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Engler, Thomas Albert

SYNTHESIS OF PERI-METHANOARENES

The Ohio State University

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SYNTHESIS OF PERI-METHANOARENES

DISSertation

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Thomas Albert Engler, B.S.

* * * * *

The Ohio State University

1981

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STATEMENT OF PROBLEM

1H-Cyclobuta[de]naphthalene (1), a naphthalene nucleus whose peri positions are spanned by a single methylene unit, and a number of its derivatives have recently been synthesized.

These single atom peri-bridged naphthalenes, although highly strained, are unexpectedly stable.

Preparation of 1 is inefficient and time consuming and better syntheses of 1 are desired. The present research investigates preparation of 1 from 1,8-dimetallonaphthalene and 1-naphthylidene precursors. The mechanisms of these unique reactions are also explored. A purpose of this study is extension of the methods developed for synthesis of 1 to a general, simple and efficient route to 1,8-methanoarenes.
Synthesis of Single Atom Peri-Bridged Naphthalenes

Single atom peri-bridged naphthalenes have interested chemists because of their unique and fascinating structures. Several of these compounds have been synthesized and are stable in spite of their high strain. These unusual molecules show interesting and sometimes surprising chemistry.

Naphtho[1,8-bc]thiete-1,1-dioxide (2), the first single atom peri-bridged naphthalene synthesized, is prepared by photolysis of naphtho-[1,8-bc]1,2,3-thiadiazene-1,1-dioxide (3, Eq. 1). Naphtho[1,8-bc]-thiete (4) is the photolysis product of naphtho[1,8-bc]1,2-dithiole-1,1-dioxide (5, Eq. 2) and has more recently been prepared from carbon
disulfide and 1,8-dehydrodronaphthalene (7), generated in situ from 
1-aminonaphtho[1,8-de]triazene (6) and lead tetraacetate (Eq. 3).\(^2\)

1. R.W. Hoffmann and W. Sieber, Angew. Chem., 77, 810 (1965) and 
R.W. Hoffmann and W. Sieber, Justus Liebigs Ann. Chem., 703, 
96 (1967).
and J. Nakayama, S. Dan and M. Hoshino, J.C.S. Perkin 1, 413, 

The first arene bridged across the peri positions by a single 
carbon moiety, 1-bromo-lH-cyclobuta[de]naphthalene (8), is prepared 
in 40–50% yield by photolysis of sodium 8-bromo-l-naphthaldehyde 
\(p\)-tosylhydrazone (9) or 8-bromo-l-naphthylidazomethane (10) in diethyl 
ether (Eq. 4). The parent hydrocarbon of 8, lH-cyclobuta[de]naphthalene (1) is synthesized from 8 by reduction with sodium bis(2-methoxy-
ethoxy) aluminum hydride or lithium aluminum hydride.\(^3\)
1,8-Dimetallonaphthalenes 11 and 12 also form hydrocarbon 1 with the proper alkylating agent, although the yields are low and unreliable (Eq. 5). A naphthalene nucleus whose peri positions are spanned by silicon has been prepared in a similar manner using 1,8-dilithionaphthalene (12) and dialkyldichlorosilanes (Eq. 6).

\[ \text{M} = \text{MgI}, 11 \quad \text{M} = \text{Li}, 12 \]

\[ + \ CH_2X_2 \rightarrow \text{2MX} \]

\[ \begin{align*}
\text{M} = \text{MgI}, & \quad X = \text{OTs}, \\
\text{M} = \text{Li}, & \quad X = \text{Cl},
\end{align*} \]

\[ 19\% \quad 9\% \]

\[ \begin{align*}
\text{Li} & \quad \text{Li} \\
\text{12} & \quad + \ R_2\text{SiCl}_2 \rightarrow \quad R_{\text{Si}}^\text{R}
\end{align*} \]

\[ \begin{align*}
\text{R} & = \text{CH}_3 \text{ or } \text{CH}_2\text{CH}_3
\end{align*} \]

4. L.S. Yang, private communication, The Ohio State University.

During the present investigation, sodium 1-naphthaldehyde p-tosylhydrazone (13) was reported to give 1 in 40% yield upon flash vacuum pyrolysis, presumably via 1-naphthylidene (14, Eq. 7).
Photolytic extrusion of nitrogen from 7-bromo-6-perinaphthyl-diazomethane (15) gives 1-bromo-1,4,5,6-tetrahydrocyclobuta[de]-phenalene (16), an air stable crystalline compound. Traces of 1H-1,4,5,6-tetrahydrocyclobuta[de]phenalene (17), presumably formed by loss of bromine from 16 during photolysis, are also found (Eq. 8). Hydrocarbon 17 can be obtained from sodium 6-perinaphthencarboxaldehyde p-tosylhydrazone (18) upon flash vacuum pyrolysis (Eq. 9). It is only one component of a complex, inseparable mixture and the
yield is poor. Attempts at a similar ring closure with 6-bromo-5-acenaphthyldiazomethane (20) fail probably because of the enormous ring strain in 21. Vacuum pyrolysis of sodium 5-acenaphthenecarboxyaldehyde p-tosylhydrazone (22) likewise does not yield the desired product, 4,5-dimethylene-1H-cyclobuta[de]naphthalene (23, Eq. 10).

\[
\begin{align*}
\text{Br} & \quad \text{CH=N}_2 \\
\begin{array}{c}
\text{Na} \\
\text{CHNNTs}
\end{array} & \quad \begin{array}{c}
\text{hv} ; \Delta \\
\text{hv} ; \Delta
\end{array} \\
\text{20} & \quad \text{hv} ; \Delta \\
\text{21} & \quad \text{hv} ; \Delta \\
\text{22} & \quad \text{hv} ; \Delta \\
\text{23}
\end{align*}
\]

(10)

Efforts to generate 1H-cyclobuta[de]naphthalene-1-ylidine-methanone (24) by Wolff rearrangement of α-diazoacenaphthenones (25) have
generally failed. Chapman has reported that irradiation of 25 in argon matrix at 80 K apparently gives 24 (Eq. 11). Identification of 24 is based on a ketene IR absorption band but 24 has not been isolated or characterized further. The steric and electronic nature of the aromatic nucleus have been varied in attempts to facilitate ring contraction in 2-diazoacenaphthenones 26 – 31 and 2-diazoanthrenone (32); the desired ketenes, however, have not been observed (Eq. 12). Carbenic reactions with solvent and 1,3-dipolar additions were found.

\[
\begin{align*}
\text{hv; } \Delta \\
Z &= 5\text{-nitro, } 26 \\
Z &= 5,6\text{-dinitro, } 27 \\
Z &= 3,8\text{-dimethoxy, } 28 \\
\end{align*}
\]

\[
\begin{align*}
Z &= 5,6\text{-dimethyl, } 29 \\
Z &= 5,6\text{-diphenyl, } 30 \\
Z &= 5,6\text{-di-m-tolyl, } 31 \\
\end{align*}
\]

\[
\begin{align*}
\text{hv; } \Delta \\
Z &= 5,6\text{-dinitro, } 27 \\
\end{align*}
\]

\[
\begin{align*}
Z &= 5,6\text{-diphenyl, } 30 \\
\end{align*}
\]

\[
\begin{align*}
Z &= 5,6\text{-di-m-tolyl, } 31 \\
\end{align*}
\]


The thermal and photolytic behavior of 2-diazo-1,1-dimethylacenaphthene (34), 1-diazoacenaphthene (33) and 2-diazoacenaphthenone ethylene glycol ketal (35) has been studied in attempts to form 1-alkylidene-1H-cyclobuta[de]naphthalenes (36) via migration of an aryl group to divalent carbon (Eq. 13). As in the previous examples, ring contraction does not occur, presumably due to prohibitive strain.

\[
\begin{align*}
1H\text{-Cyclobuta[de]naphthalene-1-one (37)} & \text{ has been prepared via a Wittig Reaction from 1-triphenylphosphonium-1H-cyclobuta[de]naphthalene bromide (38, prepared from bromide 8 and triphenylphosphine) and} \\
8 & \xrightarrow{P\phi_3} 38 \\
38 & \xrightarrow{1)RLi, 2)CH_2O} 39 \\
39 & \xrightarrow{1)O_3, 2)DMS} (14) \\
47 & \xrightarrow{h, 10^\circ K, -N_2, -CO} (15)
\end{align*}
\]
formaldehyde to give olefin 39, ozonolysis of which yields 37 (Eq. 14). Ketone 37 is also a reported photolysis product of diazolactone 40 in argon matrix at 100K (Eq. 15). As with ketene 24, identification of 37 is based solely on IR carbonyl absorbance. At present, isolation of ketene 24 and ketone 37 by matrix techniques are not of preparative value.

A more complete account of the synthesis and reactions of single atom peri-bridged naphthalenes is summarized in the Ph.D. dissertations of Bailey, Card, Friedli, Chang, Shankar and Blair.

**Generation of Carbenes via α-Elimination and Thermolysis of Organometallics**

Formation of carbenes generally involves α-elimination (Eq. 16). The driving force for such processes is formation of a stable product X-Y. Indeed, photolysis or thermolysis of diazoalkanes and ketenes to carbenes and nitrogen or carbon monoxide are classic examples of 1,1 eliminations of the above type.

Further examples of α-eliminations are pyrolytic (1050°C) fragmentation of benzyl fluoride to hydrogen fluoride and phenyl carbene (41, Eq. 17), elimination of lithium halides from α-haloorganolithiums (Eq. 18) and thermolysis of halomethyl-(or hydroxymethyl) organometallic compounds to methylenes and alkyl metal halides (or alkoxides, Eq. 19).
For the sequence in Eq. 18, it is not clear whether free carbenes or lithium halide-carbene complexes (carbenoids) are formed. Much of the mechanistic work for such systems involves cyclopropanation and C-H bond insertion processes. In reactions of 42 with olefins to form cyclopropanes, the reactivity of an olefin with 42 depends on the halide (X), the alkyllithium used to generate 42 and the order of addition of reagents. These data suggest that the carbenoid is complexed with the alkyllithium aggregate. Also, α-haloalkyllithium compounds are more selective in their intramolecular C-H insertion reactions than are "free" carbenes generated from diazoalkanes;

discrimination in insertion into tertiary and secondary C–H bonds is more pronounced in the organometallic systems.

In contrast, halomethylmercury compounds appear to decompose to free carbenes (Eq. 19). Thus, in thermolysis of phenyl(bromodichloro-
methyl)mercury in the presence of olefins or triethylsilane, the rates

\[
R-\text{Hg-}CR_2X \quad \rightarrow \quad R-\text{Hg-}X + \text{C}^R_R \tag{19}
\]

of cyclopropanation and Si-H insertion of the dichloromethylene reagent are first order in mercurial (Eq. 20) but independent of olefin or triethylsilane concentrations.¹²

\[
\phi\text{HgCCl}_2\text{Br} \quad \rightarrow \quad \phi\text{HgBr} + \text{Cl}_2
\]

Thermolysis of trialkyl(halomethyl)tin compounds also generate carbenic products and trialkyltin halides. Thus, trimethyl(trifluoromethyl)tin gives perfluorocyclopropane when heated with tetrafluoroethylen, presumably via difluorocarbene (Eq. 21). Similarly, thermal

---

\[
(\text{CH}_3)_3\text{SnCF}_3 \xrightarrow{\text{CF} \equiv \text{CF}_2} (\text{CH}_3)_3\text{SnF} + F_2
\]  
(21)


decomposition of trimethyltin and triphenyltin trichloroacetates (43 and 44) in cyclooctene yields 9,9-dichlorobicyclo[6.1.0]octane (45, 80%, Eq. 22). α-Bromotin compounds 46 and 47 thermolyze with

\[
\text{R}_3\text{SnOCCC}1_3 \xrightarrow{\Delta} \text{R}_3\text{SnCl}_3
\]  
(22)

R=CH\(_3\), 43
R=Ph, 44


extrusion of bromotrimethyltin to 7-norcar-2-enylidene (48) and vinyl cyclopropylidene (49) which then form 50, 51 and 52, 53. Carbenes


48 and 49, as generated from the N-nitrosourea 55 and geminal dibromide 56, give the same products (Eq. 23 and 24). Support for the
presumed 7-norcar-2-enylidene to 7-norbornenyldene (48 to 54) rearrangement is supplied by decomposition of the lithium salt of tosylhydrazone 57 to 50 and 51.

\[
\begin{align*}
\text{(23)} \\
46 \xrightarrow{\Delta} 48 \xrightarrow{\Delta} 54 \\
\text{Li} \\
\text{TsNN} \\
57
\end{align*}
\]

\[
\begin{align*}
\text{(24)} \\
47 \xrightarrow{\Delta} 49 \xrightarrow{\text{MeLi}} 52 \\
\text{MeLi} \\
\text{56}
\end{align*}
\]

Formation of carbenes and silicon-containing products occurs upon thermolysis of appropriate silanes (Eq. 25). Thus pyrolysis of trichlorosilane 58 in cyclohexene results in transfer of dichlorocarbene
\[
R_3SiCR_2X \xrightarrow{\Delta} R_3SiX + \overset{\cdot}{C}R
\]
(25)

X=F, Cl, OR

(Eq. 26). Silanes 59 and 60 also thermolyze in the presence of olefin, to form cyclopropane 61 in near-quantitative yield (Eq. 27).16

![Chemical structure]

\[
\text{CHF}_2\text{CF}_2\text{SiR}_3 \xrightarrow{\Delta} \text{CHF}_2 + R_3\text{SiF}
\]
(27)

R=CH₃, 59
R=F, 60

Further examples of generation of carbenes from silicon-containing precursors are as follows. Thermolysis of (dimethoxymethyl)trimethoxy-silane (62) with olefins in condensed phase gives high yields of methoxycyclopropanes 63 (Eq. 28).17 In the presence of methanol, dimethoxymethane is formed.

![Chemical structure]
The thermolyses of $\text{62}$ are first order in $\text{62}$ and zero order with respect to drastically different trapping agents. Also, $\alpha,\alpha$-dimethoxybenzylsilanes eliminate phenylmethoxy carbene which is trappable by olefins, acetylenes and by insertion into $\text{Si-H}$ and $\text{Ge-H}$ bonds (Eq.29).\textsuperscript{18}

\[
\text{R}_3\text{SiC\phi(OMe)}_2 \xrightarrow{\Delta} \phi\text{COCH}_3 \xrightarrow{\text{trap}}
\]  

\text{(29)}


Generation of methylene and phenylcarbene from $\alpha$-silylmethyl methyl ethers $\text{64}$ and $\text{65}$ fail however (Eq. 30), thus suggesting that only

\[
\begin{align*}
\text{(CH}_3\text{O)}_3\text{SiCH}_2\text{OCH}_3 & \xrightarrow{300^\circ\text{C}} \text{no } \triangle \\
\text{64} & \\
\phi_3\text{SiCHOCH}_3 & \xrightarrow{250^\circ\text{C}} \text{no reaction} \\
\text{65} &
\end{align*}
\]

(30)

stabilized carbenes, i.e. those bearing atoms with lone pairs for resonance donation to the carbenic center, can be generated by thermolytic extrusion of $\text{R}_3\text{SiX}$ in the condensed phase. A report to the contrary, however, is thermolysis of diphenylmethylsilyl(diphenyl)methyl methyl ether ($\text{66}$) in oxygen at $250^\circ\text{C}$ to give benzophenone ($\text{67}$, Eq. 31), presumably via diphenylcarbene.\textsuperscript{18}
During the present research, alkyltrimethylsilylcarbenes (68) were reported to be formed from gas phase pyrolysis of 1,1-bis(trimethylsilyl)alkanols (69, Eq. 32). The vinylsilanes presumably arise from

\[
\text{Si(} \text{CH}_3\text{)}_3 \text{COH} \xrightarrow{\Delta} \text{RCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3 \rightarrow \text{RCH}_2\text{CH} = \text{CHSiMe}_3
\]  

(32)

hydrogen migration in carbene 68. Phenyl(trimethylsilyl)carbene was also reported as an intermediate in the thermolysis of bis(trimethylsilyl)phenylmethanol 70 (Eq. 33).


Recently, generation of phenylcarbenes 71, 72 and 73 by pyrolytic elimination of trimethylsilanol from trimethylsilylalcohols 74, 75 and 76 (Eq. 34, 35, 36) has been reported.

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{SiOH} & \xrightarrow{600^\circ\text{C}} \text{CH}_2\text{CH}_2\text{M(} \text{CH}_3\text{)}_3 \\
\text{M} & = \text{C, Si}
\end{align*}
\]  

(34)
α-Silylethers, 77, which have two free radical stabilizing
groups, (i.e. phenyl) one attached to carbon which bears the silyl
group (R_1) and the other bonded to oxygen (R_2), do not collapse to
carbenes at \( \sim 200^\circ C \), but rearrangement rather than fragmentation occurs
(Eq. 37).

\[
\begin{align*}
R_1 & \quad \text{Si} \\
R & \quad \text{C} \quad \text{O} \quad \text{CH}_2 R_2 \\
\text{Si} & \quad \text{R}_3
\end{align*}
\]

21. For a more complete review of the present discussion, see

Crossover, radical trapping, and ESR experiments indicate occurrence
of a radical fragmentation-recombination mechanism (Scheme 1, path a).
Migration of the silyl group occurs with complete retention of configu-
ration. An oxygen-ylide intermediate 78 might also be involved
(Scheme 1, path b). The rate of rearrangement is insensitive, however,
to solvent polarity (\( k_{rel} \) (benzene to acetonitrile) = 1.4). Although
a carbenic mechanism can also explain the products, carbene traps fail to afford adducts, thus path c appears unlikely.

Scheme 1

Carbene-Carbene Rearrangements of Arylcarbenes

Arylcarbenes undergo profound rearrangements in gas phase at elevated temperatures. Thus, phenylcarbene (41) as generated by prolysis of the sodium salt of benzaldehyde p-tosylhydrazone (79) at 300-450°C isomerizes to cycloheptatrienylidene (80) which dimerizes to heptafulvalene (81, Eq. 38).
Isomerization of \( \text{41} \) is believed to involve ring closure to cyclopropene \( \text{82} \) which undergoes ring opening at bond b; cleavage at bond a leads to regeneration of \( \text{41} \). Reversability in rearrangement of \( \text{82} \) to \( \text{80} \) explains isomerization of o-, m- and p-tolylcarbenes in the gas phase at 420°C to benzocyclobutane (83) and styrene (84, Eq. 39).

W.J. Baron, M. Jones, Jr., and P.P. Gaspar, J. Am. Chem. Soc., 92, 4739 (1970); G.G. Vander Stouw, A.R. Kraska and H. Shechter, J. Am. Chem. Soc., 94, 1655 (1972), and ref. 22. Unlike the meta- and para-isomers, only o-tolylcarbene can form stable products through C-H insertions and rearrangement. Thus, the methyl substituent serves as a trap for the carbenic center and shifts the equilibrium toward the observed products.
At lower temperatures ($225^\circ$C), tolylcarbenes dimerize to dimethylstilbenes; at greatly increased temperatures ($600^\circ$C), phenylcarbene (41) ring contracts to fulvenallene (Eq. 40).²⁵

\[
\text{CH}_4 \xrightarrow{\text{41}} \text{C} = \text{CH}_2
\]


Conversions of cycloheptatrienyldienes to arylcarbene products are known and the intermediate bicyclo[4.1.0]heptatrienes have been intercepted. Although such rearrangements occur freely in the gas phase, one or two prerequisites is necessary for rearrangement in solution: 1) substituents which retard dimerization in a cycloheptatrienyldiene or 2) stabilizing benzannulation which reduces the loss in aromaticity in conversion of cycloheptatrienyldienes to subsequent cyclopropenes.²⁶


Thus, in solution cycloheptatrienyldiene (80) gives heptafulvalene (81) whereas 2,7-diphenylcycloheptatrienyldiene (85) yields 9-phenylfluorene (86, Eq. 41). Also, 4,5-benzocycloheptatrienyldene (87) and 2,3:4,5-dibenzocycloheptatrienyldene (88) generated via
photolysis of the corresponding tropone tosylhydrazone salts 89 and 90 convert to products of 2-naphthylcarbene (91) and 9-phenanthryl-carbene (92), respectively (Eq. 42 and 43). In the presence of furan and cyclopentadiene, Diels-Alder adducts of bicyclo[4.1.0]heptatrienes 93 and 94 are formed, i.e. 95 and 96.27
Examples of cycloheptatrienylidene-derived products from arylcarbenes in the gas phase are common. As indicated earlier, phenylcarbene (41) isomerizes and dimerizes to heptafulvalene (81, Eq. 38); also, diphenylcarbene yields diphenylheptafulvalene (97) and fluorene (98) in a 3:1 ratio (Eq. 44).23
Fluorene is the product of multiple carbene-carbene rearrangements followed by intramolecular C-H insertion. In solution, however, rearrangements of arylcarbenes to cycloheptatrienyldienes are rare.  

The carbene-carbene rearrangement of naphthylcarbenes in the gas phase is highly temperature dependent. At 350°C, the isomerization of 2-naphthylcarbene is highly regiospecific, i.e. only the C1-C2 bond migrates to the carbenic center (Fig. 1).

Figure 1. Bond migration in 2-naphthylcarbene.

Carbene-carbene rearrangement has not been observed in 1-naphthylcarbenes. Thus, vinylnaphthalenes are not produced on pyrolysis of diazo precursors of 2-methyl-1-naphthylcarbene (99) or 4-methyl-1-naphthylcarbene (100).
Although 1-vinylnaphthalene (101) is not formed from 1-methyl-2-naphthylcarbene, 3-methyl-2-naphthylcarbene (102) isomerizes to 2-vinylnaphthalene (103, Eq. 45). A rational mechanism for formation of 103 from 102 involves methyl(2-naphthyl)carbene (104), as derived from 102 via 2-methyl-4,5-benzocycloheptatrienylidene (105, Eq. 45). Supporting evidence for involvement of 105 comes from thermolysis of the sodium salt of 2-methyl-4,5-benzotropone tosylhydrazone resulting in 2-vinyl-naphthalene (103). Bicyclo[4.1.0]heptatrienes 106 and 107 may be intermediates in Eq. 45.

Thus, at 350°C a "2-naphthylcarbene" isomerizes to a "3-naphthylcarbene" but not to a "1-naphthylcarbene" (the bond of highest order migrates); a "1-naphthylcarbene" does not rearrange, however, to a "2-naphthylcarbene". The following rationale has been proposed to
account for these results.\textsuperscript{31} Rearrangement of 2-naphthylcarbene (108) to 1-naphthylcarbene (109), or vice versa, requires a series of "pseudo-aromatic" intermediates (Scheme 2) where none of the six-membered rings have benzenoid character. Isomerization, however, of a 2-naphthylcarbene to a 3-naphthylcarbene (Scheme 3) involves intermediates in which aromaticity is preserved in one of the benzene rings.

\textbf{Scheme 2}

\begin{align*}
\text{108} & \rightleftharpoons \text{109} \\
\text{108} & \rightleftharpoons \text{109}
\end{align*}

\textbf{Scheme 3}

\begin{align*}
\text{108} & \rightleftharpoons \text{109} \\
\text{108} & \rightleftharpoons \text{109}
\end{align*}

Recently, 2-naphthylcarbene (108) is reported to isomerize to 1-naphthylcarbene (109) at 600°C.\textsuperscript{6} The higher temperature apparently allows the barriers to rearrangement to be overcome (see Results and Discussion).

RESULTS AND DISCUSSION

The present research is directed toward development of a short, efficient synthesis of 1H-cyclobuta[de]naphthalene (1) and expanding the method to preparation of other peri-methano-bridged arenes. Although 1H-cyclobuta[de]naphthalene (1) and some of its derivatives have been investigated (see Historical), further elaboration of the behavior of these bridged arenes has been hampered by their unavailability. When this research was initiated 1 was obtainable from disodium 1,8-naphthalate in 12-14% yields by the seven step sequence in Scheme 4.³ Thus, a more convenient synthesis of 1 was desired.

In this laboratory, Yang⁴ found that 1 is formed from 1,8-di-dithionaphthalene (12) and dichloromethane and from 1,8-naphthylimagnesiunm iodide (11) and methylene bis-tosylate (Eq. 46 and 47). In the study by Yang, 1 was preparable unreliably and in only 9% yield from

\[
\begin{align*}
M = & \text{Li, 12} & X = & \text{Cl} & 1, & \text{9% (46)} \\
M = & \text{MgI, 11} & X = & \text{OTs} & 1, & \text{20% (47)}
\end{align*}
\]
Scheme 4

1) NaOH
2) Hg(0Ac)$_2$

100%

1) SOCl$_2$
2) LiAlH$_4$

83%

Br CH$_2$OH
NCS/DMS

88%

Br CHO

88%

Br CH=NNHTs
1) NaH
2) hv

46%

Red-Al

100%

1
1,8-dilithionaphthalene (Table 1). Grignard reagent \( 11 \) is difficult to prepare and the yields of \( 1 \) vary with the magnesium used and were not reproducible (Table 2).

A major effort has now been made of synthesis of \( 1 \) from 1,8-dimetalonaphthalenes and investigation of the mechanism by which \( 1 \) is formed. The 1,8-dilithionaphthalene precursors, 1,8-dibromo- and 1,8-diiodonaphthalenes (110 and 111) are preparable in quantity from commercial 1,8-diaminonaphthalene upon bis-diazotization and Sandmeyer displacement (Eq. 48). \(^{32}\) Bromination of anhydro-8-hydroxymercuri-1-naphthoic acid (112) also affords 110 (along with 8-bromo-1-naphthoic acid) in yields (16%, Eq. 49) comparable to those found for the Sandmeyer method (17%). \(^{33}\)

\[ \begin{align*}
\text{NH}_2 \quad \text{NH}_2 & \quad 1) \text{NaNO}_2 \quad \text{I} \quad \text{I} \\
\text{Br} \quad \text{Br} & \quad 2) \text{KI or CuBr} \quad \text{111} \quad \text{110}
\end{align*} \]


<table>
<thead>
<tr>
<th>Reactant</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Yield&lt;sup&gt;a&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Br&lt;sub&gt;2&lt;/sub&gt;</td>
<td>--</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;0</td>
<td>0 or 96</td>
<td>0</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Br&lt;sub&gt;2&lt;/sub&gt;</td>
<td>--</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;0</td>
<td>0 or 96</td>
<td>0</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>--</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;0</td>
<td>0 or 34</td>
<td>0</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;(OT&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>--</td>
<td>THF</td>
<td>66</td>
<td>0</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;(OT&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>--</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;0</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;(OT&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>MgBr&lt;sub&gt;2&lt;/sub&gt;, excess</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;0</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;(OT&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>MgCl&lt;sub&gt;2&lt;/sub&gt;, excess</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;0</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>--</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Ni(Acac)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;0</td>
<td>25</td>
<td>9</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Ni(Acac)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;0</td>
<td>25</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup> Yield of 1H-cyclobuta[de]naphthalene (1).
### TABLE 2

Reactions of 1,8-Naphthyldimagnesium Iodide and Methylene Compounds

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Type of Mg</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Yield (%)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂(OTs)₂</td>
<td>turnings</td>
<td>Et₂O</td>
<td>34</td>
<td>&gt; 20</td>
</tr>
<tr>
<td>CH₂(OTs)₂</td>
<td>turnings</td>
<td>C₆H₆, THF</td>
<td>reflux</td>
<td>&gt; 20</td>
</tr>
<tr>
<td>CH₂(OTs)₂</td>
<td>Rieke's, 8 equiv</td>
<td>THF</td>
<td>66</td>
<td>&gt; 20</td>
</tr>
<tr>
<td>CH₂(OTs)₂</td>
<td>Rieke's, 8 equiv</td>
<td>THF</td>
<td>66</td>
<td>&gt; 20</td>
</tr>
<tr>
<td>CH₂(OTs)₂</td>
<td>Rieke's, 4 equiv</td>
<td>THF</td>
<td>66</td>
<td>&gt; 20</td>
</tr>
<tr>
<td>CH₂(OTs)₂</td>
<td>T. S. c</td>
<td>THF</td>
<td>66</td>
<td>0</td>
</tr>
</tbody>
</table>

a) Yield of 1H-cyclobuta[de]naphthalene (1) based on diiodide.


c) Triple-sublimed magnesium.
Treatment of either 110 or 111 with t-butyllithium (4 equiv) or n-butyllithium (2 equiv) in diethyl ether or tetrahydrofuran at (-78)-25°C yields 1,8-dilithionaphthalene (12) quantitatively as determined by conversion by D₂O to 1,8-dideuteronaphthalene.

34. R.L. Letsinger, J.A. Gilpin and W.J. Vullo, J. Org. Chem., 27, 672 (1962) and . Occasionally, n-butyl halides interfere with the desired reaction and use of t-butyllithium is recommended for preparation of 12 since the t-butyl halide by-product is destroyed by excess t-butyllithium to the innocuous products lithium halide and isobutylene.

The behavior of 12 toward methylene halides was then studied. Reaction of 1,8-dilithionaphthalene (12) with dichloromethane in diethyl ether produces naphthalene (113), 1H-cyclobuta[de]naphthalene (1) and acenaphthylene (114, Eq. 50).
The yields of 1 and 113 do not vary much with reaction temperature or equivalents of dichloromethane (Table 3). The yield of 114 does increase substantially with excess dichloromethane. No 1 is observed when tetrahydrofuran is used as solvent. Dibromomethane, diiodomethane and methylene bis-tosylate fail to yield 1.

35. The conditions were essentially identical to those of Yang summarized in Table 1.

Addition of nickel(II) acetylacetonate (4 mole %) to a tetrahydrofuran solution of 1,8-dilithionaphthalene (12) at room temperature prior to addition of dichloromethane results in a 9% yield of 1H-cyclobuta[de]naphthalene (1), along with naphthalene (113, 15%, Eq. 51). Using diethyl ether as the reaction solvent, lower temperature or substituting dichloro[1,2-bis(diphenylphosphino)ethane] nickel(II) for Ni(Acac)₂ results in lower yields of 1 (Table 4).

Nickel(II) is at present unique in its ability to catalyze formation of 1 from 12 as is dichloromethane is its ability to serve as an alkylating agent for 12. Alkynyl copper compounds, copper(I) or (II) halides or iron(III) chloride fail to yield 1 with either dichloro-(115) dibromo-(116) or diiodomethanes (117) or methylene
TABLE 3

Effects of Reaction Temperature and Equivalents of Dichloromethane and the Yields of \( \mathbf{1} \), \( \mathbf{113} \) and \( \mathbf{114} \) from 1,8-Dilithionaphthalene (12).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Equiv of CH₂Cl₂</th>
<th>Yield (%)</th>
<th>( \mathbf{113} ), ( \mathbf{1} ), ( \mathbf{114} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et₂O</td>
<td>-78</td>
<td>1.0</td>
<td>30</td>
<td>4 N.D. (^a)</td>
</tr>
<tr>
<td>Et₂O</td>
<td>0</td>
<td>2.2</td>
<td>31</td>
<td>3 13</td>
</tr>
<tr>
<td>Et₂O</td>
<td>25</td>
<td>4.5</td>
<td>37</td>
<td>4 22</td>
</tr>
</tbody>
</table>

\(^a\) N.D. = not determined
bis-tosylate(118) under a variety of conditions (Tables 4 and 5).


Methylene compounds 116, 117 or 118 also do not form L even in the presence of nickel(II).

The proposed mechanism for Ni(II) catalyzed cross-coupling reactions between Grignard reagents and organic halides is shown in Scheme 5. The two equivalents of a Grignard reagent react with the

**Scheme 5**

1) $L_4Ni + 2RMgX \rightarrow L_2NiR_2$

2) $L_2NiR_2 + R'X \rightarrow L_2Ni(R')(X) + RR$

3) $L_2Ni(R')(X) + RMgX \rightarrow L_2Ni(R')(R) + MgX_2$

4) $L_2Ni(R')(R) + R'X \rightarrow L_2Ni(R')(X) + R'R$
TABLE 4

Reaction of 1,8-Dilithionaphthalene (12) with Dichloromethane in the Presence of Transition Metal Salt Catalysts

<table>
<thead>
<tr>
<th>Catalyst (mole %)</th>
<th>Equiv of CH₂Cl₂</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(Acac)₂ (2)</td>
<td>1.1</td>
<td>Et₂O</td>
<td>-60</td>
<td>31  2.5&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni(Acac)₂ (4)</td>
<td>1.0</td>
<td>THF</td>
<td>25</td>
<td>15  9</td>
</tr>
<tr>
<td>NiCl₂&lt;sub&gt;p&lt;/sub&gt;&lt;sub&gt;2&lt;/sub&gt; (27)</td>
<td>2.0</td>
<td>Et₂O</td>
<td>0</td>
<td>34  2</td>
</tr>
<tr>
<td>Li₂CuCl₄ (2)</td>
<td>2.0</td>
<td>Et₂O/THF</td>
<td>-78</td>
<td>14 trace&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>CuBr (200)</td>
<td>excess</td>
<td>THF</td>
<td>-78</td>
<td>- 0</td>
</tr>
<tr>
<td>CuBr (100)</td>
<td>excess</td>
<td>THF</td>
<td>-78</td>
<td>- 0</td>
</tr>
<tr>
<td>CuBr (50)</td>
<td>excess</td>
<td>THF</td>
<td>-78</td>
<td>- 0</td>
</tr>
<tr>
<td>FeCl₃ (10)</td>
<td>2.0</td>
<td>Et₂O</td>
<td>0</td>
<td>- 0</td>
</tr>
</tbody>
</table>

---

a) Acenaphthylene (4%) is also observed.

b) 1,2-Di-(1-naphthyl)ethylene is produced in 29% yield.
TABLE 5

Attempted Preparation of \( 1 \) from 1,8-Dilithionaphthalene (12)
and Dibromomethane, Diiodomethane and Methylene Bis-Tosylate

<table>
<thead>
<tr>
<th>Alkylation agent (equiv)</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Catalyst (mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_2)I(_2) (1.0)</td>
<td>Et(_2)O</td>
<td>0</td>
<td>CuI (100)(^a)</td>
</tr>
<tr>
<td>CH(_2)(OTs)(_2) (1.0)</td>
<td>Et(_2)O/THF(2:1)</td>
<td>0</td>
<td>Ni(Acac)(_2) (4)</td>
</tr>
<tr>
<td>CH(_2)Br(_2) (1.0)</td>
<td>THF</td>
<td>25</td>
<td>Ni(Acac)(_2) (5)</td>
</tr>
<tr>
<td>CH(_2)I(_2) (1.0)</td>
<td>THF</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>CH(_2)(OTs)(_2) (1.0)</td>
<td>THF/Et(_2)O/HMPA</td>
<td>-75</td>
<td>n-PrC(=)CCu (200)(^b)</td>
</tr>
<tr>
<td>CH(_2)(OTs)(_2) (1.0)</td>
<td>THF/Et(_2)O</td>
<td>-65</td>
<td>TMEDA (350)</td>
</tr>
<tr>
<td>CH(_2)(OTs)(_2) (1.0)</td>
<td>THF/Et(_2)O</td>
<td>-78</td>
<td>CH(_3)O(CH(_3))(_2)C(=)CCu (200)(^c)</td>
</tr>
</tbody>
</table>

\(^a\) The products isolated were naphthalene (18%) and 1,1'-binaphthyl (5%).

\(^b\) Naphthalene 23% was isolated.

\(^c\) Naphthalene 32% was isolated.
nickel(II) species forming a σ-organonickel complex, 119, from which the two organic groups are released for coupling by the action of an organic halide with the formation of a (halo)(organo)nickel complex (step 2). A third equivalent of Grignard reagent reacts with 120 to form a σ-organonickel compound 121 (step 3). The cross-coupled product, R'R, is then expelled from 121 by action of a second equivalent of organic halide and complex 120 is regenerated to continue the process.

Applying the mechanism in Scheme 5 to 1,8-dilithionaphthalene (12) and dichloromethane (Eq. 51) leads to Scheme 6 for the formation of 1. Due to the difunctional nature of both 12 and dichloromethane other variations of Scheme 6, based on a similar theme, can be imagined.

Organic chlorides are especially reactive for cross-coupling as in Scheme 5 and may explain dichloromethane in its reactions with 12 to form 1. Different mechanisms apparently operate in cross-coupling catalyzed by copper and iron compounds, thus rationalizing why nickel is unique in the present conversions of 12 to 1.

---

37. Iron(III) salts are thought to react via radical processes involving generation of Fe(II). Copper catalysis apparently involves alkylcopper and alkylcuprate intermediates which effect S_N^2 displacement of organic halides, see 36.

---

The limited success of the transition metal-catalyzed reactions led to study of the mechanism of formation of 1 from 12 in the absence of transition metals. As described earlier,
Scheme 6

\[ \text{L}_2\text{NiR}_2 \xrightarrow{\text{CH}_2\text{Cl}_2} \text{L}_2\text{NiCl}(\text{CH}_2\text{Cl}) \xrightarrow{\text{Li Li}} \text{L}_2\text{Ni(Li)} \]

\[ \xrightarrow{\text{CH}_2\text{Cl}_2} \text{L}_2\text{NiCl}(\text{CH}_2\text{Cl}) \xrightarrow{\text{L}_2\text{NiR}_2} \text{L}_2\text{NiCl}(\text{CH}_2\text{Cl}) \xrightarrow{-\text{RR}} \text{L}_2\text{NiCl}(\text{CH}_2\text{Cl}) \]

\[ \xrightarrow{-\text{LiCl}} \text{L}_2\text{NiCl}(\text{CH}_2\text{Cl}) \]

\[ \xrightarrow{\text{L}_2} \text{L}_2\text{NiCl}(\text{CH}_2\text{Cl}) \]

\[ \xrightarrow{\text{L}_2} \text{L}_2\text{NiCl}(\text{CH}_2\text{Cl}) \]

\[ \xrightarrow{\text{L}_2\text{NiR}_2} \text{L}_2\text{NiCl}(\text{CH}_2\text{Cl}) \xrightarrow{-\text{RR}} \text{L}_2\text{NiCl}(\text{CH}_2\text{Cl}) \]

\[ \xrightarrow{-\text{LiCl}} \text{L}_2\text{NiCl}(\text{CH}_2\text{Cl}) \]

\[ \xrightarrow{\text{L}_2} \text{L}_2\text{NiCl}(\text{CH}_2\text{Cl}) \]

\[ \xrightarrow{\text{L}_2} \text{L}_2\text{NiCl}(\text{CH}_2\text{Cl}) \]
1,8-dilithionaphthalene (12) and dichloromethane yield naphthalene (113), 1H-cyclobuta[de]naphthalene (1) and acenaphthylene (114, Eq. 50). Since 12 is apparently being destroyed in major quantity by protonation to give naphthalene (113), determination of the proton source responsible is important. Hydrolytic work up of the reaction product from 12 and 115 with D₂O does not yield deuterated naphthalene(s). However, the naphthalene produced in reaction of dichloromethane-d₂ with 12 has much deuterium at its 1,8- (62%) and 1- (25%) positions (Eq. 52), thus indication that dichloromethane is deprotonated by 12. Since strong bases are known to deprotonate dichloromethane, an interesting mechanistic question is posed as to whether lithium dichloromethane is an intermediate in the formation of 1.

Several mechanisms for formation of 1 from 12 are conceivable (Scheme 7). Path a involves step-wise S_N2 displacement of chloride from dichloromethane; an intermediate in this process would be 8-lithio-1-chloromethylnaphthalene.

Lithium dichloromethane, formed from deprotonation of CH₂Cl₂ by 12, might also react with 1,8-dilithionaphthalene to form 8-lithio-1-chloro-(lithio)methyl(naphthalene (122, path b) via chloride ion displacement or a ligand exchange process. Repeating the same operation intramolecularly results in 1-lithio-1H-cyclobuta[de]naphthalene (123).
from 122. A second equivalent of dichloromethane could then be deprotonated by 123 to form 1.

The ligand exchange process in step 1 of path b may involve α-elimination of lithium chloride from lithium dichloromethane resulting in chlorocarbene, which is trapped by 12 to form 124.

α-Elimination of lithium chloride from 124 would give 8-lithio-1-naphthylidene (125) in which the carbene center is trapped intramolecularly by the C-8 carbon lithium moiety to give 123. In reactions of α-metalloorganic halides, it is not clear if free carbenes or metal halide-complexed carbenoids are involved (see Historical) and thus differentiation of paths b and c is not yet possible.

Production of acenaphthylene (114, Eq. 50) can be explained by modifying paths a or b of Scheme 7. Thus, 8-lithio-1-chloromethyl-naphthalene (126), an intermediate in path a of Scheme 7, could displace chloride from dichloromethane to form 1,8-bis(chloromethyl) naphthalene (127, Eq. 53). Deprotonation of a benzylic hydrogen in 127 followed by ring closure and loss of lithium chloride forms 1-chloroacenaphthene (128), dehydrochlorination of which would yield 114.
Alternatively, 8-lithio-1-chloro(lithio)methylnaphthalene (122, path b, Scheme 7) might trap lithium dichloromethane forming 129 (Eq. 54). Loss of two molecules of lithium chloride from 129, either via ligand exchange or by α-elimination, would yield 114.

\[
\begin{align*}
\text{Li} & \quad \text{LiCl} \\
\text{CHCl} & \quad \text{LiCHCl}_2 \\
122 & \quad \text{LiCl} \quad \text{-LiCl} \\
\text{C1CH} & \quad \text{CHCl} \\
129 & \quad 114
\end{align*}
\]

(Eq. 54)

In Scheme 7, formation of 1 via path a is unlikely since methylene bis-tosylate, diiodomethane and dibromomethane fail to yield 1 in reactions with 1,8-dilithionaphthalene (12). The success of dichloromethane in producing 1 from 12 therefore may be attributed to formation and capture of lithium dichloromethane. Tetramethylethylenediamine (TMEDA) is known to stabilize α-lithio-organic halides (i.e. carbenoids) and its use as a co-solvent in reactions of 1,8-dilithionaphthalene (12) and dichloromethane (115) significantly increases the yields of 1 (Eq. 55). The best yields

\[
\begin{align*}
\text{Li} & \quad \text{Li} \\
\text{C1CH} & \quad \text{CHCl} \\
12 & \quad 115 \\
+ \quad \text{CH}_2\text{Cl}_2 \quad \text{2TMEDA} \\
\text{Et}_2\text{O} & \quad 78^\circ \\
\quad & \quad 31\% \\
\quad & \quad 21\% \\
\end{align*}
\]

(Eq. 55)
of 1 are obtained with ethyl ether as principal solvent at -78°C to -100°C and the use of two equivalents each of tetramethylethylenediamine and dichloromethane with respect to 1,8-dilithionaphthalene (12, Table 6). The major reaction product under all the conditions is naphthalene (113), and Ni(Acac)₂ retards formation of 1. 1-Chloromethylnaphthalene (130, 2%) and 1,2-bis(1-naphthyl)ethylene (131, 2%) are minor products in reaction of 115 with 12. Methylene bis-tosylate does not yield 1 when reacted with 1,8-dilithionaphthalene (12) under the above conditions.

Dichloromethane-d₂ and 1,8-dilithionaphthalene (12) in diethyl ether/tetramethylethylenediamine produce naphthalene (132) and 1H-cyclobuta[de]naphthalene (133) both highly deuterated as summarized in Eq. 56. Hydrolysis of such reaction mixtures with D₂O does not significantly alter the deuterium content of 132 or 133 (Table 7), thus implying that the above deuteronaphthalenes (132 and 133) are produced by dedeuteration of CD₂Cl₂ by 12.

$$\text{Li}_2 \text{Li} + \text{CD}_2\text{Cl}_2 \xrightarrow{\text{TMEDA}} \xrightarrow{\text{Et}_2\text{O}, -78^\circ\text{C}} \begin{array}{c} 12 \rightarrow \text{132} \text{ (42%)}; \text{60% } d_2 \text{ (19%)}; \text{>90% } d_1 \text{ (27%)} \\ \text{133} \end{array}$$

It thus appears that lithium dichloromethane (134) is also generated in reactions of 12 with 115 in tetramethylethylenediamine and much of 12 is used to produce 113. Efforts were then directed to independent generation of lithium dichloromethane (134) for reaction
### TABLE 6

Reactions of 1,8-Dilithionaphthalene (12) with Dichloromethane in Ethyl Ether/Tetramethylethylenediamine (TMEDA)

<table>
<thead>
<tr>
<th>Equiv of CH₂Cl₂</th>
<th>Equiv of TMEDA</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>2.3</td>
<td>Et₂O</td>
<td>-100</td>
<td>31</td>
</tr>
<tr>
<td>12.0</td>
<td>5.2</td>
<td>Et₂O</td>
<td>-100</td>
<td>46</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>Et₂O</td>
<td>-78</td>
<td>28</td>
</tr>
<tr>
<td>5.0</td>
<td>2.1</td>
<td>Et₂O</td>
<td>-60</td>
<td>42</td>
</tr>
<tr>
<td>20.0</td>
<td>2.0</td>
<td>Et₂O</td>
<td>-60</td>
<td>42</td>
</tr>
<tr>
<td>1.1</td>
<td>2.3</td>
<td>Et₂O</td>
<td>-60</td>
<td>48</td>
</tr>
<tr>
<td>1.1</td>
<td>2.0</td>
<td>Et₂O</td>
<td>0</td>
<td>16</td>
</tr>
<tr>
<td>2.1⁺b</td>
<td>2.0</td>
<td>THF</td>
<td>0</td>
<td>34</td>
</tr>
<tr>
<td>3.8⁺b</td>
<td>2.2</td>
<td>Hexane</td>
<td>-78</td>
<td>24</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>Et₂O/THF</td>
<td>0</td>
<td>10</td>
</tr>
</tbody>
</table>

+ 7 mole % Ni(Acac)₂

---

a) Small amounts of 1-chloromethylnaphthalene (130, 2%) and 1,2-(1-naphthyl) ethylene (131, 2%) were also found.

b) In these experiments, 1,8-dilithionaphthalene (12) was generated in tetrahydrofuran and hexane, respectively, at 0°C.

c) 1,1-Binaphthyl (3%) was also isolated.
TABLE 7
Reactions of 1,8-Dilithionaphthalene (12) with Dichloromethane-d₂

<table>
<thead>
<tr>
<th>Equiv of CH₂Cl₂</th>
<th>Equiv of TMEDA</th>
<th>Temp (°C)</th>
<th>Work-up</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>2.3</td>
<td>-60</td>
<td>D₂O</td>
<td>38</td>
</tr>
<tr>
<td>1.2</td>
<td>2.1</td>
<td>-60</td>
<td>H₂O</td>
<td>42</td>
</tr>
</tbody>
</table>

<sup>a</sup> The deuterium percentages in the naphthalene (132) recovered are d₂:d₁:d₀ = 63:29:9; the 1H-cyclobuta [de] naphthalene (133) contains 90% d₂.

<sup>b</sup> For the naphthalene (132) recovered the deuterium percentages are d₂:d₁:d₀ = 60:27:12; the 1H-cyclobuta [de] naphthalene (133) is 90% d₂.
with 1,8-dilithionaphthalene (12). Lithium dichloromethane (134) has been prepared from dichloromethane and n-butyllithium at -100°C and is stable below -65°C. A diethyl ether solution of lithium dichloro-

\[ \text{Li}_2 \text{Li} + \text{LiCHCl}_2 \xrightarrow{\text{TMEDA}, \text{Et}_2\text{O}} -80-25^\circ\text{C} \quad \text{113} \quad \text{1} \]

methane is generated from t-butyllithium and dichloromethane at -100°C, and addition of 1,8-dilithionaphthalene (112) in diethyl ether/tetramethylethylenediamine to the LiCHCl₂ reagent and allowing the mixture to warm to 25°C does give 1H-cyclobuta[de]naphthalene (1, 18%) along with naphthalene (113, 34%). The yield of 1 is not improved, however, by this method under a variety of conditions (Table 8).

Hydrolysis of the reaction product with D₂O reveals that all of the dilithionaphthalene (12) is consumed before quenching (there is no deuterated naphthalene). Naphthalene (113) possibly arises from reaction of 1,8-dilithionaphthalene (12) with 1,2-dichloroethylene, a product of decomposition of lithium dichloromethane in diethyl ether, or other chloro-intermediates. While the above experiments do not prove that lithium dichloromethane is an intermediate in forma-


TABLE 8

Reaction of 1,8-Dilithionaphthalene (12) with Lithium Dichloromethane in Diethyl Ether/Tetramethylethenediamine (TMEDA)

<table>
<thead>
<tr>
<th>Equiv of LiCHCl₂</th>
<th>Equiv of a TMEDA</th>
<th>Temp (°C)</th>
<th>Yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>-</td>
<td>-100</td>
<td>25 8</td>
</tr>
<tr>
<td>1.0</td>
<td>2.2</td>
<td>-90</td>
<td>30 9</td>
</tr>
<tr>
<td>4.1</td>
<td>2.2</td>
<td>-90</td>
<td>34 18</td>
</tr>
<tr>
<td>3.9</td>
<td>4.4</td>
<td>-100</td>
<td>34 9</td>
</tr>
<tr>
<td>21</td>
<td>2.2</td>
<td>-75</td>
<td>35 13</td>
</tr>
<tr>
<td>4.4 b</td>
<td>2.1</td>
<td>-100</td>
<td>28 c 15 c</td>
</tr>
</tbody>
</table>

a) With respect to 1,8-dilithionaphthalene.
b) D₂O was used in work-up.
c) No d-incorporation as evidenced by ¹H NMR or mass spectra.
tion of \text{1} \text{ from 12}, they do show that the reagent reacts with
1,8-dilithionaphthalene (12) to give \text{1}.

Chloromethyl methyl ether (135) is converted to the carbenoid,
LiCH(Cl)OCH$_3$, by alkyl lithiums.\textsuperscript{40} Study was then made of reactions


of chloromethyl methyl ether and 1,8-dilithionaphthalene (12) to
give \text{1}. Addition of chloromethyl methyl ether to 1,8-dilithio-
naphthalene (12) in diethyl ether/tetramethylethylenediamine at -70°C
produces 1-methoxymethylnaphthalene (136) and naphthalene (113, Eq. 58)
as the only identifiable products. When two equivalents of chloro-
methyl methyl ether are used, 1,8-bis(methoxymethyl)naphthalene
(137, 44\%) results along with 136 (8\%) and 113 (7\%). Naphthalene
(113) probably arises from deprotonation of chloromethyl methyl ether
and 136 and 137 may result from displacement of chloride from

\begin{equation}
\begin{array}{c}
\text{L1} \text{L1} \\
\text{12} \\
\text{ClCH}_2\text{OCH}_3 \\
\text{L1} \text{L1} \\
\text{12} \\
\text{2ClCH}_2\text{OCH}_3
\end{array}
\begin{array}{c}
\text{113} \\
\text{136} \\
\text{137}
\end{array}
\end{equation}
chloromethyl methyl ether by \(^{12}\) or from carbenoids \(^{138}\) and \(^{139}\), formed from \(\text{12}\) and \(\text{LiCH(Cl)OCH}_3\), and hydrolysis. Ether \(^{137}\) is identified from its elemental analysis, exact mass and spectral properties (see Experimental).

![Diagram](image)

Experiments were then designed to generate 8-lithio-1-chloromethylnaphthalene (126), the proposed intermediate in the displacement mechanism in Eq. 50 (Scheme 7, path a). 8-Bromo-1-naphthalene-methanol (140) is converted to 8-bromo-1-chloromethylnaphthalene (141) with thionyl chloride (Eq. 59). Addition of \(\text{t-butyllithium}\) (2 equiv) to 141 in diethyl ether at \(-100^\circ\text{C}\) followed by methyl alcohol-0-d results in 1-chloromethylnaphthalene (130, 55%) containing 85% deuterium at \(C_8\) of its naphthalene ring (Eq. 59). The solution of 8-lithio-1-chloromethylnaphthalene (126) on warming to room temperature,


42. Specific lithium-bromine exchange has been reported with 2-bromo-1-chloromethylbenzene and \(n\)-butyllithium at \(-100^\circ\text{C}\) to afford 2-lithio-1-chloromethylbenzene, see W. Parham, L.D. Jones and Y.A. Sayed, J. Org. Chem., 41, 1184 (1979).
however, does not give 1H-cyclobuta[de]naphthalene (1H); only complex coupling products are observed. Using tetramethylethylenediamine as a co-solvent also does not yield 1H. Two equivalents of t-butyllithium with 141 leads to 1-neopentynaphthalene (142, 6%) and 1,2-di(1-naphthyl)ethane (143, 46%, Eq. 60). 1-Neopentynaphthalene (142) can arise from 8-lithio-1-chloromethylnaphthalene (126) by displacement with t-butyllithium and protonation. Ethane 143 possibly results
from exchange between t-butyllithium and 8-lithio-1-chloromethyl-naphthalene (126) to give 144 which then reacts with 126 to form 145 (Eq. 61), hydrolysis of which affords 143.

Thus, it appears that 8-lithio-1-chloromethylnaphthalene (126) is not an intermediate in production of 1 from 12. The carbene or carbenoid mechanisms for formation of 1 (path b and c in Scheme 7) best fit the experimental data.

It was hoped that replacing chlorine in 8-lithio-1-chloromethyl-naphthalene (126) with other leaving groups would facilitate ring closure of 146 to form 1 as shown in Eq. 62. Bromine or iodine

\[
\begin{array}{c}
\text{Br} \quad \text{CH}_2X \\
\text{RLi} \\
\text{Li} \quad \text{CH}_2X \\
\text{146} \\
\text{-LiX} \\
\text{1} \\
\end{array}
\]

(62)

are inappropriate because benzylic halogen-lithium exchange to 8-halo-1-naphthylmethylolithiums would be faster than the desired aryl halogen-lithium exchange to 146. The reported intramolecular displacement of methoxide in 2-lithio-1-methoxymethylbenzene (147) and 5-lithio-4-methoxymethylbenzocyclobutene (148) to form benzo(cyclopropene) (149) and cyclopropacyclobutabenzene (150), respectively (Eq. 63 and 64) led to investigation of the chemistry of 8-lithio-1-methoxymethylnaphthalene and related compounds (146, X=OR).

44. The analogous reaction with 2-lithio-1-chloromethylbenzene fails to produce benzo(cyclopropene), see ref. 42.
Methyl (8-bromo-1-naphthyl)methyl ether (151) is prepared from 8-bromo-1-naphthalenemethanol (140) sodium hydride and then dimethyl sulfate (Eq. 65). Treatment of a diethyl ether/tetramethylethylene-
diamine solution of 151 with two equivalents of t-butyllithium at -75°C, and then refluxing the mixture results in α-methyl-1-naphthalene-
methanol (152, 22%), 1-methoxymethyl naphthalene (136, 18%) and 1,2-di(1-naphthyl)ethylene (131, 4%, Eq. 65).

Alcohol 152 is identified by comparison with an authentic sample. A likely mechanism for formation of 152 from 151 involves lithium-
bromine exchange between 151 and t-butyllithium followed by proton transfer from the benzylic methylene moiety to form α-lithio-1-
methoxymethyl naphthalene (154, Scheme 8). Wittig rearrangement of 154 would then yield alkoxide 155 which affords alcohol 152 upon
Scheme 8

[Diagram showing the reactions and intermediates]

hydrolysis. Ether 136 results from protonation of 154 or 156. Olefin 131 probably originates from bimolecular displacements of 154 and elimination of lithium methoxide (Eq. 66).

The behavior of benzyl (8-bromo-1-naphthyl)methyl ether (157) with alkyl lithiums is similar to methyl (8-bromo-1-naphthyl)methyl ether (151). Benzyl (8-bromo-1-naphthyl)methyl ether is prepared from 8-bromo-1-bromomethylnaphthalene (158), benzyl alcohol and sodium hydride (Eq. 67) and addition of n-butyllithium to 157 in tetrahydrofuran at -40°C followed by refluxing yields α-(phenylmethyl)-1-naphthalenemethanol (159, 42%). Identification of 159 is based on
its molecular weight and spectral characteristics including IR absorptions at 3560 (free OH), 3400 (OH), $^1$H NMR absorptions at $\delta$ 2.0 (broad s, 1H, OH), 3.5 (m, 2H, CH$_2$), 5.0 (m, 1H, CHCH$_2$), 7.2-8.2 (m, 12H, aromatic) and off-resonance $^{13}$C NMR including signals at $\delta$ 43.31 (t, CH$_2$) and 74.47 (d, CH; see Experimental for remaining signals). The $^1$H NMR spectrum of 159 is not first order because of its asymmetric center.

Phenoxide is a better leaving group than methoxide, and thus the possible conversion of 8-lithio-1-phenoxyethylmethyl naphthalene (160) to 1 was studied. The precursor to 160, phenyl methyl ether (161), is synthesized from 8-bromo-1-bromomethyl naphthalene (158) and sodium phenoxide in acetonitrile (88%, Eq. 68). Reaction of a tetrahydrofuran solution of 161 at -33°C with 1 equivalent of n-butyllithium followed by refluxing produces $\alpha$-(n-butyl)-1-naphthylmethyl phenyl ether (162, 25%) and 1-naphthylmethyl phenyl ether (163, 23%, Eq. 68).

\[
\begin{align*}
\text{Br} & \quad \text{CH}_2\text{Br} & \quad \text{Br} & \quad \text{CH}_2\text{O}\Phi \\
\text{158} & \quad & \text{161} & \\
\text{NaO}\Phi & \quad & & \\
& \quad & & \\
n-\text{BuLi} & \quad (-33)^\circ \text{C}-66^\circ \text{C} & \quad & \text{162} \\
& & & \text{163}
\end{align*}
\]

The structure of 162 is assigned from its exact mass and spectral properties including $^1$H NMR absorptions at $\delta$ 0.68-2.20 (m, 9H, n-butyl), 5.80 (t, 1H, CHO, $J = 6$ Hz), 6.79-7.92 (m, 11H, aromatic), and 8.00-8.23 (m, 1H, peri-hydrogen). Presumably 162 results from initial
lithium-bromide exchange to 160 followed by proton transfer, either intramolecularly or intermolecularly, from the benzyl methylene forming 164 (Scheme 9). Alkylation of 164 with n-butyl bromide, formed in the initial lithium-halogen exchange, gives 162. 1-Naphthylmethyl phenyl ether (163) results from protonation of 160 or 164.

Using t-butyllithium for the lithium-bromide exchange (to avoid the interference of alkyl halide by-products) with 161 in diethyl ether/tetramethylethlenediamine affords 1H-cyclobuta[de]napthalene (1, 7%), 1,2-di(1-naphthyl)ethylene (131, 12%) and 1-naphthylmethyl phenyl ether (163, 21%, Eq. 69). In the absence of tetramethylethlenediamine, only 131 (3%) and 163 (30%) are obtained and are believed to originate from 164 via processes discussed earlier. It is assumed that 1 results from intramolecular displacement of phenoxide in 160.

Providing a better leaving group than phenoxide, perhaps benzoate, may lead to a better yield of 1. 8-Bromo-1-naphthylmethyl benzoate (165) is prepared from 8-bromo-1-naphthalenemethanol (140), pyridine and benzoyl chloride (88%, Eq. 70). Lithium-bromide exchange between

\[
\begin{align*}
\text{Br} & \quad \text{CH}_2\text{OH} & \quad \text{O}^\text{CCl} \quad \text{py} & \quad \text{Br} & \quad \text{CH}_2\text{O}_2\text{C}^\phi \\
& & & & (70)
\end{align*}
\]
165 and tert-butyllithium at -78°C in diethyl ether/tetramethylethylenediamine and then refluxing gives 1-phenyl-1H,3Hnaphtho[1,8-cd]pyran-1-ol (166, 59%) and 1-naphthalenemethanol (167, 23%, Eq. 71). Structural assignment of 166 is made from its combustion analysis, spectral features (see Experimental) and its preference for the hemi-ketal form. The structure is confirmed by the absence of IR carbonyl stretching frequency and the ¹H NMR spectrum of its benzylic moiety as an AB pattern centered at δ 5.15 (J = 15 Hz).

Pyranol 166 apparently results from attack of the 8-lithio-moiety of 168 on the benzoate ester function, either intra- or intermolecularly, giving 169 (Scheme 10) or 170 and 171. Hydrolytic work up affords 166 and 157.
Alkyl lithium reagents add to aldehyde p-tosylhydrazone salts with the loss of lithium p-toluenesulfinate and nitrogen to yield hydrocarbons upon work up (Eq. 72).\textsuperscript{45} It is conceivable that a similar intramolecular process will occur with lithium 8-lithio-1-naphthaldehyde p-tosylhydrazone (172) to yield 142. Treatment of 8-bromo-1-naphthaldehyde p-tosylhydrazone (9) in diethyl ether at -78°C with \textit{t}-butyllithium, either 3 equivalents or an excess, results in 1-neopentyl naphthalene (142, Eq. 73). The absence of bromine in the product indicates that lithium-bromide exchange occurs to give 172 (Scheme II). The aldehyde tosylhydrazone moiety in 172 then reacts with \textit{t}-butyllithium rather than intramolecularly, and upon loss of lithium p-toluenesulfinate and nitrogen yields anion 173 which gives 142 on work up.

Similar processes occur when n-butyllithium reacts with 9 in diethyl ether. The 8-lithio-alpha-lithio-1-n-pentynaphthalene (174) formed from addition of n-butyllithium to lithio 8-lithio-1-naphthaldehyde p-tosylhydrazonate (175) then reacts with n-butyrbromide and 5-(1-naphthyl)nonane (176, 38%) results after hydrolysis (Eq. 74). Identification of 176 is based on 1H NMR and mass spectral data.

A synthesis of 1H-cyclobuta[de]naphthalene (1) based on 1-metal-lomethyl-7,8-naphthylene (177) was then investigated (Eq.75). Benzocyclobutanes 178 and 179 are obtained via similar intramolecular cyclizations from reactions of o-chlorohydrocinnamondinitile (180) and ethyl o-chlorohydrocinnamate (181) with potassium amide.

Elimination-addition of 8-bromo-1-naphthylacetonitrile (182) with potassium amide affords 7-amino-1-naphthylacetonitrile (183, 24%) and 8-amino-1-naphthylacetonitrile (134, 13%, Eq. 76) along with recovered 182 (27%). None of the desired 1-cyano-1H-cyclobuta[de]-naphthalene is observed. Amines 183 and 184 are identified from their $^1$H NMR, IR, [for 184, 3460, 3370(NH), and 2250(CN); for 183, 3460, 3380 (NH) and 2250(CN)] and mass spectra, m/e 182 ($M^+$) for both 183 and 184.

The downfield shift of the benzylic methylene signal in the $^1$H NMR of

\[ 182 \xrightarrow{\text{NaNH}_2} 185 \]
184 (4.05) as compared to 183 (δ 3.90) confirms the positional assignments of the amine moieties of 183 and 184. It is likely that amines 183 and 184 result from aryne 185 formed from dehydrobromination of 182.


Diradical 186 might close to 1H-cyclobuta[de]naphthalene (1).

A route to 182 would be thermal or photochemical elimination of nitrogen, carbon monoxide or sulfur dioxide from precursors 187, 188 and 189, respectively.

\[
\text{N-Isopropylidene-1-aminonaphtho[1,8-de]triazene (190) photochemically eliminates two molecules of nitrogen to give 1-isopropenylnaph-}
\]

\[
\text{190} \xrightarrow{hv} \text{191} \rightarrow \text{192}
\]
A similar process with N-methylidene-1-aminonaphtho[1,8-de]triazene (193) would afford diradical 186 which may then give 1. Elimination of nitrogen from 193 would involve 187 and was thought to be an easier route to 186 than from 187 which prefers to exist in its tautomeric form 194. Synthesis of 193 is shown in Scheme 12.

Diazotization of 1,8-diaminonaphthalene (195) gives 1H-naphtho[1,8-de]triazene (196, 100%) which is aminated by hydroxylamine-O-sulfonic acid and potassium hydroxide to give 1-aminonaphtho[1,8-de]-

Scheme 12
triazene (6, 16%). Condensation of 6 with formaldehyde affords 
N-methylidene-l-aminonaphtho[1,8-de]triazene (193, 56%). Photolysis 
of 193 in benzene, however, produces only intractables of high mole­
cular weight. No evidence for 1 is found.

The next system studied was 2H-naphtho[1,8-bc]thiophene-1,1-
dioxide (189) and its synthesis is summarized in Scheme 13. The hydrox-
amic acid resulting from 1,8-naphthalic anhydride and hydroxylamine is 
tosylated, refluxed with base (Lossen Rearrangement) and acidification 
(-CO₂) yields 2-oxo-2H-benzo[cd]indole (197, 62%). Basic hydrolysis of 
Scheme 13

amide 197, diazotization and sulfurization with potassium ethyl xanthate 
gives 2-oxo-2H-naphtho[1,8-bc]thiophene (198, 35%) which is reduced with 
sodium borohydride/boron trifluoride-etherate to 2H-naphtho[1,8-bc]thio-
phene (199, 47%). Oxidation of 199 with m-chloroperoxybenzoic acid gives 2H-naphtho[1,8-bc]thiophene-1,1-dioxide (189, 80%).

A practical alternate synthesis of thiophene 199 (52%) presently developed involves bromide displacement from 8-bromo-1-bromomethylnaphthalene (158) by sodium sulfide (Eq. 78).

\[
\begin{align*}
\text{Br} & \quad \text{CH}_2\text{Br} \\
\text{Na}_2\text{S} & \quad \text{DMF} \\
\text{158} & \quad \text{199}
\end{align*}
\]

A similar displacement occurs with hydrazine and (8-bromo-1-naphthyl) phenyl ketone to give 3-phenyl-1H-benzo[de]cinnoline (200, 16%, Eq. 79). Formation of 200 involves condensation of hydrazine with 201 to give

\[
\begin{align*}
\text{Br} & \quad \text{O} \quad \text{C} \quad \text{Ar} \\
\text{NH}_2\text{NH}_2 & \quad \Delta \\
\text{201} & \quad \text{202} \quad \text{200}
\end{align*}
\]

hydrazone 202 which reacts then intramolecularly to give 200.

The thermal and photochemical behavior of sulfone 189 was then studied. Photolysis of 189 in benzene results in evolution of sulfur

\[
\begin{align*}
\text{CH}_2\text{S}=\text{O} & \quad \text{hv} \\
\text{189} & \quad \text{1} \quad \text{198}
\end{align*}
\]
dioxide; however, only an amorphous brown solid is obtained along with major recovery of initial 189 (Eq. 80).

Upon pyrolysis of 189 at 750°C at 0.2-0.3 mm, 1H-cyclobuta[de]-naphthalene (1), intrace amounts, and 2-oxo-2H-naphtho[1,8-bc]thiophene (198, 19%) are isolated. Hydrocarbon 1 probably arises from elimination of sulfur dioxide to give biradical 186 which then closes to 1.

A reasonable explanation for 198 from 189 is cleavage of the carbon sulfur bond in 189 to diradical 203 which forms sultine 204 (Scheme 14). Rupture of the oxygen-sulfur bond in 204 produces biradical 205 and aldehyde 206 is formed from hydrogen atom transfer.

\[ \text{Scheme 14} \]

\[
\begin{align*}
189 & \rightarrow 203 \rightarrow 204 \rightarrow 205 \\
& \rightarrow 206 \rightarrow 207 \\
& \rightarrow 198
\end{align*}
\]

Attack of the sulfur atom on the peri-aldehyde moiety in 206 followed by hydrogen migration gives 207 which loses water to form thiolactone.
198. Alternately, the 206 to 198 rearrangement may involve hemiacetal 208 which loses water and then rearranges to 198. Analogous sulfone to sultine rearrangements have been observed and a process similar to that for conversion of sultine 204 to thiolactone 198 has been postulated in the thermolysis of benzo[l]thiophene-1,1-dioxide to benzothiete 209 (Scheme 15).

Scheme 15


Acenaphthenone (210) is also pyrolyzed in an attempt to eliminate carbon monoxide. At 750°C and 0.6-0.7 mm, however, 210 (95%) is recovered.
During the present investigation, 1H-cyclobuta[d]naphthalene (1) was reported to be a product (40%) of flash vacuum pyrolysis (400-800°C; 10^{-4} Torr) of sodium 1-naphthaldehyde p-tosylhydrazonate (211, Eq. 81). The method is of limited preparative value because of the low pressures and the special equipment needed. The intermediacy of 1-naphthylidazomethane (212) in the above synthesis was presumed upon demonstrating its thermal decomposition to 1. Sodium 2-naphthaldehyde p-tosylhydrazonate also thermolyzes to 1, although in lower yield, thus implying further that 1-naphthylcarbene (14) is the actual precursor to 1.

\[
\begin{align*}
\text{Na} & \quad \text{CHNNTs} \\
\begin{array}{c}
\text{211} \\
\end{array} & \rightarrow \\
\begin{array}{c}
\text{CHN}_2 \\
\end{array} & \rightarrow \\
\begin{array}{c}
\ddot{\text{CH}} \\
\end{array} & \rightarrow \\
\begin{array}{c}
\text{1} \\
\end{array}
\end{align*}
\]

(81)

\[
\begin{align*}
\text{Na} & \quad \text{CHNNTs} \\
\begin{array}{c}
\text{211} \\
\end{array} & \rightarrow \\
\begin{array}{c}
\text{CHN}_2 \\
\end{array} & \rightarrow \\
\begin{array}{c}
\ddot{\text{CH}} \\
\end{array}
\end{align*}
\]

50. a) This is the first report of the interconversion of 2-naphthyl carbene to 1-naphthylcarbene. Apparently the higher temperatures of the pyrolysis minimize the barriers to rearrangement experienced in other experiments (see Historical).

b) Ref. 6
As part of the present program, study was initiated of a large scale synthesis of \( \text{JL} \) based on generation of 1-naphthylcarbene. It was also hoped that such a process would provide more workable routes to peri-methanoarenes than methods based on peri-dilithioarenes (as previously discussed) for which preparation of peri-dibromo or diidoarene precursors are difficult.

The low volatilities of salt 211 and of diazomethane 212, even at very low pressures, necessitates their direct introduction into the pyrolysis zone as free flowing solids. To avoid the difficulties in handling large quantities of a hygroscopic salt or an unstable diazo compound and the use of very high temperatures and special equipment to attain the low pressures, generation of 14 from 1-naphthaldehyde p-tosylhydrazone under more manageable conditions was explored.

Pyrolysis of 211 at 280-290°C in evacuated flasks upon immersion into a salt bath and collection of the distillate fails to produce 1. 1-Naphthonitrile (213, 14%) and 1-naphthaldehyde (214, 5%) were the only volatile products isolated (Eq. 82).

\[
\begin{align*}
\text{Na} & \quad \text{CHNNTs} \\
\begin{array}{c}
\text{211} \\
\text{280-290°C} \\
\end{array} & \quad \begin{array}{c}
\text{CHO} \\
\text{214} \\
\text{C=N} \\
\text{213} \\
\end{array}
\end{align*}
\]

(82)

Nitriles and aldehydes have been previously observed in thermolyses of

tosylhydrazone salts and are believed to result from decomposition of intermediate azines and alkyl sulfinates.\textsuperscript{51}

Photolysis of lithium 1-naphthaldehyde p-tosylhydrazone as prepared from t-butyllithium and 1-naphthaldehyde p-tosylhydrazone (13) was then investigated. Irradiation in diethyl ether yields, however, 1-neopentylnaphthalene (142, 8%), 1,2-di(1-α-naphthyl)ethane (143, 8%) and ethyl α-(1-naphthylmethyl)ethyl ether (215, 27%, Eq. 83). Attack of t-butyllithium on 13, as previously discussed, presumably gives 142. Ethane 143 possibly results from environmental hydrogen atom abstraction by 1-naphthylidene (14) followed by

\[
\begin{align*}
\text{CH} &= \text{NNHTs} \\
\text{13} & \xrightarrow{1) t-\text{BuLi}} \xrightarrow{2) \text{hv, Et}_2\text{O}} \text{142} + \left[ \text{143} \right]_2 + \text{215} \\
\end{align*}
\]

dimerization of 1-naphthylmethyl radicals. Insertion of 14 into an α-C-H bond of the solvent will result in 215.

The structure of 215 is deduced from its exact mass, 200 MHz \(^1\text{H} \text{NMR}\) absorptions at \(\delta\ 1.132(t, 3\text{H}, \text{OCH}_2\text{CH}_3, J=7\text{Hz}), 1.145(d, 3\text{H}, \text{CH}_2\text{CH(CH}_3)_0, J=6\text{Hz}), 3.01(m, 1\text{H}, \text{one of the benzylic protons}), 3.48(m, 3\text{H}, \text{one of the benzylic protons and OCH}_2\text{CH}_3), 3.79(m, 1\text{H}, \text{CH}_2\text{CH(CH}_3)-), \text{and 7.3-7.5(m, 4H, aromatic), 3 peri-hydrogen multiplets at }\delta\ 7.69-7.74,\)
7.81-7.85, and 8.03-8.08 (see Experimental for specific assignments), and off-resonance $^{13}$C NMR signals at 6 15.63 (q, CH$_3$), 20.15 (q, CH$_3$), 40.49 (t, CH$_2$CH), 64.18 (t, OCH$_2$), and 75.83 (d, CH$_2$CH(CH$_3$)-). The $^1$H NMR spectrum of 215 is not first order because of its asymmetric center. The resonances of each hydrogen of the benzylic methylene as well as of the methylene component of the ethyl group are not equivalent. Specific assignments of the multiplets are based on decoupling experiments.

These and other experiments suggest that 1-naphthylmethylenec (14) must be generated in the gas phase at high temperature to form 1. Since tetrazoles have been thermally decomposed to carbenes, the pyrolytic behavior of 5H-(1-naphthyl)tetrazole (216) was then examined. Tetrazole 216 is a crystalline solid readily prepared from hydrazoic acid and 1-naphthonitrile (Eq. 84). Decomposition of 216 however in a quartz tube packed with quartz chips and heated to 600°C at 0.05-0.1 mm

\[
\begin{align*}
\text{C}=\text{N} & \quad \text{HN}_3 \quad \text{N}=\text{N} \\
\text{213} & \quad \rightarrow \quad \text{216} & \quad \Delta \rightarrow \quad \text{213}
\end{align*}
\]

(84)

does not yield 1H-cyclobuta[de]naphthalene. Only 1-naphthonitrile, presumably from loss of hydrazoic acid from 216, was formed (Eq. 84).

A desirable property of the carbene precursor required for the present investigation is volatility at a readily accessible pressure, allowing its introduction into the hot zone via simple volatilization, and of course an expedient synthesis. The observation that products
resulting from alkyl \( \alpha \)-lithio-\( \beta \)-naphthylmethyl ethers (217) are produced from 8-bromo-\( \beta \)-alkoxymethylnaphthalenes and alkyllithiums (Eq. 85).

\[
\begin{align*}
\text{Br} \quad \text{CH}_2\text{OR} & \quad \xrightarrow{\text{RLi}} \quad \text{Li} \quad \text{CH}_2\text{OR} \\
& \quad \rightarrow \quad \text{H} \quad \text{CH}_2\text{OR} \\
\end{align*}
\]

(85)

\(217\)

suggested that 217 may be used to prepare other \( \alpha \)-metalloalkoxymethyl-naphthalenes (218) which upon pyrolysis might fragment to \( \beta \)-naphthylidene and metal alkoxides (Eq. 86). There is literature precedence for such eliminations (see Historical) and efforts at exploiting this hypothesis will now be described.

\[
\begin{align*}
217 & \quad \xrightarrow{\text{R'MX}} \quad \text{MR'CHOR} \\
& \quad \xrightarrow{\Delta} \quad \text{CH} \quad \text{CH} \\
& \quad + \quad \text{R'MOR} \\
\end{align*}
\]

(86)

\(217\)

\(218\)

\(M=\text{Si, Sn, Hg}\)

1-Methoxymethylnaphthalene (136) is preparable (86%) from commercially available 1-naphthalenemethanol via a Williamson ether synthesis (sodium hydride and then dimethyl sulfate). Deprotonation of 136 with \text{t-butyl}lithium in tetramethylethlenediamine/diethyl ether at \(-78^\circ\text{C}\) and trapping the resulting dark purple-black anion (219) with chlorotrimethylsilane gives [methoxy(1-naphthyl)methyl]trimethylsilane (220) quantitatively (Eq. 87).

52 The structure of 220 is determined from its elemental analysis, exact mass and spectral properties.
including $^1$H NMR absorptions at $\delta$ -0.02(s, 9H, Si(CH$_3$)$_3$), 3.33(s, 3H, OCH$_3$), 4.83(s, 1H, CH), and 7.3-8.2(m, 7H, aromatic).


The thermal behavior of 220 was then investigated. Vacuum pyrolysis of 220 is achieved by distillation at 0.05-0.10 mm through a quartz tube at 650°C. 1H-Cyclobuta[de]naphthalene (1) is the major product.
(39%) accompanied by naphthalene (113, 5%), 1-methylnaphthalene (221, 3%), 1-methoxymethylnaphthalene (136, 8%), 1-naphthaldehyde (214, 9%) and α-methyl-1-naphthalenemethanol (152, 7%, Eq. 88). 1H-Cyclobuta-

\[
\begin{align*}
\text{220} & \xrightarrow{650^\circ C, 0.05-0.1 \text{ mm}} \text{[de]naphthalene (1)} + \text{naphthalene (113)} + \text{1-methylnaphthalene (221)} \\
& \quad + \text{1-naphthaldehyde (214)} + \text{1-methoxymethylnaphthalene (136)} + \text{α-methyl-1-naphthalenemethanol (152)}
\end{align*}
\]

[de]naphthalene (1) is obtainable, after chromatography of the pyrolysate, as the major component (60-70% by 1H NMR) of a mixture containing naphthalene, 1-methylnaphthalene and unidentified minor products. This mixture can be used conveniently for preparation of derivatives of as demonstrated by nitration with acetyl nitrate to give pure 4-nitro-1H-cyclobuta[de]naphthalene 222. Further purification (90%) of can be effected by fractional distillation, preparative VPC (5% SE-30, isothermal at 140°C), or formation of the picrate of 1 followed by recrystallization and decomposition of the complex on silica gel.

Pyrolysis of 220 is conducted with simple equipment (see Experimental) at readily attainable temperatures and pressures, and as much as 10 g of 220 have been pyrolyzed in a single experiment. Since the synthesis of 220 is nearly quantitative from commercially available material, the method represents a short, efficient route to sizeable
quantities of 1H-cyclobuta[de]naphthalene.

Varying the pyrolysis temperature and pressure greatly affects the yield of 1. As shown in Table 9, temperatures of at least 500°C are required and the best yields are obtained at lower pressures (< 0.10 mm). Shorter contact times, i.e. lower pressures, also result in less minor products. Temperatures greater than 750°C, even at low pressures, give poor yields of 1 and tar formation is extensive.

The mechanism for formation of 1 is presumed to involve elimination of methoxytrimethylsilane from 220 to form 1-naphthylcarbene (14) which then inserts into the peri-C-H bond of the naphthalene ring (Eq. 89). Although the details of the insertion are not known, a rational explanation is attack of the carbenic center on the naphthalene π-

\[
\begin{align*}
220 & \xrightarrow{-(CH_3)_3SiOCH_3} 14 & 1 \\
& \text{(89)}
\end{align*}
\]

system at C_8 followed by hydrogen migration from C_8 to the bridging carbon (223 Scheme 16). Alternatively, the carbene might attack via its triplet and thus involve biradical 224. Intramolecular hydrogen abstraction-recombination via biradical 186, although intuitively less attractive, cannot be excluded at this time.

1-Methylnaphthalene 221 presumably results from environmental hydrogen transfer to 1-naphthylcarbene (14). The other minor products are readily explained by non-carbenic mechanisms. α-Methyl-1-naphthalenemethanol (152) is believed to arise by silicon complexation as in
TABLE 9  
Effect of Pyrolysis Temperature and Pressure on Yield of 1 from 220

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Pressure (mm)</th>
<th>Yield (%)(^a) 1, (%) SM(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>434-440</td>
<td>2.0-2.7</td>
<td>0, 59</td>
</tr>
<tr>
<td>490-510</td>
<td>0.005</td>
<td>0, 92</td>
</tr>
<tr>
<td>500-510</td>
<td>2.0</td>
<td>6-11(9-12), 35</td>
</tr>
<tr>
<td>500-510</td>
<td>0.35-0.40</td>
<td>17(35), 51</td>
</tr>
<tr>
<td>510-530</td>
<td>0.15-0.20</td>
<td>5(17), 69</td>
</tr>
<tr>
<td>560</td>
<td>0.07-0.10</td>
<td>11(32), 65</td>
</tr>
<tr>
<td>650</td>
<td>0.25-0.30</td>
<td>22, N.D.(^c)</td>
</tr>
<tr>
<td>650</td>
<td>0.10-0.15</td>
<td>32, N.D.</td>
</tr>
<tr>
<td>650</td>
<td>0.05-0.15</td>
<td>39, N.D.</td>
</tr>
<tr>
<td>695-700</td>
<td>0.05-0.07</td>
<td>27, N.D.</td>
</tr>
<tr>
<td>750</td>
<td>0.05-0.07</td>
<td>4(^d), N.D.</td>
</tr>
<tr>
<td>800</td>
<td>3</td>
<td>0, N.D.</td>
</tr>
</tbody>
</table>

\(^a\) Numbers in parentheses represent yield of 1 based on recovered starting material.
\(^b\) SM represents starting material.
\(^c\) N.D. equals not detected.
\(^d\) Only 8% of a complex mixture.
(as discussed in the Historical for similar rearrangements) and isomerization (similar to a Wittig Rearrangement) to silyl ether 226 (Eq. 90), which cleaves hydrolytically on chromatography. 1-Naphthaldehyde probably comes from β-elimination of tetramethylsilane, either by radical processes or possibly involving 225. 1-Methoxymethylnaphthalene is assumed to result from homolytic cleavage of the Si-C bond in 220 and hydrogen scavenging from the environment. The source of naphthalene, 113, is unknown.
To obtain evidence that a carbene is formed in the pyrolysis of 220, the thermal chemistry of [methoxy(2-naphthyl)methyl]trimethylsilane (227) was studied. The synthesis of 227 is shown in Scheme 17. Bromination of 2-methylnaphthalene with N-bromosuccinimide yields 2-bromomethylnaphthalene (228, 65%), displacement of which by methoxide in methanol/tetrahydrofuran affords 2-methoxymethylnaphthalene (229, 75%). Deprotonation of 229 with t-butyllithium/tetramethylethylene-diamine and trapping the intermediate (black) anion with chlorotrimethylsilane yields 227 (82%). Identification of 227 is based on its elemental analysis and spectral properties including exact mass. The $^1$H NMR spectra consists of three alkyl C-H resonances at $\delta$ 0.23(s, 9H, Si(CH$_3$)$_3$), 3.48(s, 3H, OCH$_3$) and 4.18(s, 1H, CHOCH$_3$) in agreement with the assigned structure.

Pyrolysis of 227 at 640-650°C (0.2-0.3 mm) does give 1, albeit in lower yield than from 220, accompanied by intractables (Eq. 91). The difference in the yields of 1 from 117 and 123 may be attributable
to the difficulty in the rearrangement of 2-naphthylcarbene to 1-naphthylcarbene for reasons discussed in the Historical.\(^5\)

The thermal behavior of substituted \([\text{methoxy}(1\text{-naphthyl})\text{methyl}]\)-trimethylsilanes (230) then became of interest for synthesis of substituted 1H-cyclobuta[de]naphthalenes (231, Eq. 92).

Many derivatives of 231 have been prepared by electrophilic aromatic substitution reactions (see Historical). This method, however provides only 4- (and 5-for disubstitution) substituted derivatives. Thus, 1H-cyclobuta[de]naphthalene with substituents in ortho (2) or meta (3) positions are currently unavailable and the above sequence (Eq. 92) was viewed as potentially useful. It was also of interest to explore

\[ \phi\text{-CH(Si(CH\(_3\))\(_3\))OH} \longrightarrow \phi\text{CH} + \text{CH\(_3\))\(_3\)SiOH} \]

53. During the course of this investigation, α-trimethylsilylbenzyl alcohols were reported to thermolyze to phenylcarbenes (A. Sekiguchi and W. Ando, J. Org. Chem., 45, 5286 (1980)).
whether carbene formation or ring closure could tolerate, or perhaps be enhanced by, ring substituents.

The first molecule studied was [methoxy(4-methoxy-1-naphthyl)-methyl]trimethylsilane (232). Synthesis of 232 is similar to that for 220 and 227. Commercial 4-methoxy-1-naphthaldehyde (233) is reduced with sodium borohydride to 4-methoxy-1-naphthalenemethanol (234, 100%) which is converted to 4-methoxy-1-methoxymethylnaphthalene (235, 87%) by reaction with hydrogen chloride followed by displacement of chloride by methoxide (Scheme 18). The \(_{\text{t}}\)-butyllithium/tetramethylethylenediamine complex efficiently deprotonates 235, and the resulting dark purple anion reacts with chlorotrimethylsilane to form 232 (89%, 77% yield from 233). The structure of 232 is confirmed by elemental analysis and spectral data including alkyl \(^1\)H NMR resonances at \(\delta\) 0.02(s, 9H, Si-(CH\(_3\))\(_3\)), 3.31(s, 3H, OCH\(_3\)), 4.00(s, 3H, OCH\(_3\)) and 4.69(s, 1H, CHOCH\(_3\)), indicating benzylic substitution.
Pyrolysis of 232 at 510°C and 0.05-0.1 mm yields 4-methoxy-1H-cyclobuta[de]napthalene (236), a pale yellow liquid, in 42% yield (Eq. 93). Bridged naphthalene 236 is storable at 0°C but decomposes when open to the atmosphere at room temperature. Product 236 is assigned from its elemental analysis, exact mass, 1H NMR absorptions at δ 3.90(s, 3H, OCH₃), and 4.60(s, 2H, CH₂) and 13C NMR signals at 45.95(CH₂) and 55.76(OCH₃), see Experimental for further spectral data. Methanonaphthalene 236 represents the first 1H-cyclobuta[de]napthalene with an oxygen substituent on the aromatic ring. Presumably 236 is formed from 4-methoxy-1-naphthylidene (237, generated from 232 by loss of methoxytrimethylsilane) via reaction at the C₈-H peri position by a process similar to that for formation of 1.

Conversion of 232 to 236 is much more sensitive to the pyrolysis temperature (Table 10) than is conversion of 220 to 1. Temperatures greater than 450°C are required to eliminate methoxytrimethylsilane from 232; however, at 520°C extensive decomposition to tars occurs.

To probe the preference of 1-naphthylmethylene for reaction with an ortho substituent compared to a peri C₈-H center, pyrolysis of [methoxy(2-methoxy-1-naphthyl)methyl]trimethylsilane (238) was investigated. Silane 238 is synthesized in a manner similar to 220 and 227
TABLE 10

Effect of Pyrolysis Temperature and Pressure on Yield of $1$ from $232$

<table>
<thead>
<tr>
<th>Temp ($^\circ$C)</th>
<th>Pressure (mm)</th>
<th>Yield (%)$^a$ $236$, SM$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>445-455</td>
<td>0.2-0.3</td>
<td>87</td>
</tr>
<tr>
<td>510</td>
<td>0.05-0.10</td>
<td>27(42) 35</td>
</tr>
<tr>
<td>510</td>
<td>0.05-0.10</td>
<td>30(37) 13</td>
</tr>
<tr>
<td>520</td>
<td>0.05-0.10</td>
<td>27(35) 21</td>
</tr>
<tr>
<td>535-545</td>
<td>0.1-0.4</td>
<td>6 10</td>
</tr>
<tr>
<td>560</td>
<td>0.2-0.3</td>
<td>trace</td>
</tr>
</tbody>
</table>

a) Numbers in parentheses represent yields of $236$ based on recovered starting material.

b) SM denotes starting material.
Reduction of 2-methoxy-1-naphthoic acid (239) with lithium aluminum hydride yields 2-methoxy-1-naphthalenemethanol (240, 97%). Treatment of 240 with anhydrous hydrogen chloride gives 1-chloromethyl-2-methoxynaphthalene which is converted to 2-methoxy-1-methoxy- methylnaphthalene (241, 97%) by sodium methoxide in methanol/tetrahydrofuran.

The deprotonation/trimethylsilylation procedure used for preparing 220, 227 and 232 is not as successful with 238. The color of anion 242, as generated from 241, and the tert-butyllithium/tetramethylethylenediamine complex at -78°C, is completely discharged upon addition of chlorotrimethylsilane at -78°C. A yield of 238 of only 25-30% is obtained, however, along with initial ether 241. A 55% yield of 238 (89% based on recovered 241) results if the ethereal solution of anion 242 is warmed to -30°C before addition of chlorotrimethylsilane. Again 36% of 241 is recovered. Allowing the anion solution to warm to 0°C before quenching with chlorotrimethylsilane results in a complex mixture
of products. The low yield (compared to 220, 227 and 232) of 238 may reflect some steric inhibition of silylation of anion 242 by its o-methoxy substituent, and proton transfer from chlorotrimethylsilane to anion 242 may be occurring. Such deprotonation of chlorotrimethylsilane has been previously observed. Adduct 238 is identified by its elemental analysis, exact mass and spectral properties including $^1$H NMR absorptions at δ 0.02 (s, 9H, Si(CH$_3$)$_3$), 3.24 (s, 3H, OCH$_3$), 3.88 (s, 3H, OCH$_3$), 5.18 (s, 1H, CHOCH$_3$) and 7.2-8.8 (m, 6H, aromatic).

When 238 is pyrolyzed at 610°C and 0.05-0.1 mm, naphtho[2,1-b]-furan (243, 31%) and 1,2-dihydronaphtho[2,1-b]furan (244, 64%), are isolated along with starting material (3%, Eq. 94). The structures of 243 and 244 are assigned from their exact masses and by comparison of their $^1$H NMR, IR and mass spectra with literature values.

Ether 244 apparently results from insertion of 2-methoxy-1-naphthylcarbene (245) into a C-H bond of its o-methoxy group. Dehydrogenation of 244 gives 243. Such cyclizations have been reported for
arylcarnes bearing o-dialkylamino, o-thioalkyl, o-methoxy, and some o-alkyl substituents. The material balance for the above reaction is excellent and there was no evidence for 2-methoxy-1H-cyclobuta[de]-naphthalene.


The behavior of 6-methyl-1-naphthylidene (246), as generated from [methoxy(6-methyl-1-naphthyl)methyl]trimethylsilane (247) was then examined. Synthesis of 247 proceeds in excellent overall yield (Scheme 20) and is uneventful.

6-Methyl-1-naphthalenemethanol (249, 100%) is obtained from 6-methyl-1-naphthoic acid (248) after reduction with borane-dimethylsulfide complex and is methylated via sodium hydride and dimethyl sulfate to yield 6-methyl-1-methoxymethylnaphthalene (250, 78%). [Methoxy-(6-methyl-1-naphthyl)methyl]trimethylsilane (247) is prepared by (100%)}
deprotonation of 250 with t-butyllithium/tetramethylethylenediamine and reaction of the red-black anion generated with chlorotrimethylsilane. Assignment of 247 is based on its elemental analysis, exact mass and spectral properties. The $^1$H NMR spectrum consists of absorptions at -0.08(s, 9H, Si(CH$_3$)$_3$), 2.41(s, 3H, CH$_3$) 3.19(s, 3H, OCH$_3$), 4.67(s, 1H, CHOCH$_3$) and 7.1-8.0(m, 6H, aromatic).

Pyrolysis of 247 at 510°C is interesting in that two isomeric hydrocarbons possessing the 1,8-methanonaphthalene structure are generated, in an 11:1 ratio, (25% combined yield) along with 1,6-dimethylnaphthalene (251, 2%). The three products could be partially separated by VPC allowing 251 and the major peri-bridged naphthalene 252 to be isolated pure. However, the minor isomer 253 could not be obtained free of 251 or 252 and its analysis is based on spectra acquired from mixtures of 251 and 253 or 252 and 253 in which 253 is the major component. Hydrocarbon 251 is identified by comparison of its $^1$H NMR spectrum and VPC retention times to those of authentic 1,6-dimethylnaphthalene.

The major 1,8-dimethanonaphthalene obtained is identified as 3-methyl-1H-cyclobuta[de]naphthalene (252) and the minor isomer as 2-methyl-1H-cyclobuta[de]naphthalene (253, Eq. 95). The structural
assignment of 252 is based on spectral, exact mass and elemental analyses. The most significant spectral data are the $^1$H NMR absorptions at $\delta$ 2.55(s, 3H, CH$_3$), 4.76(s, 2H, CH$_2$) and 6.97-7.48(m, 5H, aromatic) and $^{13}$C NMR signals at $\delta$ 23.66 (CH$_3$) and 47.10(CH$_2$). Isomer 253 is assigned from its $^1$H NMR absorptions at 2.38(s, 3H, CH$_3$), 4.70(s, 2H, CH$_2$), 7.02(d, 1H, H-7) and 7.2-7.8(m, 4H, aromatic).

Differentiation between 252 and 253 is based on their $^1$H NMR spectra. A characteristic feature of the $^1$H NMR spectra of 1H-cyclobuta[de]naphthalenes is that the aromatic protons ortho to the peri-methylene bridge are upfield (at 5.7-7.1 ppm) from the meta and para protons (at 7.2-8.1 ppm). In the symmetrical 1-substituted-1H-cyclobuta[de]naphthalenes, the ortho protons are observed as a doublet of doublets whereas the meta and para protons appear as a multiplet. The aromatic region of 252 at 300 MHz consists of a singlet at $\delta$ 6.97 (1H), a doublet at 7.04 (1H, $J = 6$ Hz) and a multiplet at 7.35-7.48 (3H), which corresponds to a structure having two protons ortho to the 1,8-methano-bridge; H$_2$ appears as the singlet (meta coupling to H$_4$ is small) and H$_7$ as a doublet, coupled to H$_6$. In their 90 MHz spectra H$_7$ and H$_2$ partially overlap; however, H$_7$ is split into a doublet of doublets, indicating further coupling to H$_5$ and H$_2$ still appears as a singlet at 90 MHz.

The aromatic region of 253 at 90 MHz is observed as a doublet at 7.05 (1H, $J = 5$ Hz) and a multiplet at 7.3-7.9 (4H). This pattern is consistent with a structure having only one proton ortho to the peri-methylene bridge, H$_7$ which is split by H$_6$. However, coupling between H$_5$ and H$_7$ is too small to be observed.
A rational explanation (Scheme 21) for formation of 251, 252, and 253 involves loss of methoxytrimethylsilane from 247 to generate 6-methyl-1-naphthylidene (246). Hydrogen abstraction by 246 from the environment yields 1,6-dimethynaphthalene (251). Reaction of 246 at C8-H of the naphthalene nucleus gives 252. 2-Methyl-1H-cyclobuta[de]naphthalene (253) probably arises from carbene-carbene isomerization of to 7-methyl-1-naphthylmethylene (254) which undergoes ring-closure at its adjacent peri C-H position.

As seen for the pyrolyses of 220 and 232, the yields of 1,8-methanonaphthalenes 252 and 253 vary with the temperatures and pressures of the pyrolyses (Table 11). Better yields of 252 are found with lower temperatures and smaller amounts of minor products are produced making
TABLE 11

Effect of Pyrolysis Temperature and Pressure on Yields of 251, 252, and 253 from 247.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Pressure (mm)</th>
<th>Yields (%)b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>252, 253, 251, SMa</td>
</tr>
<tr>
<td>510</td>
<td>0.1-0.2</td>
<td>22(31) 3(4) 2(2) 28</td>
</tr>
<tr>
<td>540</td>
<td>0.05-0.10</td>
<td>15(20) 2(3) 1.2(1.5) 25</td>
</tr>
<tr>
<td>610-620</td>
<td>0.12-0.15</td>
<td>12 6 2 -</td>
</tr>
<tr>
<td>660-670</td>
<td>0.1-0.2</td>
<td>trace</td>
</tr>
</tbody>
</table>

a) SM denotes starting material.

b) Numbers in parentheses represent yields based on recovered starting material.
purification of 252 easier. The ratio of 252 to 253 formed as a function of pyrolysis temperature is dramatic (Table 12). Higher temperatures result in larger amounts of the product of the rearranged carbene 253 relative to 252.

An investigation was then initiated of the thermal behavior of benzannelated naphthylcarbenes as generated from methyl α-trimethylsilylaryl methyl ether precursors. The first system studied was the phenanthrene network. The pyrolytic precursor to 9-phenanthrylmethylene (255) is [methoxy(9-phenanthryl)methyl]trimethylsilane (256) and its synthesis is depicted in Scheme 22.

Addition of bromine to the phenanthrene 9,10-double bond followed by elimination of hydrogen bromide yields 9-bromophenanthrene (257, 85%). Conversion of 257 to its Grignard reagent and reaction with paraformaldehyde affords 9-phenanthrenemethanol (258, 60%) which is methylated with sodium hydride and dimethyl sulfate to 9-methoxymethylphenanthrene (258, 100%). As with the other methoxymethylenarenes studied, deprotonation of 259 with t-butyllithium/tetramethylethylene diamine at
<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Pressure (mm)</th>
<th>252/253&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>510</td>
<td>0.1-0.2</td>
<td>11</td>
</tr>
<tr>
<td>540</td>
<td>0.05-0.10</td>
<td>6.7</td>
</tr>
<tr>
<td>610-620</td>
<td>0.12-0.15</td>
<td>4.2</td>
</tr>
<tr>
<td>660-670</td>
<td>0.1-0.2</td>
<td>1.9</td>
</tr>
</tbody>
</table>

<sup>a</sup> Ratio was determined by 300 MHz NMR.
-78°C occurs exclusively at the benzylic position. The brown anion is trapped quantitatively with chlorotrimethylsilane to afford 256. The overall yield of 256 from phenanthrene is 52%.

Pyrolysis of 256 at 590°C and 0.1 mm gives two isomeric hydrocarbons, 4H-cyclobuta[jk]phenanthrene (260) and 4H-cyclopenta[def]phenanthrene (261), in a 9:1 ratio and a combined yield of 72% (Eq. 96). The major isomer 260 is obtained pure by recrystallization and is assigned from its combustion analysis, exact mass and spectral characteristics. The important features are the 1H NMR absorptions at δ 4.80(s, 2H, CH2), 7.20(d, 1H, H3 on the phenanthrene nucleus, J = 2 Hz) 7.31(s, 1H, H5), 7.5-8.5(m, 7H, aromatic), and 13C NMR absorption at 46.56(CH3) as well as the proper number of aromatic C-H and quaternary signals. Identification of 261 results from 1H NMR and HPLC comparison of the pyrolysis mixture of 260 and 261 with independently synthesized 4H-cyclopenta[def]phenanthrene (261). 4H-Cyclobuta[jk]phenanthrene (260) is a stable white crystalline material and forms a bright orange complex with 2,4,7-trinitrofluoren-9-one.

It is believed 260 arises from insertion of 9-phenanthrylidene (255) into its peri-C1-H bond (Eq. 97). 4H-Cyclopenta[def]phenanthrene (261) results from carbene-carbene rearrangement of 255 to
4-phenanthrylcarbene (262) which inserts into the C-H bond at C5. Rearrangement 255 to 262 is unique in that carbenic migration through a fused ring juncture occurs (Scheme 23).

\[
\begin{align*}
\text{255} & \xrightarrow{152} \text{260} & \xleftrightarrow{262} & \text{261}
\end{align*}
\]

The yield of 4H-cyclobuta[jk]phenanthrene (260) and the ratio of 260 to 261 vary greatly with the pyrolysis conditions (Tables 13 and 14). Indeed, no 4H-cyclopenta[def]phenanthrene (261) is produced when the pyrolysis is conducted at low conversion of starting material to product and, in general, purification of 260 is much simpler at the lower temperatures. As with 6-methyl-1-naphthyldene (246), the conversion of 256 to rearrangement product 261 increases with temperature.

Another polycyclic aromatic of interest is the pyrene system and efforts to generate 1,10-methanopyrene (263) were begun. [Methoxy(1-pyrenyl)methyl]trimethylsilane (264) was viewed as the proper precursor and its synthesis is shown in Scheme 24.

Reduction of commercially available 1-pyrenecarboxaldehyde (265) with sodium borohydride yields 1-pyrenemethanol (266, 93%). Hydrogen chloride converts alcohol 266 to 1-chloromethylpyrene which is reacted with sodium methoxide in methanol/tetrahydrofuran affording 1-methoxymethylpyrene (267, 100% from 266). The dark purple-black anion of 267, generated with t-butyllithium/tetramethylethylenediamine at
### TABLE 13

Effect of Pyrolysis Temperature on Yield of 4H-Cyclobuta [jk] -phenanthrene (260) and 4H-Cyclopenta [def] phenanthrene (261) from 256.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Pressure (mm) (or N₂ flow rate)</th>
<th>Yields (%)</th>
<th>S.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>500-520</td>
<td>5 ml/min</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>500-520</td>
<td>0.05-0.10</td>
<td>7(31); 100⁵</td>
<td>80</td>
</tr>
<tr>
<td>590</td>
<td>0.3-0.5</td>
<td>21(56); 10:1</td>
<td>63</td>
</tr>
<tr>
<td>590</td>
<td>0.10</td>
<td>37(72); 8.5:1</td>
<td>48</td>
</tr>
<tr>
<td>600</td>
<td>0.2-0.3</td>
<td>15(52); 8.5:1</td>
<td>71</td>
</tr>
<tr>
<td>600-650</td>
<td>0.2-0.4</td>
<td>35(57); 6:1</td>
<td>39</td>
</tr>
<tr>
<td>650</td>
<td>0.1-0.15</td>
<td>56(77); 4:1⁵</td>
<td>27</td>
</tr>
<tr>
<td>650</td>
<td>0.10-0.15</td>
<td>63(70); 3:1</td>
<td>10</td>
</tr>
</tbody>
</table>

---

a) Numbers in parentheses represent yield of 260 based on recovered starting material.

b) Combined yield of 260 and 261.

c) Ratio of 260 to 261 determined by 90 MHz ¹H NMR.
**TABLE 14**

Ratio of 4H-Cyclobuta[ajk]phenanthrene (260) versus 4H-Cyclopenta[def]phenanthrene (261) as a Function of Pyrolysis Temperature and Pressure

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Pressure (mm)</th>
<th>260/261&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>500-520</td>
<td>0.05-0.10</td>
<td>100</td>
</tr>
<tr>
<td>590</td>
<td>0.1</td>
<td>9</td>
</tr>
<tr>
<td>600</td>
<td>0.2-0.3</td>
<td>8.5</td>
</tr>
<tr>
<td>650</td>
<td>0.1-0.15</td>
<td>3</td>
</tr>
</tbody>
</table>

<sup>a</sup> Ratio determined by <sup>1</sup>H NMR.
Scheme 23

\[
\begin{align*}
\text{Scheme 23} & \quad \text{Diagram of chemical reactions.}
\end{align*}
\]
-78°C in diethyl ether, is quenched with chlorotrimethylsilane and [methoxy(1-pyrenyl)methyl]trimethylsilane (264, 77%) is obtained. Structure 264 is assigned on the basis of combustion and spectral data (see Experimental). The overall yield of 264 from 265 is 67%.

Volatilization of 264 through a quartz tube at 520-525°C at 0.05-0.07 mm produces 3H-cyclobuta[cd]pyrene (263) in 86% yield (Eq. 98). Identification of 263 is made from exact mass and spectral characteristics including $^1$H NMR absorptions at $\delta$ 5.19 (s, 2H, CH$_2$),
7.50(s, 1H, H\textsubscript{10} on aromatic ring), 7.62(d, 1H, H\textsubscript{2}, J = 6 Hz), and 7.8-8.2(m, 6H, aromatic) and \textsuperscript{13}C NMR signal at δ 52.97(CH\textsubscript{2}, see Experimental for remaining signals). Pyrene 263 is a white crystalline solid which colorizes on standing in air at room temperature. Combustion data suggests that 263 picks up oxygen readily (see Experimental); 263 forms an air stable bright maroon-purple complex with 2,4,7-trinitrofluoren-9-one.

The yield of 263 is very sensitive to pyrolysis temperature (Table 15). It is assumed the formation of 263 from 264 proceeds via 1-pyrenylcarbene (268) which inserts into the peri-C-H bond.

A third arene system of interest involves the anthracene moiety and efforts toward synthesis of 1H-cyclobuta[de]anthracene (269) are now described. An obvious route is by way of 9-anthrylidene (270). Pyrolysis of sodium 9-anthraldehyde p-tosylhydrazonate (271) at 500-520°C at 0.3 mm does not yield 269, however. 9-Methylanthracene (272, 20%) and intractables are obtained (Eq. 99). Environmental hydrogen abstraction by 9-anthrylcarbene (270) will account for 272. Thermolysis of 271 in chlorobenzene affords intractables.

Focus was then shifted to generation of 9-anthrylidene (270) via pyrolytic elimination of methoxytrimethylsilane from [methoxy(9-anthryl)methyl]trimethylsilane (273, Eq. 100). 9-Methoxymethylanthracene
TABLE 15
Effect of Pyrolysis Temperature and Pressure on Yield of

263 from 264

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Pressure (mm)</th>
<th>Yields (%)&lt;sup&gt;a&lt;/sup&gt; 263, SM&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>510-530</td>
<td>0.02-0.05</td>
<td>29(47) 39</td>
</tr>
<tr>
<td>520-530</td>
<td>0.02-0.05</td>
<td>27(54) 50</td>
</tr>
<tr>
<td>520-540</td>
<td>0.05-0.10</td>
<td>31(47) 34</td>
</tr>
<tr>
<td>520-525</td>
<td>0.05-0.07</td>
<td>32(86) 62</td>
</tr>
<tr>
<td>660</td>
<td>0.05-0.20</td>
<td>16&lt;sup&gt;c&lt;/sup&gt; 26</td>
</tr>
</tbody>
</table>

<sup>a</sup> Numbers in parentheses represent yields of 263 based on recovered starting material.

<sup>b</sup> SM denotes starting material.

<sup>c</sup> Only 35% of a complex mixture.
(274) is preparable by reaction of technical 9-anthracenemethanol (275) with thionyl chloride followed by sodium methoxide in tetrahydrofuran/methanol (63% yield from 275, Eq. 101).

Treatment of 274 with t-butyllithium/tetramethylethylenediamine in diethyl ether at -78°C followed by chlorotrimethylsilane does not give the expected [methoxy(9-anthryl)methyl]trimethylsilane (273). [9,10-Dihydro-10-(methoxymethylene)-9-anthryl]trimethylsilane (276, 40%) and 9-neopentylantracene (277, 16%) are obtained (Eq. 102).
Hydrocarbon 277 is identified from its exact mass and upon comparison of its physical and spectral properties with those reported (see Experimental). A rationalization for formation of 277 is electron transfer from t-butyllithium to 274 forming the t-butyl radical and radical anion 278 which loses methoxide yielding the 9-anthrylmethyl radical 279 (Scheme 25). Radical 279 may then be attacked by t-butyllithium to form a new radical anion 280 which transfers an electron to starting 9-methoxymethylantracene continuing the chain process. Alternatively, t-butyl radical and 279 may combine to form 9-neopentylanthracene (277). Other mechanisms for the formation of 277 could be postulated.

Assignment of 276 is based on its combustion analysis, exact mass and spectral characteristics in which the important features are a vinylic \(^1\)H NMR absorption at \(\delta 6.55\) (1H, =CHOCH\(_3\)) and \(^{13}\)C NMR absorptions at \(\delta 43.21\) (C\(_9\)) and 144.92 (=CHOCH\(_3\)) as well as 8 aromatic
56. Direct displacement of methoxide by \( \text{t-BuLi} \) could give 277. Deprotonation of 274 followed by \( \alpha \)-elimination of lithium methoxide to give 9-anthryl carbene (270) and trapping 270 with \( \text{t-BuLi} \) followed by hydrolysis would yield 277. Such mechanisms are not likely however, because 1) reaction of 274 with \( \text{n-BuLi} \) (more nucleophilic than \( \text{t-BuLi} \)) does not yield 9-\( \text{n-pentylanthracene} \) and 2) there is no relationship between the yield of 277 and the equivalents of alkylithium used.

C-H signals and 4 quaternary carbon signals (see Experimental for the complete spectral data). It is expected that 273 would show 9 aromatic C-H signals and 5 quaternary aromatic carbon absorptions. The electronic spectrum of 276 confirms the absence of an anthracene chromophore (see Experimental).

Silane 276 is a white crystalline solid prone to air oxidation and hydrolysis to 9-anthraldehyde (281, Eq. 103). Flash chromatography (see Experimental) can be used to separate 276 and 277; normal column chromatography yields only 277 and 281. Stirring 276 in hexane over silica gel open to the atmosphere also results in 281. The details of the conversion of 276 to 281 are unknown but reasons for the instability of 276 can be found by examining its structure.
X-ray and $^1H$ NMR data of various 9-methylene-10-alkyl-9,10-dihydroanthracenes indicate that the central ring exists in a "boat" or butterfly conformation and the C$_{10}$ alkyl group prefers a pseudo axial position to avoid confrontation with the peri hydrogens. Thus, the large trimethylsilyl group in 276 probably occupies a pseudo axial orientation. Because of interaction between the methoxy group and the
peri hydrogen at C₁, space filling models of 276 show a dihedral angle of 20° between the p orbitals of the exo-methylene unit. The ¹H NMR spectrum of 276 exhibits the H₁ proton downfield (7.8–8.0 ppm) with respect to the other aromatic hydrogens, thus indicating considerable deshielding by the oxygen which is presumably very close to H₁.

These structural features may account for the high reactivity of 276 toward oxidation and hydrolysis. Oxygen might attack the trimethylsilyl group yielding radicals 282 and 283 which could recombine to form acetal 284 (Scheme 26). Hydrolysis would then yield 281. Alternatively, oxygen could add to the distorted exo-methylene moiety to give biradical 285. Transfer of the trimethylsilyl group from C₁₀ to oxygen in 285 yields 284 which may then be hydrolyzed to 281. A third possibility is hydrolysis of the twisted enol ether unit in 276 to an aldehyde moiety giving 10-trimethylsilyl-9,10-dihydro-9-carboxaldehyde (286) followed by air oxidation of 286 to 281. The steric and thermodynamic driving forces for conversion of 276 to 281 are probably considerable.

Formation of 276 is believed to involve deprotonation of 274 and silylation of anion 287 at the C₁₀ ring position with chlorotrimethylsilane (Eq.104). Similar 9-anthrylmethyl anions react with carbon electrophiles and proton traps to form C₁₀ alkylated or protonated adducts under conditions where product formation is kinetically

\[
\begin{align*}
274 & \overset{\text{t-BuLi}}{\longrightarrow} & 287 & \overset{\text{CHOCH₃}}{\longrightarrow} & 276 & \overset{\text{CHOCH₃}}{\longrightarrow} & \text{TMSCl} & \overset{\text{H}}{\longrightarrow} & 276 \\
& & & & & (104) & & &
\end{align*}
\]
Scheme 26

\[ \text{Scheme 26} \]

\[ \text{276} \]

\[ \text{281} \]

\[ \text{282} \]

\[ \text{283} \]

\[ \text{284} \]

\[ \text{285} \]

\[ \text{286} \]
controlled. For example, reaction of 9-chloromethylanthracene with methylmagnesium iodide yields 288, presumably via 289 (Eq. 105) and deprotonation of 9-diphenylmethylanthracene followed by quenching anion

\[ \text{CH}_2\text{Cl} \rightarrow \text{CH}_2\text{MgCl} \]

Compounds similar to \( \text{288} \) and \( \text{291} \), i.e. 9-methylene-9,10-dihydroanthracenes (292) are isolable when the \( C_{10} \) substituent, \( R \), is secondary or tertiary or if bulky substituents are at peri positions 4 and 5 (i.e. \( R_1 \)). Proton migration to form 9,10-dialkylanthracene (293) from 292 is retarded by steric interaction between \( R \) and the peri substituent \( R_1 \). However, the 9,10-dialkylanthracene isomers are thermodynamically more stable; treatment of 292 with mild base in the presence of a proton source yields 293 (Eq. 107).
Reactions of anion 287 were then studied with other electrophiles. Quenching 287 with D$_2$O results in 9,10-dihydro-9-methoxymethylene-10-d-anthracene (294, 17%, identified from its $^1$H NMR and mass spectra) and 9-anthraldehyde (281, 39%) with 64% deuterium at C-10 (Eq. 108).

9-Neopentylanthracene (277) is also formed in the reaction of t-butyllithium with 274. 9-Anthraldehyde (281) might originate from 294 via oxidation-hydrolysis as discussed earlier for 276. The lower deuterium content in 281 compared to 294 indicates some of the deuterium is lost in the oxidation process of 294 to 281. The actual yield of 294 is therefore probably much higher than found since 294 is unstable to work up.

Reaction of 287 with dimethyl sulfate affords 9,10-dihydro-9-methoxymethylene-10-methylanthracene (295, 75%, Eq. 109), as assigned from its elemental analysis, exact mass, $^1$H NMR absorptions at $\delta$ 1.36 (d, 3H, CH$_3$, $J$ = 6.8 Hz), 3.86(s, 3H, OCH$_3$), 4.02(q, 1H, CHCH$_3$, $J$ = 6.8 Hz).
Hz), 6.76 (s, 1H = CHOCH₃), 7.2-7.9 (m, 8H, aromatic) and ¹³ C NMR signals at δ 25.97 (CH₃), 41.99 (CH), 60.93 (OCH₃), 113.75 (C₉), 145.89 (CHOCH₃) as well as 8 aromatic C-H resonances and 4 quaternary aromatic carbon absorptions (see Experimental). Vinylic absorption in the ¹H NMR, the ¹³C NMR of C₁₀ and the number of aromatic signals in the ¹³C NMR confirm the structure of 295. 9-Neopentylanthracene (277, 20%) is also obtained in the reaction of 274 with t-butyllithium.

Benzoyl chloride, acetaldehyde, benzaldehyde and acetone react with 287 to give products of attack at C₁₀ (296 a-d, Eq. 110).

\[
\begin{align*}
\text{287} & \quad R = \phi \text{CCl} & \quad \text{296 a}; R = \phi \text{C}^- \\
& = \text{CH₃CHO} & \quad \text{296 b}; R = \text{CH₃CH(OH)}^- \\
& = \phi \text{CHO} & \quad \text{296 c}; R = \phi \text{CH(OH)}^- \\
& = (\text{CH₃})₂\text{C}=\text{O} & \quad \text{296 d}; R = (\text{CH₃})₂\text{COH}^- \\
\end{align*}
\]

Structures 296 a-d have proper exact masses and spectra including vinylic ¹H NMR absorptions at δ 6.50-6.85 and methoxymethylene ¹³C NMR absorptions at δ 145.66-146.59 (see Experimental for complete spectral data). In each experiment, 9-neopentylanthracene (277, in 23-36% yields) is also formed from the reaction of t-butyllithium with 274. Products 296 a-d are unstable oils which decompose to aldehyde derivatives as evidenced by ¹H NMR spectra. The decomposition products were
not isolated or identified.

Thus, reactions of anion 287 with electrophiles under kinetically-controlled conditions yield 9-methoxymethylene-10-substituted-9,10-dihydroanthracenes (276, 294, 295, and 296 a-d) regardless of the electrophile. It was of interest to study the behavior of 9-anthrylmethyl anions bearing heteroatoms other than oxygen on the benzylic carbanionic center (297). The behavior of these anions toward benzylic versus ring substitution may show trends with respect to the benzylic heteroatom and the electrophile used to trap 297.

The first system studied was methyl 9-anthrylmethyl sulfide (298) which is synthesized from 9-chloromethylanthracene (294) and sodium thiomethoxide (77%, Eq. 111). Attempts to deprotonate 298 with amide bases fail (see Experimental). Reaction of 298 with n-butyllithium and then chlorotrimethylsilane yields 9-n-pentylanthracene (300, 29%),

possibly by direct displacement of thiomethoxide (Eq. 112); no silylated products are observed.
Treatment of 298 with t-butyllithium at -78°C in diethyl ether/tetramethylethylenediamine results in a dark green solution which gives previously unknown 9-anthrylmethyltrimethylsilane (301, 91%) upon quenching with chlorotrimethylsilane (Eq. 113.). Silane 301 is identified from its combustion analysis, exact mass and spectral properties including $^1$H NMR absorptions at $\delta$ 0.02(s, 9H, Si(CH$_3$)$_3$), 3.18(s, 2H, CH$_2$), 7.4-8.3(m, 9H, aromatic), a 9 line $^{13}$C NMR spectrum (one quaternary carbon signal is buried) and an UV spectrum showing the anthracene chromophore (see Experimental). Formation of 301 possibly results from electron transfer from t-butyllithium to 298 forming radical anion 302 (Scheme 26). Loss of methylthio radical from 302 and reaction of the
resulting 9-anthrylmethyl anion (303) with chlorotrimethylsilane gives 301. The fate of the methylthio radical is unknown but it may combine with the t-butyl radical forming methyl t-butyl sulfide (not isolated).

Silane 301 can also be synthesized by reductive silylation of 9-anthrylmethyloxysilane (304) with lithium in the presence of chlorotrimethylsilane (Eq. 114), and anion 303 may be a common intermediate in equations 113 and 114. It is noteworthy that anion 303 is silylated at its benzylic methyl position yielding 301 whereas alkylation of yields ring (C\textsubscript{10}) alkylated adducts (for example 288) as discussed earlier. Reasons for these phenomena will be discussed later.

Generation of α-lithio-9-anthrylmethyltrimethylsилane (305) and its reactions with electrophiles were then studied. A dark emerald green solution is produced upon addition of n-butyllithium to a diethyl ether/tetramethylethylenediamine or tetrahydrofuran/tetramethylethylenediamine solution of 9-anthrylmethyltrimethylsilane (301) at 0°C. After quenching with D\textsubscript{2}O, silane 301 is recovered quantitatively which is 70% deuterated at the benzylic position as based on \textsuperscript{1}H NMR and mass
spectral analyses (Eq. 115). Since no deuterium is detected at C₁₀, initial formation of [9(10H)-anthrylidene-10-d-methyl]trimethylsilane (306) followed by prototopic shift to 301 does not occur.

Reaction of anion 305 with dimethyl disulfide yields [9-anthryl-(methylthio)methyl]trimethylsilane (307, 97%, Eq. 116), whose structure is proven by its combustion analysis, exact mass and spectral features including ¹H NMR absorptions at δ 0.10 (s, 9H, Si(CH₃)₃), 1.84 (s, 3H, SCH₃), 4.80 (s, 1H, CH), 7.3-8.9 (m, 9H, aromatic). The ¹³C NMR spectrum of 307 displays absorptions at δ -0.43 (Si(CH₃)₃), 17.28 (SCH₃) and 33.64 (CH); the aromatic region consists of 9 C-H signals and 5 quaternary absorptions. Although the anthracene ring is symmetrically
substituted, all its carbons are nonequivalent due to the asymmetric center at the benzylic position and possibly to hindered rotation about the 9-anthryl -α-trimethylsilyl(methylthio)methyl bond. The anthracene chromophore is clearly evidenced in the UV spectrum of 307 (259 nm, ε = 140,000), indicating benzylic rather than ring substitution.

Conversely, quenching anion 305 with chlorotrimethylsilane yields the product of ring (C^q) silylation, [9,10-dihydro-10(trimethylsilylmethylene)-9-anthryl]trimethylsilane (308, 55%, Eq. 117). Structure 308 is identified by ^1H NMR absorptions at -0.05 (s, 9H, Si(CH_3)_3), 0.20 (s, 9H, CHSi(CH_3)_3), 3.64 (s, 1H, CH), 6.10 (s, 1H, CHSi(CH_3)_3) and 7.1-8.3 (m, 8H, aromatic); further characterization is prevented by the inability to separate 308 from initial silane 301 in the reaction product.

The regioselectivities in reactions of anions 287, 303 and 305 at benzylic versus C^q ring positions are summarized as follows:

1) alkylation of 9-anthrylmethyl anion (303) occurs at C^q whereas silylation takes place at the benzylic position,
2) products of C^q ring protonation, alkylation and silylation are observed from α-lithio-9-methoxymethylandanthracene (287), and
3) [9-anthryl(lithio)methyl]trimethylsilane (305) reacts at its benzylic position with proton sources and with dimethyl disulfide but is silylated with chlorotrimethylsilane at C\textsubscript{10}.

Electrical factors in anions 287, 303 and 305 as well as the electronic and steric character of the electrophiles must be considered to explain the above observations. Since simple Hückel Theory predicts equal electron density on the benzylic and C\textsubscript{10} ring carbons in 9-anthrylmethyl anion 303 (Fig. 2),\textsuperscript{61} the apparent discrepancy between the regioselectivity of its alkylation and silylation is probably due to steric factors. Since chlorotrimethylsilane is a much more reactive electrophile than is an alkyl halide, it is presumed that bond formation between the anionic center in 303 and the electrophile is not as far advanced in the transition state for silylation as for alkylation.


Figure 2. Electron Density Map of 303 as Predicted by Hückel Theory. (Fig. 3). Thus, steric interaction between the benzylic reaction center and the peri hydrogens on the anthracene nucleus is greater during alkylation than silylation and alkylation is relatively
kinetically favored at the more open ring position. Also the greater length of the C-Si bond keeps the trimethylsilyl group further away from the peri hydrogens and silylation leads to the more thermodynamically stable 9-anthrylmethyltrimethylsilane.

62. It is expected that anion 303 exists in a "pseudo boat" or twisted conformation because contact between the peri hydrogens and the exo-methylene moiety prevent planarity. As reaction proceeds at the benzylic position the central ring will flatten and increase interaction between the peri hydrogens and the groups attached to the benzylic carbon.

The steric factors for reactions of 9-methoxymethyleneanthryl anion 207 are even greater than for 303 because of the larger methoxy substituent at the benzylic center. Therefore, approach of the electrophile to the benzylic position suffers from severe crowding at the reaction center due to the peri hydrogens (Fig. 3) and the C₁₀ ring position is preferentially attacked. Of interest is that simple Hückel calculations show C₁₀ as the site of highest electron density (Fig. 4) and electrophilic attack should be faster at this position even in the absence of steric factors.
Hückel calculations were performed on a Hewlett-Packard Model 9830A calculator with an augmented Basic language program written by Micheal J. Skoglund, The Ohio State University. To account for the difference in the parameters for the coulombic integral, $\alpha$, for the oxygen atom in 287 and the resonance integral $\beta$, for the C-O bond in 287, the $\alpha$ and $\beta$ parameters were set $\alpha = \alpha_0 + \beta_0 = 2$ and $\beta_{\text{C-X}} = k_{\text{C-X}} \beta_0 = 0.8$ as recommended in Greenwood, H.H., "Computing Methods in Quantum Organic Chemistry"; Wiley-Interscience: New York, 1972 and Streitwieser, A., "Molecular Orbital Theory for Organic Chemists"; Wiley, New York, 1961.

To account for the nonplanarity of the system due to the interaction between H$_2$ and OCH$_3$ in 287, the resonance integral, $\beta$, for the exo-methylene C-C bond was further corrected, as recommended in the references cited above. Thus, $\beta = \cos \theta \beta_{\text{C-X}}$ where $\theta = 20^\circ$.

The 9-anthryl(trimethylsilyl)methyl anion 305 yields products of ring substitution and of benzylic substitution depending on the electrophile. It is likely that the size of the electrophile has considerable influence on the course of these reactions. Deuterium oxide ($D_2O$) is small and presumably delivers deuterium to the benzylic carbon without forcing much contact between the benzylic center and the peri hydrogens. On the contrary, the transition state for silylation at the benzylic carbon involves two trimethylsilyl groups, and the steric hindrance due to the peri hydrogens is enormous; thus, reaction is favored at the C$_{10}$ ring position.
Sulfur in dimethyl disulfide is much more accessible to attack than tetrasubstituted silicon in chlorotrimethylsilane and thus the transition state for reaction of 305 with dimethyl disulfide at the benzylic carbon is not as clustered as it is for silylation. The more thermodynamically stable product 307 is then formed faster.

It is also possible that 307 is not the product of initial sulfuration. Thus, trimethyl[(10-(methylthio)-9(10H)-anthrylidene)methyl]silane (309) might have been formed first and then isomerized in the presence of thiomethoxide to 307 (Eq. 118). Indeed such isomerizations have been observed with 10-substituted-9-benzylidene-9,10-dihydroanthracenes (Eq. 119).

Further research on the ambident nature of anions 287, 303, 305 and other α-substituted-9-anthrylmethyl anions is needed to determine the electronic and steric factors which control the regiochemistry of their reactions with electrophiles.
Efforts were then directed at oxygenating or halogenating the benzylic position of 9-anthrylmethyltrimethylsilane, anticipating the products to be potential 9-anthrylidene (270) precursors (Scheme 27). Reaction of anion 305 with benzoyl peroxide or t-butyl peroxybenzoate fail to produce 310 and 311 respectively, only complex product mixtures are obtained. Similarly, attempted halogenation of anion 305 with N-bromosuccinimide or N-chlorodiethylamine did not yield isolable products.

Attempts to place oxygen or halogen functionality at the benzylic position in 301 via free radical processes also fail. Thus, reaction of 301 with N-bromosuccinimide, either thermally or photochemically, or t-butyl hypochlorite did not produce the desired products (Eq. 120). Likewise, the products of reaction of silane 301 and t-butyl peroxybenzoate in the presence of copper(I) bromide (Eq. 121) could not be separated and identified.64

Solvolysis of sulfide 307 to usable products (Eq. 122) was attempted. The thioether linkage in 307 is stable, however, to mercuric ion even on prolonged contact in refluxing methanol.

Alkylolithiums add to anthracene to form 9-alkyl-9,10-dihydroanthracenes (312, Eq. 123). α-Lithio-methoxymethyltrimethylsilane (313), however, does not yield an adduct with anthracene. Displacement of 9-bromoanthracene (314) by 313 also fails. Anthracene and 9-bromoanthracene are recovered from these experiments. Further,

α-lithiomethoxymethylsilane (313) does not form an addition product with 9-anthrone.

Since trimethylsilyllithium (315) adds to aldehydes, the reaction

of 315 and 9-anthraldehyde (281) was studied. Lithium reagent 315 is generally prepared by cleavage of hexamethyldisilane in hexamethylphosphoramide (HMPA). Unexpectedly, the reaction of 315 with 281 followed by dimethyl sulfate yields a phosphorus containing product identified as \( P-(9\text{-anthrylmethoxymethyl})-N,N',N'-\text{tetramethylphosphonic diamide} \) (316) from its combustion analysis, exact mass and spectral data including \(^1\text{H NMR}, \; ^{13}\text{C NMR}, \; ^{31}\text{P NMR} \) and UV (Eq.124). The \(^1\text{H NMR} \) spectrum is very definitive. The dimethylamino groups are non-equivalent in 316 because of the asymmetric center. Additional hydrogen-phosphorus coupling (\( J = 9 \text{ Hz} \)) causes the dimethylamino groups to appear as two sets of doublets. The methine CH is a doublet because of phosphorus-hydrogen coupling (\( J = 15 \text{ Hz} \)). The methoxy group appears as a singlet however, indicating H-C-O-C-P coupling is too small to be observed at 90 MHz. The \(^{13}\text{C NMR} \) spectrum displays the dimethylamino moiety again as two sets of doublets (\( J_{P-N-C} = 3 \text{Hz} \)), the methine carbon as a doublet (\( J_{P-C} = 137 \text{ Hz} \)) and the methoxy carbon is now a doublet (\( J_{P-C-O-C} = 15' \text{ Hz} \)). The UV spectrum clearly shows the anthracene chromophore (255 nm, \( \varepsilon = 142,000 \)).

The mechanism for the formation of 316 is unknown. However, a possible route is illustrated in Scheme 28. Equation 124 represents
an unusual and unique reaction involving HMPA, and the behavior of trimethylsilyllithium/HMPA reagent towards aromatic aldehydes might be an interesting study.

Scheme 28

\[
(CH_3)_3SiLi + \text{CHO} \rightarrow \text{CHO}^- + (CH_3)_3Si^+ \\
((CH_3)_2N)_3P=O + (CH_3)_3Si^- \rightarrow ((CH_3)_2N)_3PSi(CH_3)_3 \\
((H_3C)_2N)_3POSi(CH_3)_3 \rightarrow (H_3C)_2NPSi(CH_3)_2 \\
((H_3C)_2N)_3POSi(CH_3)_3 \rightarrow (H_3C)_2NPSi(CH_3)_2 \\
\]

Final attempts to generate 9-anthrylmethylene in the gas phase pyrolyses of 276 and 307 (Eq. 125 and 127). It was hoped that on pyrolysis of 276 methoxytrimethylsilane would eliminate possibly as in Equation 125. Thermolysis of 276 at 600–650°C and 0.05–0.1 mm, however, gives intractables and minor amounts of anthracene, 9-methylanthracene, 9-methoxymethylanthracene and 9-anthraldehyde (Eq. 126). 1H-cyclobuta[de]anthracene (269) is not detected. Similarly, attempts to thermally eliminate methylthiotrimethylsilane (320) from 307 at 650°C and 0.05–0.1 mm results in intractables.
It was then decided to study synthesis of 1H-cyclobuta[de]anthracene (269) from 1-anthrylidene (321) as generated by pyrolysis of [methoxy(1-anthryl)methyl]trimethylsilane (322). The synthesis of is summarized in Scheme 29 and described below.
Benzanthrone (323) is oxidized with chromic acid to 9,10-anthraquinone-1-carboxylic acid (324) which is reduced to 1-anthracene-carboxylic acid (325, 47% from 323) with zinc in ammonium hydroxide. Reduction of acid 325 to 1-anthracenemethanol (326, 78%) with lithium aluminum hydride followed by reaction with phosphorus tribromide gives 1-bromomethylanthracene which is converted to 1-methoxymethylanthracene (327, 95% from 326) with sodium methoxide in methanol/tetrahydrofuran.
Deprotonation of 327 with t-butyllithium/tetramethylethylenediamine in diethyl ether at -110°C and reaction of the purple-black anion generated with chlorotrimethylsilane yields [methoxy(1-anthryl)methyl]trimethylsilane (322, 68%). The low temperature used for deprotonation and silylation is critical for good yields of 322; at -78°C the yield of 322 is only 23-33%. Silyl ether 322 is assigned from its elemental analysis, exact mass and spectral properties including $^1$H NMR absorptions at $\delta$ 0.04 (s, 9H, Si(CH$_3$)$_3$), 3.40 (s, 3H, OCH$_3$), 4.95 (s, 1H, CH), 7.4-7.6 (m, 4H, H-2,3,6,7 of anthryl), 7.9-8.1 (m, 3H, H-4,5,8 of anthryl), 8.5 (s, 1H, H-10), and 8.7 (s, 1H, H-9).

Pyrolysis of 322 at 560-570°C and 0.02-0.07 mm yields 1H-cyclobuta[de]anthracene (269, 52%) and intractables (Eq. 128). Bridged anthracene 269 is identified by its exact mass and spectral characteristics. Important spectral features are a $^1$H NMR absorption at $\delta$ 4.98 (s, 2H, CH$_2$), 6.98 (d, 1H, H-2 on anthryl, $J$ = 5 Hz), 7.3-8.0 (m, 6H, anthryl), 8.05 (s, 1H, H-5 on anthryl) and a $^{13}$C NMR signal at $\delta$ 46.34 (CH$_2$) as well as 8 aromatic CH signals and 6 quaternary aromatic carbon resonances. The anthracene UV chromophore of 269 is distinct (256 nm, $\epsilon$ 204,000).
As with the previous peri-methanoarenes generated thermally, the yield of \( 269 \) varies with the pyrolysis temperature and pressure (Table 15). Temperatures greater than \( 500^\circ\text{C} \) are necessary to effect fragmentation of \( 322 \) whereas temperatures greater than \( 630^\circ\text{C} \) result in extensive decomposition. The best yields are obtained at low pressures (< 0.1 mm).

The mechanism of formation of \( 269 \) presumably involves thermal elimination of methoxytrimethylsilane from \( 322 \) to give 1-anthrylidene (321) which then inserts into the peri CH bond at \( C_9 \) of the anthracene nucleus.

Hydrocarbon \( 269 \) is a light yellow solid which rapidly changes to a red-orange oil when open to the atmosphere at room temperature. Mass spectral analysis of the converted material reveals peaks at \( M^+16 \) and \( M^+30 \) as well as other higher molecular weight fragments indicating oxidation and/or polymerization may be occurring. The 9,10-positions of the anthracene ring in \( 269 \) may be highly susceptible to oxidation because of the strain due to the cyclobutyl moiety (Eq. 129).

\[
\begin{align*}
269 & \xrightarrow{O_2} \text{Complex (129)} \\
& \text{Mixture}
\end{align*}
\]

Bridged anthracene rapidly decolorizes a carmine red solution of N-phenyl-1,3,4-triazoline-2,5-dione in benzene at room temperature; however, attempts to isolate and identify the product of this reaction have failed. Hydrocarbon \( 269 \) is storable at room temperature as its
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a) Numbers in parentheses represent yield of 269 based on recovered starting material.
b) SM denotes starting material.
c) N. D. means not determined.
2,4,7-trinitrofluoren-9-one complex, a dark red crystalline solid.

Spectral and Physical Properties of Peri-Methanoarenes

The nuclear magnetic resonance spectra ($^1$H and $^{13}$C) of peri-methylene-bridged arenes are very distinct with respect to the positions of their peri-methano hydrogen and carbon resonances. The $^1$H spectra show methylene signals at 4.39-5.19 ppm, depending upon ring substituents and the $^{13}$C spectra display carbon signals at 44.20-52.97 ppm (Table 17). These resonances clearly indicate formation or retention of a peri-methanoarene structure in determining the products of a new reaction.

The mass spectra of aromatic hydrocarbons 252, 260, 263, and 269 reveal intense molecular ion patterns and very little fragmentation.

The ultraviolet-visible spectra of 236, 252, 260, 263, and 269 are compared with those of similar compounds in Tables 18-22. There is little correlation of the effect of the cyclobutyl ring on the energy or intensity for the absorptions of these bridged species with those of their parent hydrocarbons 113, 327, 328 and 329.

Hydrocarbons 260, 263 and 269 are low melting sublimable solids. Arenes 263 and 269 rapidly colorize (hours to 1 day) upon storing open to the atmosphere at room temperature. Phenanthrene analog 260, however, only slowly decomposes under similar conditions (appears to be stable for weeks). 2,4,7-Trinitrofluoren-9-one forms highly colored, air and thermally stable crystalline complexes with 260, 263 and 269 and these complexes are a convenient way to store 263 and 269; the hydrocarbons can easily be regenerated by decomposing the complexes on
silica gel with hexane eluent.
TABLE 17: $^1$H NMR and $^{13}$C NMR Chemical Shifts of the Methylene Moieties in Peri-Methanoarenes

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TABLE 18: UV Data for Naphthalene Derivatives

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a) Wavelength in nanometers.
**TABLE 19**

UV Data for 1-Naphthol and 4-Methoxy-1H-cyclobuta[de]naphthalene

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*a) Wavelength in nanometers.*
### TABLE 20

UV Data for Anthracene Derivatives

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a) Wavelength in nanometers.

b) Shoulder.
### TABLE 21

UV Data for Phenanthrene Derivatives

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a) Wavelength in nanometers

b) Shoulder
TABLE 22
UV Data for Pyrene Derivatives

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EXPERIMENTAL

Melting Points: Melting points were determined using a Thomas Hoover capillary melting point apparatus or a Fisher melting point block and are uncorrected.

Elemental Analyses: Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, or Microanalysis, Inc., Wilmington, Delaware.

Infrared Spectra: Infrared spectra were obtained using a Perkin Elmer, Model 457 recording spectrophotometer. Spectra were calibrated against a polystyrene absorption at 1601 cm\(^{-1}\).

Mass Spectra: Mass spectra were determined on a MS-9 mass spectrometer at 70 eV by Mr. C.R. Weisenberger, unless otherwise described.

Gas Chromatography-Mass Spectra: Gas chromatography-mass spectra were determined by Mr. C.R. Weisenberger on a DuPont 21-490 Mass Spectrometer interfaced with a single stage metal jet from a Perkin Elmer Model 990 gas chromatograph.

Ultraviolet-Visible Spectra: Ultraviolet-visible spectra were obtained with a Cary 14 recording spectrophotometer.

\(^1\)H Nuclear Magnetic Resonance Spectra: Proton nuclear magnetic resonance spectra were obtained on Varian Associates nuclear magnetic resonance spectrometers, Models A-60A, EM-360, EM-390 and HA-100, and Bruker nuclear magnetic resonance spectrometers, Models WP-200 and WM-300\(^*\).
Chemical shifts, unless otherwise specified, were measured in ppm downfield from tetramethylsilane.

$^{13}$C Nuclear Magnetic Resonance Spectra: $^{13}$C Nuclear magnetic resonance spectra were obtained on Bruker spectrometers, Models WP-80, WP-200, and WM-300* operating at 20.1, 50.3 and 75.3 MHz, respectively. Chemical shifts were measured in ppm from tetramethylsilane.

$^{31}$P Nuclear Magnetic Resonance Spectra: $^{31}$P Nuclear magnetic resonance spectra were obtained on a Bruker Model HX-90 spectrometer operating at 36.43 MHz. Chemical shifts are measured in ppm relative to 85% phosphoric acid. Trimethylphosphate was used as an internal standard.

Anhydro-8-hydroxymercuri-1-naphthoic Acid. 1,8-Naphthalic anhydride (99.1 g, 0.50 mol) was suspended in aqueous sodium hydroxide (70.2 g, 1.75 mol in 3000 mL of water) and refluxed until the solid material dissolved. The excess base was neutralized with glacial acetic acid (50 mL) and a solution of mercuric acetate, prepared by dissolving mercuric oxide (110 g, 0.51 mol) in hot glacial acetic acid (250 mL) and diluting with water (500 mL), was added in one portion. After refluxing the mixture 30 min, additional glacial acetic acid (90 mL) was added to the white slurry, resulting in slow evolution of carbon dioxide. The slurry was refluxed 48 hr, cooled and filtered. The tan

*300 MHz FT-NMR spectra were obtained at The Ohio State University Chemical Instrument Center (funded in part by National Science Foundation Grant CHE-7910019) with the help of Dr. C.E. Cottrell.
solid, anhydro-8-hydroxymercuri-1-naphthoic acid, was washed with water and dried under vacuum at 105°C overnight (184 g, -100%).

8-Bromo-1-naphthoic Acid. Anhydro-8-hydroxymercuri-1-naphthoic acid (190 g, 0.514 mol) suspended in glacial acetic acid (750 mL) and water (120 mL) was stirred vigorously at 0°C. Sodium bromide (341 g, 1.66 mol) in water (620 mL) and bromine (84.5 g, 29 mL, 0.53 mol) were added slowly while maintaining the reaction temperature at 0-5°C. The resulting slurry was then slowly heated to 100°C and poured on ice (1500 g). The precipitate was washed with water, dissolved in hot aqueous sodium hydroxide (120 g, 3 mol in 2500 mL of water) and filtered through Celite. Upon acidifying the filtrate with concentrated hydrochloric acid (250 mL), 8-bromo-1-naphthoic acid was obtained as white crystals (85.6 g, 67.4%), mp 174-175°C, lit mp 175-176°C. Extraction of the Celite with benzene (750 mL) and concentration of the extract yielded 1,8-dibromonaphthalene as yellow crystals (11.4 g, 8%), mp 106-109°C, lit mp 109-110°C.

8-Bromo-1-naphthalenemethanol (140). 8-Bromo-1-naphthoic acid (35.2 g, 0.14 mol) was refluxed in thionyl chloride (105 mL) for 4 hr and the thionyl chloride removed under reduced pressure. The remaining oily residue was dissolved in diethyl ether (450 mL) and filtered. The ethereal solution was added dropwise, at a rate to cause gentle
reflux, to a lithium aluminum hydride (4.5 g, 95%, 0.11 mol) suspension in diethyl ether (100 mL). After refluxing 5 hr, the mixture was hydrolyzed with saturated aqueous sodium sulfate and the organic layer decanted. The white salts remaining were extracted with diethyl ether (5 x 50 mL) and the combined ethereal solutions dried (MgSO₄). Removal of solvent left 8-bromo-1-naphthalenemethanol (27.5 g, 83%) as a white solid which was spectrally identical (¹H NMR, IR) to an authentic sample.

8-Bromo-1-naphthaldehyde (Br CHO). N-Chlorosuccinimide (80.2 g, 0.60 mol) was suspended in toluene (2 L), cooled to 0°C and dimethyl sulfide (46 mL, 0.63 mol) added and the resulting mixture cooled to -33°C in a dry ice/nitromethane bath. A solution of 8-bromo-1-naphthalenemethanol (70.3 g, 0.30 mol) in toluene (700 mL) was then added slowly, keeping the temperature < -25°C throughout the addition which required 3 hr. After stirring an additional 2.5 hr, the mixture was treated with triethylamine (80 mL, 0.60 mol) and allowed to warm to room temperature overnight and then filtered to remove the succinimide. The solution was concentrated to 300 mL, diethyl ether (1 L) added and filtered. The ethereal solution was washed with 1 N hydrochloric acid, saturated aqueous sodium bicarbonate, brine and dried (MgSO₄). The solvents were removed under reduced pressure affording 8-bromo-1-naphthaldehyde (61.4 g, 88%) as a light tan solid identical to an authentic sample.
8-Bromo-1-naphthaldehyde p-Tosylhydrazone (9). 8-Bromo-1-naphthaldehyde (59.3 g, 0.25 mol) was dissolved in ethyl alcohol (200 mL) and added to p-tosylhydrazide (47.8 g, 0.26 mol) in hot ethyl alcohol. After the mixture had cooled to room temperature, the white solid that formed was filtered and recrystallized from ethyl alcohol yielding 8-bromo-1-naphthaldehyde p-tosylhydrazone (69.9 g, 69%) as white crystals, mp 192-194°C, lit3 mp 193-195°C.

1-Bromo-1H-cyclobuta[de]naphthalene (8). Sodium hydride (50% dispersion in mineral oil, 5.5 g, 0.11 mol) was washed with hexane, slurried in dichloromethane (500 mL) and cooled to 0°C. 8-Bromo-1-naphthaldehyde p-tosylhydrazone (40.4 g, 0.10 mol) was added slowly with stirring to the sodium hydride slurry. Stirring was continued 30 min after hydrogen evolution ceased and the yellow solution evaporated to dryness under reduced pressure. The yellow solid was suspended in anhydrous diethyl ether (2.4 L) and irradiated under nitrogen for 22 hr with a Hanovia 450W high pressure mercury arc lamp. The mixture was filtered, solvent removed and the residue chromatographed on silica gel. Elution with hexane yielded 8-bromo-1H-cyclobuta[de]naphthalene (6.4 g, 29%) as a white solid identical in all respects to authentic material.3

Reaction of 1,8-Dilithionaphthalene with Dichloromethane.

A. General Procedure: 1,8-Dilithionaphthalene was prepared from
1,8-diiodo-or 1,8-dibromonaphthalene\(^{70}\) (1-3 mmol) and \(t\)-butyllithium (4 equiv) in diethyl ether (20-100 mL) at \(0^\circ\text{C}\) \(^{34}\) and the mixture cooled to the desired temperature (see Table 3). Dichloromethane (1-4 equiv) was added and the solution allowed to warm to room temperature, washed with water and aqueous sodium bicarbonate and dried (MgSO\(_4\)). Removal of solvent and chromatography (silica gel, hexane as eluent) of the residue gave a mixture of naphthalene (113), 1H-cyclobuta[de]naphthalene (\(\text{I}^\text{I}\)), and acenaphthyene (114). The yields of 113, \(\text{I}^\text{I}\), and 114 were determined by \(^1\text{H}\) NMR using 1,2-dichloroethane as an internal standard.

Varying the reaction temperature or the number of equivalents of dichloromethane added had little effect on the yields of 113 and \(\text{I}^\text{I}\) (Table 3). The yields of acenaphthyene increased appreciably however with excess alkylating agent.

B. With Added Tetramethylethylenediamine: To the light yellow diethyl ether solution of 1,8-dilithionaphthalene at \(0^\circ\text{C}\) was added tetramethylethylenediamine (2-5 equiv, see Table 6). The resulting black solution was cooled to the desired temperature and dichloromethane (1-20 equiv) added. The reaction mixture was allowed to warm to room temperature and worked up and analyzed as previously described. The products observed were naphthalene (113) and 1H-cyclobuta[de]naphthalene (\(\text{I}^\text{I}\)); no acenaphthyene (114) was detected in these experiments. The yield of \(\text{I}^\text{I}\) was dependent upon reaction temperature, solvent and the amount of tetramethylethylenediamine used as shown in Table 6.

C. With Added Metal Salt Catalysts: 1,8-Dilithionaphthalene was prepared in either diethyl ether or tetrahydrofuran solution at \(0^\circ\text{C}\) (see Table 4) and cooled to the indicated temperature. The transi-
tion metal salt catalyst was added followed quickly (or simultaneously) by dichloromethane. Work up and analysis of the reaction mixture were conducted as previously described and the results summarized in Table 4.

Reaction of 1,8-Dilithionaphthalene with Dibromomethane, Diiodomethane and Methylene Bistosylate. 1,8-Dilithionaphthalene was prepared in diethyl ether or tetrahydrofuran as previously described. Dibromomethane, diiodomethane or methylene bistosylate were added neat or in solution in diethyl ether or tetrahydrofuran, and the reaction mixtures were analyzed as before. No 1H-cyclobuta[de]naphthalene was detected from the varied experiments (Table 5).

The major products from reaction with diiodomethane were iodonaphthalene (14%) and diiodonaphthalene (4%). It was concluded that lithium-halogen exchanged occurred rather than the desired alkylation.

Reaction of 1,8-Dilithionaphthalene with Dichloromethane-d$_2$. An anhydrous diethyl ether solution (50 mL) of 1,8-dibromonaphthalene (1.1 g, 4.0 mmol) was cooled to 0°C under argon and t-butyllithium (1.9 M in pentane, 9.5 mL, 18 mmol) added. After 30 min at 0°C, the light yellow mixture was cooled to -60°C. Tetramethylethylenediamine (1.2 mL, 8.2 mmol) was added followed by dichloromethane-d$_2$ (0.31 mL, 4.6 mmol) and the reaction mixture was allowed to warm to room temperature. After washing with water, saturated aqueous ammonium sulfate and brine, the solution was dried (MgSO$_4$) and concentrated. Preparative thin-layer chromatography (hexane) afforded a 69:31 mixture of naphthalene (113, 0.23 g, 42%) and 1H-cyclobuta[de]naphthalene (1, 0.10 g, 19%) as a
colorless liquid. The yields were determined by $^1\text{H}$ NMR (100 MHz) using 1,2-dichloroethane as an internal standard.

Naphthalene was sublimed from the mixture and its deuterium content determined by mass spectral analysis. The deuterium content of was determined by $^1\text{H}$ NMR. The results are shown in Table 7. Work up with deuterium oxide gave little enhancement of the d-content in 1 or 113.

**Reaction of 1,8-Dilithionaphthalene with Lithium Dichloromethane.**

An anhydrous diethyl ether solution (5 mL) of dichloromethane (1.0 mL, 16 mmol) was cooled to $-100^\circ\text{C}$ (CH$_3$OH/liquid nitrogen bath) under argon and a 1.9 M solution of t-butyllithium in pentane (9.0 mL, 17 mmol) was added dropwise ($T < -100^\circ\text{C}$). The mixture was stirred 15 min at ($-100$)--(-112)$^\circ\text{C}$, and a solution of 1,8-dilithionaphthalene, prepared from 1,8-diiodonaphthalene (1.5 g, 4.0 mmol) and t-butyllithium (1.9 M, 9.4 mL, 18 mmol) at $0^\circ\text{C}$ in diethyl ether (25 mL) and tetramethylethylenediamine (1.3 mL, 8.8 mmol), was added dropwise. Throughout the addition the reaction temperature remained between ($-80$)--(-100)$^\circ\text{C}$ and after addition was complete, the solution was allowed to warm to room temperature. After washing with water, aqueous ammonium sulfate and brine, the solution was dried and solvent removed. Chromatography of the residue on silica gel (hexane) gave a light yellow oil (0.27 g) which was a 65:35 mixture of naphthalene (0.17 g, 34%) and 1H-cyclobuta[de]naphthalene (0.10 g, 18%) as shown by $^1\text{H}$ NMR (1,2-dichloroethane was used as an internal standard).
Similar experiments were conducted with varying amounts of lithium dichloromethane and tetramethylethylenediamine and the results are shown in Table 8. Work up of the reaction mixture with deuterium oxide resulted in no deuterium incorporation in the naphthalene or the 1H-cyclobuta[de]naphthalene isolated.

Reaction of 1,8-Dilithionaphthalene with Chloromethyl Methyl Ether:

1,8-Bis(methoxymethyl)naphthalene (137). To an anhydrous diethyl ether solution (30 mL) of 1,8-diiodonaphthalene (1.5 g, 4.1 mmol) at 0°C under argon was added a 2.0 M solution of t-butyllithium in pentane (9.2 mL, 18 mmol) followed, after 30 min, by tetramethylethylenediamine (1.3 mL, 8.7 mmol). The dark yellow-green mixture was cooled to -70°C and freshly distilled chloromethyl methyl ether (0.62 mL, 8.2 mmol) added. The pale yellow mixture, after warming to room temperature, was washed with water, saturated aqueous ammonium sulfate and brine and dried (MgSO₄). Concentration of the solution and chromatography of the residue (silica gel; hexane/benzene, 1:1) yielded three products:

1) naphthalene (0.044 g, 8%),
2) 1-methoxymethylnaphthalene (136, 0.046 g, 7%), identical to an authentic sample and
3) 1,8-bis(methoxymethyl)naphthalene (137, 0.39 g, 44%) as colorless crystals, mp 56–59°C (pentane); IR (KBr, cm⁻¹) 3010, 2960, 2900, 2840, 1190, 1130, 1095, 825, 790; ¹H NMR (CDCl₃, δ) 3.39(s, 6H,
OCH₃), 4.94(s, 4H, CH₂), 7.2-7.9(m, 6H, aromatic); exact mass: calcd. 216.1150; obsd. 216.1154.

**Anal.** Calcd for C₁₄H₁₆O₂: C, 77.75; H, 7.46.

Found: C, 77.99; H, 7.58.

Reaction of 1,8-dilithionaphthalene with one equivalent of chloromethyl methyl ether yielded only naphthalene and 1-methoxymethyl-naphthalene; no 1H-cyclobuta[de]naphthalene was observed. Yields were not determined because the products were deemed trivial; there was no further analysis of the product.

8-Bromo-1-chloromethylnaphthalene (141). A thionyl chloride solution (50 mL) of 8-bromo-1-naphthalenemethanol (5.1 g, 22 mmol) was stirred 12 hr and concentrated by distillation. The brown residue was dissolved in diethyl ether and washed with water and aqueous saturated sodium bicarbonate and then dried over magnesium sulfate. Removal of solvent and chromatography (silica gel) using hexane as eluent gave 8-bromo-1-chloromethylnaphthalene (3.4 g, 61%) as a white solid, mp 63-68°C, lit71 mp 64-66°C; ¹H NMR (CDCl₃, δ) 5.50(s, 2H, CH₂); mass spectrum, m/e 258, 256, 254 (M⁺). ¹H NMR, IR and mass spectra agreed with those reported.³

**Reaction of 8-Bromo-1-chloromethylnaphthalene with t-Butyllithium.**

**A. Quench with Methyl Alcohol-0-d:** A solution of 8-bromo-1-chloromethylnaphthalene (0.32 g, 1.2 mmol) in anhydrous diethyl ether (35 mL) was cooled to -100°C (methyl alcohol/liquid nitrogen bath) under argon
and a 2.0 M solution of t-butyllithium in pentane (0.65 mL, 1.3 mmol) was added slowly. The clear light yellow solution was stirred 15 min at -100°C and methyl alcohol-0-d (1 mL) added. Hydrochloric acid (1 mL) was introduced after the solution had warmed to -50°C. The mixture was then allowed to warm to room temperature and washed with water and dried (MgSO$_4$). Concentration of the solution and column chromatography of the residue on silica gel (hexane) gave a 88:12 mixture (0.14 g, ratio by $^1$H NMR) of 1-chloromethylnaphthalene (0.12 g, 55%) and 8-bromo-1-chloromethylnaphthalene (0.02 g, 7%) as a colorless liquid. Preparative VPC (5% SE-30, 150°C) afforded pure 1-chloromethylnaphthalene. $^1$H NMR and mass spectral analysis revealed 85% deuterium incorporation in the 8-position of the 1-chloromethylnaphthalene.

B. Attempted Preparation of 1H-Cyclobuta[de]naphthalene: 8-Bromo-1-chloromethylnaphthalene (0.54 g, 2.1 mmol) was treated with n-butyl-lithium (1.6 M in hexane, 1.4 mL, 2.2 mmol) in diethyl ether (30 mL) at -100°C under argon. After having been warmed to room temperature and stirred several hr, the light yellow reaction mixture was washed with water and brine and dried over magnesium sulfate. Upon removal of solvent, no 1H-cyclobuta[de]naphthalene could be detected. The only products observed were of high molecular weight (> 280), thus indicating coupling of naphthylmethyl moieties. No further characterization of the product was made.

C. With Tetramethylethylenediamine: To a diethyl ether solution (30 mL) of 8-bromo-1-chloromethylnaphthalene (0.77 g, 3.0 mmol) and tetramethylethylenediamine (0.45 mL, 3.0 mmol) at -100°C under argon was added a 2.0 M solution of t-butyllithium in pentane (3.0 mL, 6.0 mmol).
The dark brown mixture was stirred 15 min at -100°C, then allowed to warm to room temperature and stirred 1 hr. The reaction mixture was washed with water, dried (MgSO₄) and the solvent removed. Preparative thin-layer chromatography (silica gel; hexane) afforded two products:

1) 1-neopentynaphthalene (142, 0.033 g, 6%) as a colorless oil whose ¹H NMR and mass spectra were identical to those of an authentic sample.

2) 1,2-di(1-naphthyl)ethane (143, 0.19 g, 46%) as a white solid, mp 158-160°C, lit mp 160-162°C; identical to an authentic sample by ¹H NMR and mass spectra.

Methyl (8-Bromo-1-naphthyl)methyl Ether (151). To a slurry of hexane-washed sodium hydride (0.97 g, 50% mineral oil suspension, 20 mmol) in dry dichloromethane (5 mL) at 0°C was added 8-bromo-1-naphthalene-methanol (4.0 g, 17 mmol) in dichloromethane (50 mL) dropwise. After the addition was complete, dimethyl sulfate (1.7 mL, 18 mmol) in dichloromethane (25 mL) was introduced, the mixture was stirred overnight at room temperature and the excess hydride was neutralized with saturated aqueous ammonium sulfate. The organic layer was separated, washed with water and dried over magnesium sulfate. Removal of solvent left a colorless oil which was chromatographed on silica gel (hexane as eluent) yielding methyl (8-bromo-1-naphthyl)methyl ether (2.1 g, 50%) as a colorless oil; IR (neat film, cm⁻¹) 3050, 2980, 2920, 2880, 2810, 1190, 1115, 815, 760; ¹H NMR (CDCl₃, δ) 3.47(s, 3H, CH₃), 5.25(s, 2H,
Reaction of Methyl (8-Bromo-1-naphthyl)methyl Ether with t-Butyl-
lithium. Methyl (8-bromo-1-naphthyl)methyl ether (0.70 g, 2.8 mmol) and
tetramethylethylenediamine (0.42 mL, 2.8 mmol) in dry diethyl ether (65
mL) were cooled -75°C under argon and a 2.0 M solution of t-butyllithium
in pentane (3.0 mL, 6.0 mmol) was added dropwise. The resulting bright
orange solution was warmed to room temperature, refluxed 17 hr, and then
washed with water and saturated aqueous ammonium sulfate and dried over
magnesium sulfate. Removal of solvent and preparative thin-layer
chromatography of the residue on silica gel with hexane eluent yielded
three products:

1) 1,2-di(1-naphthyl)ethylene (0.18 g, 4%) as a yellow solid identical
to an authentic sample.7

2) 1-methoxymethylnaphthalene (0.059 g, 18%) as a pale yellow oil;
identified by comparison to an authentic sample by 1H NMR and mass
spectra 83,

3) \( \alpha \)-methyl-1-naphthalenemethanol (152, 0.10 g, 22%) identical with a
sample independently synthesized (see later Experimental).

Reaction of Benzyl (8-Bromo-1-naphthyl)methyl Ether with t-Butyl-
lithium; \( \alpha \)-(Phenyl)methyl-1-naphthalenemethanol (159). An anhydrous
tetrahydrofuran solution (50 mL) of benzyl (8-
bromo-1-naphthyl)methyl ether74 (0.99 g, 3.0
mmol) was cooled under argon to -40°C in a dry
ice/acetonitrile slush bath and a 2.0 M
t-butyl lithium in pentane solution (3.5 mL, 7.0 mmol) added dropwise. The black solution was allowed to warm to room temperature then refluxed 2 hr. After cooling to room temperature, diethyl ether (200 mL) was added and the mixture was washed with saturated aqueous ammonium sulfate and water and then dried over magnesium sulfate. The yellow-brown oil obtained upon concentration of the solution was chromatographed on silica gel with hexane/benzene (1:1) as eluent yielding 1-naphthaldehyde (0.12 g, 26%), identified by $^1$H NMR, IR and mass spectra, and α-(phenyl)methyl-1-naphthalenemethanol (0.31 g, 42%), as a light yellow gum; IR (KBr, cm$^{-1}$) 3560(free OH), 3400(OH), 2070, 3040, 2930, 1601, 1520, 1500, 1460, 1090, 1060, 1035, 1025, 805, 787, 705; $^1$H NMR (CDCl$_3$, $\delta$) 2.0 (broad s, 1H, OH), 3.5(m, 2H, CH$_2$), 5.0(m, 1H, CHCH$_2$), 7.2-8.2(m, 12H, aromatic); off-resonance $^{13}$C NMR (CDCl$_3$, $\delta$, 20.1 MHz) 43.31(t, CH$_2$), 74.47(d, CH), and 10 aromatic CH absorptions at 123.75, 125.50, 125.60, 125.84(2C), 126.08, 127.54, 127.67, 127.88, 128.51(2C), 128.95 and 4 quaternary aromatic signals at 132.20, 134.09, 134.24 and 144.14; mass spectrum: m/e 248 (M$^+$).

8-Bromo-1-bromomethyl naphthalene (158). Phosphorus tribromide (6.8 mL, 72 mmol) was added to 8-bromo-1-naphthalene-methanol (5.9 g, 25 mmol) in diethyl ether (150 mL) and pyridine (2.2 mL, 27 mmol). After refluxing 25 hr, the milky white mixture was poured onto ice (300 g) and extracted with diethyl ether (600 mL). The extracts were washed with saturated aqueous sodium bicarbonate, dried (MgSO$_4$) and concentrated yielding 8-bromo-1-bromomethyl naphthalene (6.5 g, 86%) as a
white solid, mp 75-77°C, lit\textsuperscript{71} mp 76-77°C.

**Phenyl (8-Bromo-1-naphthyl)methyl Ether (161):** Sodium hydride (0.67 g, 50% dispersion in mineral oil, 14 mmol) was washed with hexane under nitrogen and a solution of phenol (1.2 g, 13 mmol) in acetonitrile (25 mL) added dropwise followed by 8-bromo-1-bromomethyl napthalene (3.9 g, 13 mmol) in acetonitrile (50 mL). The mixture was stirred 24 hr at room temperature, then poured into water (100 mL) and extracted with diethyl ether (500 mL). The ethereal extract was washed with brine, dried over magnesium sulfate and concentrated to a yellow oil. Chromatography on silica gel with hexane/benzene (4:1) eluent yielded phenyl (8-bromo-1-naphthyl)methyl ether (3.57 g, 88%) as a colorless oil which solidified on standing; IR (KBr, cm\textsuperscript{-1}) 1595, 1585, 1495, 1475, 1380, 1300, 1240, 1195, 1170, 1080, 1030, 1010, 990, 885, 845, 815, 770, 755, 690; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, δ) 5.84(s, 2H, CH\textsubscript{2}), 6.80-7.89(m, 11H, aromatic); exact mass: calcd. 312.0150; obsd. 312.0156. An analytical sample was prepared by flash chromatography on silica gel with 10% ethyl acetate/benzene followed by recrystallization from hexane, mp 62-64°C.

**Anal.** Calcd for C\textsubscript{17}H\textsubscript{13}BrO: C, 65.19; H, 4.18; Br, 25.52.

Found: C, 65.17; H, 4.31; Br, 25.41.

**Reaction of Phenyl (8-Bromo-1-naphthyl)methyl Ether (161) with n-BuLi in Tetrahydrofuran:** A solution of phenyl (8-bromo-1-naphthyl)methyl ether (0.94 g, 3.0 mmol) in dry tetrahydrofuran (50 mL) was cooled to -33°C under nitrogen and a 1.6 M solution of n-butyllithium in hexane
(2.0 mL, 3.2 mmol) added dropwise. After stirring 45 min at -33°C, the solution was refluxed 2 hr. Water was then added, the mixture diluted with diethyl ether, and the organic solution washed with water and brine, dried over magnesium sulfate and concentrated. Preparative thin-layer chromatography of the brown oily residue on silica gel (benzene: hexane, 1:9) gave two products:

1) \( \text{n-(n-butyl)-1-naphthylmethyl phenyl ether (162, 0.45 g, 52\%)} \) as a clear colorless oil; IR (neat, cm\(^{-1}\)) 3060, 2950, 2920, 2860, 1601, 1590, 1500, 1235, 800, 775, 750, 685; \(^1\)H NMR (CDCl\(_3\), \( \delta \) 0.68-2.20 (m, 9H, n-butyl), 5.82 (t, 1H, CH0, \( J=6\text{Hz} \)), 6.79-7.92 (m, 11H, aromatic), 8.00-8.23 (m, 1H, peri hydrogen); exact mass: calcd. 290.1671, obsd. 290.1662.

2) \( 1\text{-naphthylmethyl phenyl ether (163, 0.16 g, 23\%)} \), as a yellow solid, mp 70-73°C, lit mp 75°C 76-77°C, 66-67°C.

Reaction of Phenyl (8-Bromo-1-naphthyl)methyl Ether (161) with t-Butyl lithium.

A. In Diethyl Ether and Tetramethylethylenediamine: An anhydrous diethyl ether solution (30 mL) of phenyl (8-bromo-1-naphthyl)methyl ether (0.60 g, 1.9 mmol) and tetramethylethylenediamine (0.36 mL, 2.4 mmol) was cooled to -75°C under nitrogen and a 2.0 M solution of t-butyllithium in pentane (2.4 mL, 4.8 mmol) added dropwise. The resulting orange solution was stirred 30 min at -75°C and then refluxed 4 hr. The mixture was washed with water and brine, and dried over magnesium sulfate. The yellow oil obtained upon removal of solvent was chromatographed on silica gel (hexane as eluent) yielding three products:
1) 1H-cyclobuta[de]naphthalene (1, 0.018 g, 7%), a colorless liquid as identified by 1H NMR;

2) 1,2-di(1-naphthyl)ethylene (153, 0.031 g, 12%) as a yellow solid, identical to a sample identified earlier;

3) 1-naphthylmethyl phenyl ether (163, 0.094 g, 21%) as a yellow solid, mp 70-73°C, identified earlier.

B. In Diethyl Ether: A diethyl ether solution (50 mL) of phenyl (8-bromo-1-naphthyl)methyl ether (0.89 g, 2.9 mmol) was cooled to -78°C under nitrogen and a 2.0 M solution of t-butyllithium in pentane (3.2 mL, 6.4 mmol) was added dropwise. The light yellow solution mixed with a white precipitate was stirred 30 min at -78°C and then refluxed 2 hr. The resulting black solution was washed with water, dried over magnesium sulfate and concentrated. Chromatography of the residue on silica gel (10% benzene/hexane as eluent) yielded 1,2-di(1-naphthyl)ethylene (153, 0.023 g, 3%) and 1-naphthylmethyl phenyl ether (163, 0.20 g, 30%) both as previously characterized.

(8-Bromo-1-naphthyl)methyl Benzoate (165): A mixture of 8-bromo-1-naphthalenemethanol (3.37 g 22 mmol), pyridine (1.8 mL, 22 mmol) and benzoyl chloride (2.6 mL, 22 mmol) in benzene (100 mL) was refluxed 5 hr. After cooling to room temperature, the solution was washed with water, dried over magnesium sulfate and concentrated to a light yellow oil. Chromatography on silica gel (benzene as eluent) produced (8-bromo-1-naphthyl)methyl benzoate (6.63 g, 88%) as a colorless oil which slowly
solidified in a freezer, mp 49-52°C (hexane); IR (KBr, cm⁻¹) 1705 (C=O), 1600, 1455, 1375, 1330, 1275, 1110, 1075, 1030, 825, 775, 720; ¹H NMR (CDCl₃, δ) 6.20(s, 2H, CH₂), 7.2-8.3(m, 11H, aromatic); exact mass: calcd. 340.0099; obsd. 340.0104.

Anal. Calcd for C₁₈H₁₃O₂Br: C, 63.36; H, 3.84; Br, 23.42.
Found: C, 63.16; H, 3.99; Br, 23.60.

**Reaction of (8-Bromo-1-naphthyl)methyl Benzoate with t-Butyllithium:**

**1-Phenyl-1H,3H-naphtho[1,8-cd]pyran-1-ol (166).** A solution of (8-bromo-1-naphthyl)methyl benzoate (0.98 g, 2.9 mmol) and dry tetramethylethylenediamine (0.59 mL, 3.9 mmol) in dry diethyl ether (60 mL) was cooled to -79°C under argon and a 2.0 M solution of t-butyllithium in pentane (3.4 mL, 6.8 mmol) was added dropwise. After 0.5 hr the light orange solution was allowed to warm to room temperature and then refluxed 7 hr. The solution was cooled and poured into water; the organic layer was separated, washed with saturated aqueous sodium bicarbonate and dried (MgSO₄). Removal of solvent left a light yellow oil. Preparative thin-layer chromatography (silica gel, 10% ether/benzene) gave:

1) 1-phenyl-1H,3H-naphtho[1,8-cd]pyran-1-ol (0.45 g, 59%) as white crystals from hexane, mp 112.5-115°C; IR (KBr, cm⁻¹) 3390(OH), 1525, 1455, 1395, 1225, 1125, 1095, 1065, 1025, 970, 835, 810, 790, 770, 710; ¹H NMR (CDCl₃, δ) 3.45(broad s, 1H, OH), 5.15(q, 2H, center of AB pattern, δA= 5.38, δB= 4.92, J= 15 Hz) 7.0-7.9(m, 11H, aromatic); mass spectrum m/e 262 (M⁺).
Anal. Calcd for C$_{18}$H$_{14}$O$_2$: C, 82.42; H, 5.38.

Found: C, 82.01; H, 5.53.

2) 1-naphthalenemethanol (0.104 g, 23%); spectrally identical to an authentic sample.

Reaction of 8-Bromo-1-naphthaldehyde p-Tosylhydrazone (9) with n-Butyllithium and t-Butyllithium: A diethyl ether solution (30 mL) of 8-bromo-1-naphthaldehyde p-tosylhydrazone (1.00 g, 2.5 mmol) was cooled to -78°C under nitrogen and a 2.0 M solution of t-butyllithium in pentane (3.6 mL, 7.2 mmol) was added. A red solution containing a suspended orange solid was formed. The mixture was allowed to warm to room temperature and the red solution then refluxed 11 hr. After cooling to room temperature, the mixture was washed with water and saturated aqueous ammonium sulfate and dried (MgSO$_4$). Removal of the solvent and chromatography of the residue on silica gel (hexane as eluent) yielded 1-neopentynaphthalene (142, 0.079 g, 17%) as a colorless oil; $^1$H NMR (CDCl$_3$, $\delta$) 0.93(s, 9H, C(CH$_3$)$_3$), 2.95(s, 2H, CH$_2$), 7.2-8.2(m, 7H, aromatic); mass spectrum m/e 198 (M$^+$). The $^1$H NMR spectrum of the product agreed with the reported.$^{72}$

Repeating the reaction with excess t-butyllithium or n-butyl-lithium resulted in enhanced yields of 142 (39%) and 5-(1-naphthyl)-nonane (176, 38%), characterized by $^1$H NMR (CDCl$_3$, $\delta$) 0.8-2.0 (complex m, 19H, alkyl), 3.5(m, 1H, CH), 7.2-8.4(m, 7H, aromatic) and mass spectra, m/e 254 (M$^+$), 197 (M$^+$ - nBu), 141 (M$^+$ - 2nBu).

No evidence for the formation of 1H-cyclobuta[de]naphthalene (1) was obtained in any of these experiments.
(8-Bromo-l-naphthyl)acetonitrile (182): Anhydrous potassium cyanide (0.35 g, 5.3 mmol) was added to an acetonitrile solution (15 mL) of 8-bromo-l-chloromethyl-naphthalene (0.63 g, 2.5 mmol) and dicyclohexyl-18-crown-6 (0.04 g), the mixture stirred 22 hr and then poured into water. The mixture was extracted with diethyl ether, the organic extract washed with water and dried over magnesium sulfate. Removal of solvent left a light brown oil which was filtered through silica gel with benzene yielding (8-bromo-l-naphthyl)acetonitrile as a light yellow oil (0.53 g, 87%); IR (neat, cm⁻¹) 3060, 2260 (C≡N), 1600, 1540, 1500, 1425, 1370, 1200, 1020, 765; ¹H NMR (CDCl₃, δ) 4.5(s, 2H, CH₂), 7.0-7.9(m, 6H, aromatic).

Reaction of (8-Bromo-l-naphthyl)acetonitrile (182) with Potassium Amide: 7-Amino-l-naphthylacetonitrile (183) and 8-Amino-l-naphthylacetonitrile (184): An anhydrous diethyl ether solution (10 mL) of (8-bromo-l-naphthyl)acetonitrile (0.50 g, 2.0 mmol) was added to potassium amide (10 mmol), prepared from potassium and liquid ammonia, in liquid ammonia (60 mL). After stirring 15 min, saturated aqueous ammonium sulfate (20 mL) was added and the ammonia allowed to distill away. The residue was dissolved in benzene/ether (1:1), washed with water and dried over magnesium sulfate. Removal of solvent left a brown tar. Three compounds were isolated by preparative thin-layer chromatography (10% ethyl acetate/benzene): 1) starting (8-bromo-l-naphthyl)acetonitrile (0.14 g, 27%), identified
by $^1$H NMR and TLC,

2) (8-amino-1-naphthyl)acetonitrile (0.047 g, 13%) as a light brown oil; IR (neat, cm$^{-1}$) 3460, 3370, (N-H), 2930, 2250(CN), 825, 785, 750; $^1$H NMR (CDCl$_3$, δ, ethyl acetate was added as an internal standard) 4.05 (s, 2H, CH$_2$), 7.2-8.0 (m, 6H, aromatic); mass spectrum, m/e 182 ($M^+$).

3) (7-amino-1-naphthyl)acetonitrile (0.087 g, 24%) as a light red-brown oil; IR (neat, cm$^{-1}$) 3460, 3380(N-H), 2250(CN), 830; $^1$H NMR (CDCl$_3$, δ, ethyl acetate was added as an internal standard) 3.90 (s, 2H, CH$_2$), 6.8-7.6 (m, 6H, aromatic); mass spectrum, m/e 182 ($M^+$).

1H-Naphtho[1,8-de]triazene (196). Freshly distilled 1,8-diaminonaphthalene (19 g, 0.12 mol) was dissolved in boiling water (5 L) and glacial acetic acid (30 mL). Upon cooling the mixture to room temperature, a solution of sodium nitrite (9.8 g, 0.14 mol) in water (50 mL) was added in 15 min and the dark red suspension then stirred 10 min. The brick red crystals of 1H-naphtho[1,8-de]triazene were filtered, washed with water and dried (20 g, 100%), mp 225-235°C d, lit$^{76}$ mp 235-237°C. The product was of sufficient purity for further use.
1-Aminonaphtho[1,8-de]triazene (6).  1H-Naphtho[1,8-de]triazene (10 g, 60 mmol) was suspended in warm (60°C) aqueous potassium hydroxide (14 g, 242 mmol, in 200 mL) and hydroxylamine-O-sulfonic acid (7.1 g, 63 mmol) added in small portions. After stirring the suspension 1 hr at 60-70°C, additional potassium hydroxide (7.0 g, 124 mmol) and hydroxylamine-O-sulfonic acid (7.4 g, 66 mmol) were added and the mixture was stirred an hour at 60-70°C. After cooling to room temperature, the solution was filtered and the residue washed with 4% aqueous potassium hydroxide and water, and then extracted with diethyl ether until the ether extracts were nearly colorless (2500 mL). The extracts were concentrated and the residue chromatographed on silica gel. Elution with 1:3 diethyl ether/hexane gave 8-azido-1-naphthylamine (1.1 g, 10%) as light brown crystals, mp 80-82°C. Elution with ether gave a dark red solution from which 1-aminonaphtho[1,8-de]triazene separated as bright ruby red crystals (1.8 g, 16%), mp 152.5-154°C, lit77 mp 154.5-155.5°C.

N-Methylidene-1-aminonaphtho[1,8-de]triazene (193).  A solution of 1-aminonaphtho[1,8-de]triazene (1.1 g, 5.8 mmol) in absolute ethanol (125 mL) and aqueous formaldehyde (36%, 0.96 mL, 12 mmol) was refluxed 2 hr. Benzene (50 mL) was added and the water removed as an azeotrope. Removal of solvent and chromatography of the residue
on basic alumina (benzene) gave N-methylidene-1-aminonaphtho[1,8-de]-triazene as red crystals (0.063 g, 56%), mp 90-92.5°C; IR (KBr, cm⁻¹) 1585, 1375, 1290, 1045, 1000, 830, 770; ¹H NMR (CDCl₃, δ) 6.85 (d, 1H, A of AB pattern, N CH₂, J = 12 Hz), 7.92(d, 1H, B of AB, N CH₂, J = 12 Hz), 6.6-7.5(m, 6H, aromatic); mass spectrum, m/e(relative intensity) 196(M⁺, 19), 169(8), 168(62), 167(19), 141(38), 140(100), 139(73), 114(15), 113(54), 112(31).

Photolysis of N-Methylidene-1-aminonaphtho[1,8-de]triazene (193). A benzene solution (150 mL) of N-methylidene-1-aminonaphtho[1,8-de]-triazene (0.86 g, 4.4 mmol) was purged with nitrogen for 30 min and then photolyzed with a 450W Hanovia high pressure mercury arc lamp for 8 hr. The original ruby red solution turned black after 1 hr. Removal of solvent left an intractable tar. No evidence for 1H-cyclobuta[de]-naphthalene could be found by TLC or ¹H NMR.

2-Oxo-2H-benzo[cd]indole (197). 1,8-Naphthoic anhydride (131 g, 0.66 mol), hydroxylamine hydrochloride (46 g, 0.66 mol) and freshly distilled pyridine (750 mL) were refluxed 1 hr. Heating was discontinued and p-toluenesulfonyl chloride (270 g, 1.42 mol) was added to the black solution at a rate to cause controlled boiling. After refluxing an additional hr, the hot solution was poured into water (3 L) and allowed to cool. The yellow solid obtained was filtered, washed with 4% sodium hydroxide and water. After air drying, the material was refluxed with ethanol (500 mL), water (1500 mL) and sodium hydroxide (100 g,
2.4 mol) for 3 hr; during the last 2 hr, ethanol was allowed to distill off (the final solution temperature was 95°C). The hot solution was poured into a 3 L beaker and concentrated hydrochloric acid (30 mL) added slowly with gas evolution. Upon cooling the mixture, a yellow solid formed which was filtered, washed with water and dried at 100°C under vacuum. The yield of 2-oxo-2H-benzo[cd]indole was 68.9 g (62%), mp 171-175°C, lit78 mp 172-178°C; IR (KBr, cm⁻¹) 3200(N-H), 1720(C=O), 1665, 1645(N-H bending).

2-Oxo-2H-naphtho[1,8-bc]thiophene (198). 2-Oxo-2H-benzo[cd]indole (5.4 g, 30 mmol) was dissolved in hot 1.5 M sodium hydroxide (40 mL). The mixture was allowed to cool to room temperature and sodium nitrite (2.4 g, 34 mmol) added in one portion. The dark brown solution was added to cold (0°C) 2 N hydrochloric acid (200 mL) slowly to keep the temperature between 0-5°C. After stirring the mixture 1 hr at 0-5°C, the brown precipitate was filtered, washed with water and slurried in cold water (75 mL). The mixture was then added, in small portions, to an aqueous solution of potassium ethyl xanthate (5.4 g, 34 mmol, in 25 mL) at 40-50°C. After addition of sodium bicarbonate (6.0 g) in one portion, the brown solution was stirred 1 hr at 35-40°C and then refluxed 2.5 hr. After cooling the solution to room temperature, the resulting yellow crystals of 2-oxo-2H-naphtho-[1,8-bc]thiophene (2.0 g, 35%) were collected and dried, mp 143.5-146.5°C, lit79 mp 144.5-145.5°C; IR (KBr, cm⁻¹) 1690(C=O).
2H-Naphtho[1,8-bc]thiophene (199).

**Method A:** Sodium borohydride (1.7 g, 42 mmol) was suspended in dry tetrahydrofuran (20 mL) and dry bis-(2-methoxyethyl) ether (30 mL) and cooled to 0°C under argon. A solution of 2-oxo-2H-naphtho[1,8-bc]thiophene (4.4 g, 24 mmol) in freshly distilled boron trifluoride-etherate (80 mL) was added in 1.5 hr at 0–5°C. The solution was stirred 2 hr at room temperature and finally at 65-70°C for 2.5 hr while the volatiles escaped. The mixture was cooled to room temperature and poured into concentrated hydrochloric acid (100 mL) and crushed ice. The white precipitate was filtered, dissolved in diethyl ether (300 mL), washed with water (300 mL) and dried over magnesium sulfate. Removal of solvent left a tan solid which was chromatographed on silica gel with hexane as eluent yielding 2H-naphtho[1,8-bc]thiophene (1.6 g, 47%) as a white solid, mp 84.5–85.5°C (hexane), lit® mp 83–85°C; \(^1\)H NMR (CDCl\(_3\), \(\delta\)) 4.65 (s, CH\(_2\)).

**Method B:** 8-Bromo-1-bromomethylnaphthalene (1.2 g, 3.9 mmol) and sodium sulfide nonahydrate (0.97 g, 4.0 mmol) in dimethylformamide (50 mL) were refluxed 2.5 hr. The initial blue-black solution was light orange when heating was discontinued and after cooling to room temperature, was poured into water (400 mL) and extracted with diethyl ether (500 mL). The organic extract was washed with water (4 x 500 mL), dried over magnesium sulfate and the solvent removed under reduced pressure. Chromatography of the resulting dark oil on silica gel (hexane) yielded 2H-naphtho[1,8-bc]thiophene as a tan solid (0.35 g, 52%), mp 75–79°C,
which was identical with an authentic sample by TLC, \(^1\)H NMR, IR and mass spectra.

**2H-Naphtho[1,8-bc]thiophene-1,1-dioxide (189).** 2H-Naphtho[1,8-bc]thiophene (2.1 g, 12 mmol) was dissolved in dry dichloromethane (125 mL). The solution was cooled to 0-5°C under argon and m-chloroperoxybenzoic acid (5.1 g, 85%, 25 mmol) was added in small portions over a period of 30 min. The cloudy solution was stirred 90 min at 0-5°C, filtered, washed with saturated aqueous sodium bicarbonate (2 x 250 mL) and dried over magnesium sulfate. Upon removal of the solvent, 2H-naphtho[1,8-bc]thiophene-1,1-dioxide was obtained as a tan solid in quantitative yield. Recrystallization from 95% ethanol gave white needles (2.0 g, 80%), mp 201-203°C d, lit mp 198.5-199.5°C; IR (KBr, cm\(^{-1}\)) 1290, 1120(SO\(_2\)); \(^1\)H NMR (CDCl\(_3\), \(\delta\)) 4.69(s, CH\(_2\)); mass spectrum, m/e 204(M\(^+\)).

**Photolysis of 2H-Naphtho[1,8-bc]thiophene-1,1-dioxide (189).** After argon had been bubbled through a dry benzene (125 mL) solution of 2H-naphtho[1,8-bc]thiophene-1,1-dioxide (0.36 g) for 30 min, the solution was irradiated in a quartz vessel with a Hanovia 450W high pressure mercury arc lamp for 12 hr. The sulfur dioxide evolved slowly was detected via a zinc nitroprusside test, and a brown precipitate formed in the photolysis vessel. The mixture was filtered, solvent removed and the brown residue chromatographed on silica gel (benzene). Starting material (0.23 g, 64% recovery), identified by \(^1\)H NMR and TLC, and a
brown amorphous solid which defied characterization were isolated. No
evidence for \( 1H \)-cyclobuta\{de\}napthalene was detected by either TLC or
\( 1H \) NMR.

**Pyrolysis of 2H-Naphtho[1,8-bc]thiophene-1,1-dioxide (189).** 2H-Naphtho-
[1,8-bc]thiophene-1,1-dioxide (0.43 g, 2.1 mmol) was added as a neat
solid via a "Normag" solid addition funnel to a 3.5 x 35 cm quartz tube
packed with quartz chips and heated to 750°C at 0.25-0.30 mm. The black
pyrolysate was collected in a U-tube trap cooled to -78°C. Preparative
thin-layer chromatography on silica gel (benzene) gave two fractions
along with starting material (0.06 g, 14%) and intractables. Column
chromatography on silica gel of each fraction (hexane and 1:1 hexane/
benzene, respectively, used as eluent) yielded two products:
1) \( 1H \)-cyclobuta\{de\}napthalene (\( \frac{1}{1} \), trace, < 1%), identified by \( 1H \)
NMR as one component of a complex mixture;
2) 2-oxo-2H-naphtho[1,8-bc]thiophene (198, 0.063 g, 16%), identical to
an authentic sample by IR, \( 1H \) NMR, and TLC. The yield of was 19%
based on recovered starting material.

Pyrolysis at lower temperatures resulted in major, if not exclu-
sive, recovery of starting material. Higher temperatures or higher
pressures afforded only intractable tars.

**8-Bromo-1-naphthyl Phenyl Ketone (201).** Phenyl magnesium bromide was
prepared by stirring magnesium turnings (0.98 g, 40 mmol) and bromobenzene (4.2 mL, 40 mmol)
in diethyl ether (50 mL) for 3 hr. Dry cadmium chloride (3.8 g, 20 mmol) was added via a gooch
tube at 0°C and the diethyl ether allowed to distill out of the reaction vessel with simultaneous addition of dry benzene (70 mL). A benzene (70 mL) solution of 8-bromo-1-naphthoyl chloride (5.1 g, 19 mmol) was added dropwise and the solution refluxed 5 hr. After cooling the mixture to room temperature, 5% hydrochloric acid (70 mL) was added. The organic layer was separated, washed with saturated aqueous sodium bicarbonate and dried (MgSO₄). Removal of solvent left a light brown oil which was chromatographed on silica gel (benzene) and gave a light yellow oil; additional flash chromatography on silica gel (light petroleum: ethyl acetate; 20:1) gave a colorless oil which was crystallized from hexane/benzene/ethanol yielding 8-bromo-1-naphthyl phenyl ketone as a white solid (4.2 g, 72%), mp 63.5-65°C; IR (KBr, cm⁻¹) 3070, 3050, 1670, (C=O), 1600, 1585, 1500, 1455, 1320, 1275, 1205, 1075, 1025, 825, 770, 710, 685; ¹H NMR (CDCl₃, δ) 7.2-8.1(m, aromatic); mass spectrum, m/e 311 and 309(M⁺).


3-Phenyl-1H-benzo[de]cinnoline (200). 8-Bromo-1-naphthyl phenyl ketone (0.48 g, 1.5 mmol) and anhydrous hydrazine (7 mL) were heated under nitrogen at 120-125°C for 17 hr. Upon cooling the dark red solution and diluting it with ethanol, yellow crystals separated which were collected and recrystallized from benzene/hexane affording 3-phenyl-1H-benzo[de]cinnoline as yellow needles (0.058 g, 16%), mp 199-204°C, lit mp 206-208°C; IR (KBr, cm⁻¹) 3270(N-H), 3060(aromatic...
$^1$H NMR (CDCl$_3$, $\delta$) 6.2-7.3 (m, 6H), 7.3-7.7 (m, 5H), 10.92 (broad s, 1H, NH); exact mass: calcd. 244.1012; obsd. 244.1006.

**Anal.** Calcd for C$_{17}$H$_{12}$N$_2$: C, 83.58; H, 4.95; N, 11.47.

Found: C, 83.57; H, 4.95; N, 11.47.

**Attempted Pyrolysis of Acenaphthenone (210).** Acenaphthenone (0.74 g) was dropped as a neat solid via a "Normag" solid addition funnel into a quartz tube packed with quartz chips and heated to 750°C at 0.6-0.7 mm. The product collected in a U-tube trap at -78°C and purified by column chromatography on silica gel with 1:1 benzene/hexane yielded original acenaphthenone (0.70 g, 95% recovery).

**1-Naphthaldehyde p-Tosylhydrazone (13).** Freshly distilled 1-naphthaldehyde (2.6 mL, 19 mmol) dissolved in absolute ethanol (20 mL) was added to a hot absolute ethanolic solution (20 mL) of p-toluenesulfonhydrazide (3.56 g, 19 mmol) and the solution refluxed 2 hr. Upon cooling the mixture colorless crystals of 1-naphthaldehyde p-tosylhydrazone (13) formed which were collected and recrystallized from ethanol (4.92 g, 80%), mp 129-133°C, lit$^3$ mp 130-132°C.

**Pyrolysis of Sodium 1-Naphthaldehyde p-Tosylhydrazonate (211).** 1-Naphthaldehyde p-tosylhydrazone (0.51 g, 1.6 mmol) was converted to its sodium salt with dry sodium methoxide (0.22 g, 4.0 mmol) in anhydrous dichloromethane (50 mL). The solvent was removed under reduced pressure and the flask containing the dry salt fitted with a Claisen adapter and
connected to a dry ice/acetone cooled trap. A vacuum of 0.7 mm was pulled on the system and the pyrolysis flask then immersed in a salt bath at 280–290°C. A clear distillate (0.088 g) was collected in the cold trap. 1H NMR analysis of this material indicated that 1H-cyclo­buta[de]naphthalene (1) was not present. Preparative thin-layer chromatography (1:1, benzene/hexane) gave 1-naphthonitrile (213, 0.034 g, 14%) and 1-naphthaldehyde (214, 0.011 g, 5%) both as colorless liquids. Identification of 213 and 214 was based on IR and TLC comparisons with authentic samples.

Photolysis of Lithium 1-Naphthaldehyde p-Tosylhydrazone in Diethyl Ether. To an anhydrous tetrahydrofuran solution (60 mL) of 1-naphthaldehyde p-tosylhydrazone (0.80 g, 2.5 mmol) at 0°C was added a 2.0 M solution of t-butyllithium in pentane (1.31 mL, 2.6 mmol). After 30 min the light yellow mixture was concentrated to dryness in vacuo and the resulting yellow solid then suspended in dry diethyl ether (125 mL). Nitrogen was bubbled through the solution and the mixture photolyzed with a Hanovia 450W mercury arc lamp for 8.5 hr. After filtering through Celite, the reaction mixture was washed with saturated aqueous sodium bicarbonate and dried over magnesium sulfate. Removal of solvent left a brown oil which was chromatographed on silica gel. Elution with 1:1 benzene/hexane gave:

1) 1-neopentynaphthalene (142, 0.038 g, 8%) as a colorless oil; identical to an authentic sample,
2) 1,2-di(1-naphthyl)ethane (143, 0.029 g, 8%), as identified earlier.

Elution with benzene gave ethyl α-(1-naphthylmethyl)ethyl ether
(215, 0.143 g, 27%) as a light yellow oil; IR (neat film, cm⁻¹) 3060, 2980, 2940, 2880, 1120 (C-O), 795; ¹H NMR (CDCl₃, δ, 200 MHz) 1.132 (t, 3H, -CH₂CH₃, J=7Hz), 1.145 (d, 3H, -CH₂CH(CH₃)-O, J=6Hz), 3.01 (M, 1H, one of the benzylic protons), 3.48 (M, 3H, one of the benzylic protons and -OCH₂CH₃), 3.79 (m, 1H, -CH₂CH(CH₃)-O) 7.3-7.5 (m, 4H, aromatic, H-2,3,6,7), 7.69-7.74 (m, 1H, H-4 or H-5), 7.81-7.85 (m, 1H, H-4 or 5), 8.03-8.08 (m, 1H, H-8); ¹³C NMR (CDCl₃, δ) 15.63 (CH₃), 20.15 (CH₃), 40.49 (naph-CH₂-CH) 64.18 (O-CH₂CH₃), 75.83 (CH₂-CH(CH₃)-O), 6 aromatic C-H signals at 124.04, 125.45 (2C), 125.74, 126.96, 127.68 and 128.80, 3 quaternary aromatic signals at 132.39, 134.00 and 135.50; exact mass: calcd. 214.1358; obsd. 214.1362.

5-(1-Naphthyl)-1H-tetrazole (216). 1-Naphthonitrile (4.1 g, 27 mmol), ammonium chloride (1.43 g, 27 mmol) and sodium azide (1.81 g, 27 mmol) were heated in dimethylformaide at 110-120°C for 48 hr. After cooling to room temperature the reaction mixture was poured into water, and several drops of concentrated hydrochloric acid were added. The beige solid obtained was filtered and recrystallized from water/ethanol affording 5-(1-naphthyl)-1H-tetrazole as a tan solid (3.18 g, 57%), mp 104-114°C.

Pyrolysis of 5-(1-Naphthyl)-1H-tetrazole. 5-(1-Naphthyl)-1H-tetrazole (0.90 g) was added, as a neat solid via a "Normag" solid additional funnel to a quartz tube packed with quartz chips and heated to 600°C at 0.05-0.1 mm. The crude pyrolysate was a black tar from which only
1-naphthonitrile and intractables were obtained by chromatography. No evidence (TLC, $^1$H NMR) for formation of 1H-cyclobuta[de]naphthalene was found.

1-Methoxymethylnaphthalene (136). A 50% mineral oil dispersion of sodium hydride (8.6 g, 0.18 mol) was cooled to 0-5°C and washed with hexane (2 x 30 mL) under argon. 1-Naphthalenemethanol (25.6 g, 0.16 mol) in dry dichloromethane (200 mL) was added dropwise with mechanical stirring. Dimethyl sulfate (16 mL, 0.17 mol) in dry dichloromethane (75 mL) was then introduced slowly and the resulting grey slurry refluxed overnight. After careful dropwise addition of saturated aqueous ammonium sulfate (75 mL), the organic solution was washed with water and dried over magnesium sulfate. Removal of solvent left a light yellow oil. Distillation yielded 1-methoxy­methylnaphthalene as a clear colorless liquid (23.72 g, 86%), bp 109-112°C at 0.75 mm, lit bp 150.5-156.0/16 mm. Column chromatography on silica gel (hexane) of the pot residue afforded additional 136 (2.02 g, 7%) total yield 93%.

[Methoxy(1-naphthyl)methyl]trimethylsilane (220). A mixture of 1-methoxy­methylnaphthalene (5.2 g, 30.0 mol) and dry tetramethylethylene­diamine (5.3 mL, 35 mmol) in dry diethyl ether (100 mL) was cooled to -70°C under argon. Addition of t-butyllithium in pentane (1.9 M, 17 mL, 32 mmol) resulted in a deep purple-black solution. The reaction mixture was stirred 20 min at -70°C, chlorotrimethyl-
silane (5.2 mL, 33 mmol) then added and the dark green solution allowed to warm to room temperature. Water was added to the colorless solution and the organic layer was separated, washed with saturated aqueous sodium bicarbonate and dried over magnesium sulfate. Removal of solvent left a light yellow oil (7.59 g, 100%) which was pure by TLC and $^1$H NMR. Vacuum distillation yielded a colorless oil, bp 123-125°C/0.6 mm, which solidified in a freezer. Sublimation (40-60°C at 0.05 mm) yielded analytically pure [methoxy(1-naphthyl)methyl]trimethylsilane as a white waxy solid, mp 40.5-43.0°C; IR (neat, cm$^{-1}$) 3060, 2960, 2930, 2900, 2820, 1595, 1510, 1395, 1252, 1095, 940, 880, 850, 790; $^1$H NMR (CDCl$_3$, $\delta$, CH$_2$Cl$_2$ was added as an internal standard), -0.02 (s, 9H, -Si(CH$_3$)$_3$), 3.33 (s, 3H, -OCH$_3$), 4.83 (s, 1H, -CH), 7.3-8.2 (m, 7H, aromatic); exact mass: calcd. 244.1284; obsd. 244.1289.

Anal. Calcd. for C$_{15}$H$_{20}$OSi: C, 73.71; H, 8.25,

Found: C, 73.58, H, 8.13.


All pyrolyses, unless otherwise described, were performed by passing the samples through a 3 x 35 cm quartz tube packed with a 4-5 cm column of quartz chips placed approximately half way down the tube (Fig. 5). The pyrolysis tube was heated with a 110 V Hoskins electric furnace. A thermocouple was positioned between the furnace wall and the quartz tube approximately one-third of the way into the oven. Insulation material was packed around the tube at the top and bottom of the oven and a receiver, with a sidearm for carrier gas exit or vacuum connection, was attached to the bottom of the tube and cooled to -78°C.
Figure 5: Pyrolysis Unit

Figure 6: Reservoir for Introduction of Sample by Volatilization

Figure 7: Normag Solid Addition Funnel

Figure 8: Solid Addition Funnel
Introduction of sample into the hot zone was effected in one of three ways: 1) distillation or sublimation of the sample by slowly heating a reservoir containing the sample with an oil bath, flame, or nichrome wire wrapped around the reservoir (Fig. 6), 2) dropping the sample into the tube as a neat liquid using a Hersberg pressure equalized dropping funnel, or 3) dropping the sample as a neat solid into the tube utilizing a "Normag" pressure equalizing solid addition funnel (Fig. 7) or a scoop holding the sample which was fitted into an inverted Erlenmeyer flask placed on top of the pyrolysis tube (Fig. 8). Generally, the distillation technique gave better and more reproducible results since stricter control over rate and amount of addition could be maintained and there was less fluctuation in pressure during pyrolysis. When vacuum pyrolyses were conducted, pressure was monitored with a manometer fitted into the vacuum system between the receiver and the vacuum pump. The flow rates of carrier gas for pyrolyses at atmospheric pressure were monitored with a gas bubbler.

Pyrolysis of [Methoxy(1-naphthyl)methyl]trimethylsilane (220); 1H-Cyclobuta[de]naphthalene (1). Distillation of [methoxy(1-naphthyl)methyl]trimethylsilane (3.0 g, 12 mmol) through a quartz tube heated to 650°C at 0.05-0.10 mm afforded a dark brown pyrolysate which was chromatographed on silica gel, slowly changing eluent from hexane to benzene. The products obtained were:

1) a mixture (1.02 g) of 1H-cyclobuta[de]naphthalene (1, 63% of mixture, 39% yield), naphthalene (5% yield), and 1-methylnaphthalene (3% yield) as a light yellow liquid. The product was
homogeneous by TLC and identification and yields of components were
determined by $^1$H NMR (CH$_2$ClCH$_2$Cl was added as internal standard)
or VPC. Analysis of the mixture by VPC or HPLC showed numerous
other products (3%) which were not identified.

2) 1-methoxymethylnaphthalene (136, 0.11 g, 8%), identical with an
authentic sample by TLC and $^1$H NMR.

3) 1-naphthaldehyde (214, 0.12 g, 9%), characterized by comparison of
its TLC and $^1$H NMR with that of an authentic sample.

4) $\alpha$-methyl-1-naphthenemethanol (152, 0.14 g, 7%); identical to
authentic sample by TLC and $^1$H NMR.

The yield of 1H-cyclobuta[de]naphtalene (1) varied greatly
with the temperature and pressure at which the pyrolyses were conducted
as shown in Table 9.

Hydrocarbon was usually obtained after chromatography as the major
component (60-70%) of a mixture with naphtalene, methylnaphthalene and
other minor products. This mixture could be used directly for prepara-
tion of derivatives of 1 as demonstrated by the isolation, in good
purity, of 4-nitro-1H-cyclobuta[de]naphthalene (222) from nitration of
the mixture. Further purification (> 90% purity) of 1 could be ef-
rected by fractional distillation or preparative VPC (5% SE-30, 140°C).
Formation of the picric acid complex of 1 followed by recrystalliza-
tion and decomposition of the complex on silica gel (hexane eluent)
also afforded 1H-cyclobuta[de]naphthalene (1) of good purity.
Nitration of 1H-Cyclobuta[de]naphthalene Obtained from Pyrolysis.

Acetyl nitrate (6.2 mmol) was prepared by slowly adding 70% nitric acid (0.4 mL, 6.2 mmol) to acetic anhydride (5 mL) at 0.5°C. After stirring 5 min this mixture was added dropwise to 1H-cyclobuta[de]naphthalene (1.02 g of pyrolysis product, 63% pure; 4.7 mmol) in acetic anhydride (20 mL) at 0-5°C. The mixture was stirred for 1 hr at 0-5°C, allowed to warm to room temperature and stirred an additional hr. The solution was then poured into a mixture of diethyl ether (200 mL) and aqueous potassium hydroxide (40 g in 200 mL). After the mixture had been stirred 2 hr, the ether layer was separated and dried over magnesium sulfate. Removal of solvent left a yellow solid which was recrystallized from hexane to give 4-nitro-1H-cyclobuta[de]naphthalene, as yellow needles (0.29 g, 34%; mp 120-123°C, lit.3 mp 124-125°C). The product was homogeneous by TLC and spectrally identical to reported values. The mother liquor, upon chromatography on silica gel with 50% hexane/benzene, afforded additional 4-nitro-1H-cyclobuta[de]naphthalene, as a yellow solid (0.12 g, 14%).

α-Methyl-1-naphthalenemethanol (152). 1-Naphthylmagnesium bromide, prepared from 1-bromonaphthalene (1.1 g, 5.1 mmol) and magnesium turnings (0.15 g, 6.2 mmol) in dry diethyl ether (60 mL), was treated with acetaldehyde (0.4 mL, 7.2 mmol) and the solution stirred 0.5 hr at room temperature. Upon quenching the mixture with
aqueous ammonium sulfate, the organic layer was separated, washed with
water and saturated aqueous sodium bicarbonate and then dried over mag­
nesium sulfate. Removal of solvent left a yellow oil which crystal­
lized upon addition of hexane (0.63 g, 72%). Recrystallization from
hexane yielded α-methyl-1-naphthalenemethanol as colorless needles,
mp 62.5-63.5°C, lit84 65.5-66.5°C, 62.5-63.5°C, 62-63°C.

2-Bromomethyl-naphthalene (228). A mixture of 2-methyl-naphthalene
(5.9 g, 41 mmol), N-bromosuccinimide (7.6 g, 41 mmol) and benzoylperoxide (0.1 g) in carbon
tetrachloride (150 mL) was refluxed 28 hr.
After cooling, the solution was filtered and
the solvent evaporated. The brown solid ob­
tained was recrystallized from hexane to give
2-bromomethyl-naphthalene as tan crystals (6.0 g, 65%), mp 47-50°C,
lit85 52-53°C.

2-Methoxymethyl-naphthalene (229). To 2-bromomethyl-naphthalene (5.7 g,
26 mmol) in dry tetrahydrofuran (100 mL) was
added a solution of 25% sodium methoxide in
methanol (25 mL, 116 mmol) and the mixture was
stirred 51 hr at room temperature. The solu­
tion was diluted with diethyl ether (200 mL),
washed with water and with saturated sodium
bicarbonate solution and then dried over magnesium sulfate. Removal
of solvent left 2-methoxymethyl-naphthalene as a light brown liquid
which distilled as a colorless oil (3.3 g, 75%), bp 105-115°C/0.60-
0.75 mm, whose 1H NMR and IR spectra matched those reported.

[Methoxy(2-naphthyl)methyl]trimethylsilane (227). A mixture of
2-methoxymethylnaphthalene (0.46 g, 2.7 mmol) and tetramethylethlenediamine (0.5 mL, 3.3 mmol) in dry diethyl ether (50 mL) was cooled
to -70°C under argon. Dropwise addition of t-butyllithium in pentane (1.9 M, 1.7 mL, 3.2 mmol) yielded a black solu-
tion which was stirred 30 min at -70°C. Chlorotrimethylsilane (0.39 mL, 3.1 mmol) was added dropwise, the mixture allowed to warm to room tem-
perature and water (50 mL) was introduced. The organic layer was
separated, washed with aqueous saturated sodium bicarbonate and dried
over magnesium sulfate. Removal of solvent and column chromatography
on silica gel with 10% benzene/hexane as eluent yielded [methyl-
(2-naphthyl)methyl]trimethylsilane as a colorless liquid which slowly
crystallized at 0-(-10)°C, mp 33-35°C (0.53 g, 82%); IR (neat film,
cm⁻¹) 3040, 2940, 2900, 2800, 1240, 1075, 935, 890, 875, 840, 775, 730,
695; 1H NMR (CDCl₃, δ, CH₂Cl₂ was added as an internal standard) 0.23
(s, 9H, -Si(CH₃)₃), 3.48(s, 3H, -OCH₃), 4.18(s, 1H, -CH), 7.1-7.9 (m,
7H, naphthyl); exact mass: calcd. 244.1283; obsd. 244.1276.

Anal. Calcd. for C₁₅H₂₀O₂Si: C, 73.71; H, 8.25.
Found: C, 73.57; H, 8.04.

Pyrolysis of [Methoxy(2-naphthyl)methyl]trimethylsilane (227).
[Methoxy(2-naphthyl)methyl]trimethylsilane (1.0 g, 4.1 mmol) was
distilled through a quartz tube heated to 640-650°C at 0.2-0.3 mm.
then dried. Removal of solvent left a pale yellow oil which was homogeneous by TLC and exhibited the expected $^1$H NMR spectrum for 4-methoxy-1-methoxymethyl naphthalene (3.6 g, 87%); $^1$H NMR (CDCl$_3$, $\delta$) 3.32 (s, 3H, -OCH$_3$), 3.80 (s, 3H, -OCH$_3$), 4.68 (s, 2H, -CH$_2$OCH$_3$), 6.48-6.58 (d, 1H, J=7.5Hz), 7.15-7.25 (d, 1H, J=7.5 Hz), 7.35-7.50 (m, 2H), 7.90-8.10 (m, 1H), 8.15-8.35 (m, 1H).

[Methoxy(4-methoxy-1-naphthyl)methyl]trimethylsilane (232). A 2.0 M t-butyllithium in pentane solution (10 mL, 20 mmol) was added dropwise to a dry diethyl ether solution (150 mL) of 4-methoxy-1-methoxymethyl naphthalene (3.5 g, 17 mmol) and tetramethylethlenediamine (2.7 mL, 18 mmol) cooled under argon to -78°C. After stirring 45 min at -78°C, the deep purple-black mixture was treated with chlorotrimethylsilane (2.4 mL, 19 mmol) and the resulting light orange-brown solution allowed to warm to room temperature. The resulting solution contained a white precipitate and was washed with water and saturated aqueous sodium bicarbonate and then dried over magnesium sulfate. The pale yellow oil obtained from evaporation of solvent was chromatographed on silica gel with benzene:hexane (1:1) to yield [methoxy(4-methoxy-1-naphthyl)methyl]trimethylsilane as a colorless oil which slowly crystallized in the refrigerator (4.2 g, 89%, mp 55-60°C); IR (neat film, cm$^{-1}$) 3060, 2950, 1585, 1460, 1390, 1265, 1245, 1090, 1075, 865, 855, 840; $^1$H NMR (CDCl$_3$, $\delta$, CH$_2$Cl$_2$ was added as an internal standard) 0.02(s, 9H, -Si(CH$_3$)$_3$), 3.31(s, 3H, -OCH$_3$), 4.00(s, 3H, -OCH$_3$), 4.69(s, 1H, -CH$_2$OCH$_3$),
Column chromatography of the black pyrolysate on silica gel with hexane as eluent afforded a complex mixture (0.25 g) in which 1H-cyclobuta[de]-naphthalene (1) was shown to be a major component by 1H NMR (28% of mixture, 12% yield).

4-Methoxy-1-naphthalenemethanol (234). Sodium borohydride (1.1 g, 28 mmol) was added to 4-methoxy-1-naphthaldehyde (5.0 g, 27 mmol) in dioxane (100 mL) and the mixture was stirred 18 hr at room temperature. After introduction of methanol (25 mL) and removal of the solvents in vacuo, the residue was dissolved in chloroform (100 mL). The resulting solution was washed with saturated aqueous ammonium sulfate and dried over magnesium sulfate. Evaporation of solvent left 4-methoxy-1-naphthalenemethanol as a colorless oil which slowly crystallized (5.1 g, 100%), mp 77-78°C, lit87 mp 76-77°C.

4-Methoxy-1-methoxymethylnaphthalene (235). Dry hydrogen chloride was bubbled through 4-methoxy-1-naphthalenemethanol (3.9 g, 21 mmol) in chloroform (100 mL) for 30 min. After the solution had been dried over magnesium sulfate and evaporated, the resulting pale yellow oil was dissolved in dry tetrahydrofuran (100 mL) and a 25% sodium methoxide in methanol solution (40 mL) added. The mixture was stirred 23 hr at room temperature and poured into diethyl ether (500 mL). The organic layer was washed with water and with saturated aqueous sodium bicarbonate and
6.85 (d, 1H, J=8 Hz), 7.3-7.5 (m, 3H, aromatic), 8.0-8.2 (m, 1H, aromatic), 8.3-8.5 (m, 1H, aromatic); exact mass: calcd. 274.1389, obsd. 274.1398. An analytical sample was prepared by distillation at 86°C/0.1 mm.

**Anal.** Calcd. for C_{16}H_{22}O_{2}Si: C, 70.02; H, 8.08.

**Found:** C, 70.12; H, 8.28.

**Pyrolysis of [Methoxy(4-methoxy-l-naphthyl)methyl]trimethylsilane (232);**

4-Methoxy-lH-cyclobuta[de]naphthalene (236). Volatilization of [methoxy(4-methoxy-l-naphthyl)methyl]trimethylsilane (0.54 g, 2.0 mmol) through a quartz tube at 510°C and 0.05-0.10 mm gave a dark red-black oil. Preparative thin-layer chromatography on silica gel with hexane eluent yielded two fractions:

1) 4-methoxy-lH-cyclobuta[de]naphthalene

(0.10 g, 27%) as a light yellow liquid; IR (neat film) 3040, 2940, 2910, 2810, 1485, 1460, 1450, 1430, 1380, 1305, 1250, 1140, 1060, 1010, 800, 765, 740; ^1^H NMR (CDCl$_3$, δ, 90 MHz) 3.90(s, 3H, -CH$_3$), 4.60(s, 2H, -CH$_2$), 6.68(d, 1H, H-3 naphthyl, J=7 Hz), 6.84-7.48 (m, 3H, H-2, 6, 7) 7.62(d, 1H, H-5, (peri), J=9 Hz); ^13^C NMR (CDCl$_3$, δ, 75.43 MHz) 45.95(CH$_2$), 55.76(-OCH$_3$), 108.94(C-3, naphthyl), 117.72(C-7), 118.09(C-9), 118.16(2C, C-2 and C-5), 129.47 (C-6), 133.02(C-8), 140.65(C-1a), 147.05(C-7a), 153.37(C-4); UV (λ, ε, hexane) 324 nm(3,600), 315(2,500), 310(3,400), 304(3,500), 296(4,900), 292(4,900), 285(4,600), 242(20,500), 234(25,600),
216(38,400); exact mass: calcd. 170.0732 obsd. 170.0737. An analytical sample was prepared by molecular distillation (45-50°C/0.3 mm).

Anal. Calcd. for C_{12}H_{10}O: C, 84.68; H, 5.92.

Found: C, 84.89; H, 6.24.

The yield of 236 is 42% based on recovered starting material.

2) Initial [methoxy(4-methoxy-1-naphthyl)methyl]trimethylsilane as a light yellow oil; (0.19 g, 35%) which was identified by comparison to an authentic sample by TLC and $^1$H NMR.

The effect of temperature and pressure at which the pyrolysis was conducted on the yield of 236 is shown in Table 10.

2-Methoxy-1-naphthalenemethanol (240). 2-Methoxy-1-naphthoic acid (5.1 g, 25 mmol) dissolved in dry benzene (150 mL) and dry diethyl ether (150 mL) was added dropwise to lithium aluminium hydride (2.0 g, 50 mmol) suspended in dry diethyl ether (50 mL) under argon. The resulting grey suspension was stirred 25 hr and the excess hydride then quenched by the slow cautious addition of saturated aqueous sodium sulfate (50 mL). The colorless organic layer was decanted from the remaining white salts, which were extracted with benzene (100 mL) and diethyl ether (100 mL). The combined organic solution was washed with water and with brine and dried over magnesium sulfate. Removal of solvent left white crystals of 2-methoxy-1-naphthalenemethanol (4.7 g, 97%), mp 97-100°C (ethanol); IR (KBr, cm$^{-1}$) 3300(OH), 3060, 2980, 2910, 2850,
2-Methoxy-1-methoxymethylnaphthalene (241). 2-Methoxy-1-naphthalene-methanol (3.2 g, 17 mmol) dissolved in dry chloroform (100 mL) was reacted by bubbling dry hydrogen chloride through the solution for 30 min. After drying the solution over magnesium sulfate, the solvent was removed affording a tan solid (3.4 g) whose IR spectrum exhibited no OH stretch. A tetrahydrofuran solution (100 mL) of this material was treated with 25% sodium methoxide in methanol (40 mL, 170 mmol) and stirred at room temperature. After the mixture had been poured into diethyl ether (400 mL), the organic layer was separated and washed with water and with brine solution and dried over magnesium sulfate. Removal of the solvent left 2-methoxy-1-methoxymethylnaphthalene as a pale yellow oil (3.3 g, 97%), the sample was homogeneous by $^1$H NMR and TLC; $^1$H NMR (CDCl$_3$, $\delta$) 3.38(s, 3H, OCH$_3$), 3.80(s, 3H, OCH$_3$), 4.88(s, 2H, -CH$_2$OCH$_3$), 7.0-7.8(m, 5H, aromatic), 8.05(d, 1H, H-8 on naphthyl, J=8 Hz).
[Methoxy(2-methoxy-1-naphthyl)methyl]trimethylsilane (238). A dry diethyl ether solution (50 mL) of 2-methoxy-1-methoxymethylbenzthaline (0.28 g, 1.4 mmol) and tetramethylethylenediamine (0.34 mL, 2.3 mmol) was cooled to -78°C under argon and a 2.2 M t-butyllithium in pentane solution (0.80 mL, 1.8 mmol) added slowly. After stirring 10 min at -78°C, the deep purple mixture was warmed to -30°C in a dry ice/CH\textsubscript{3}NO\textsubscript{2} bath. The violet solution was then treated with chlorotrimethylsilane (0.30 mL, 2.4 mmol). After 30 min at -30°C, the mixture (clear and colorless) was allowed to warm to room temperature and then washed with water and with saturated aqueous sodium bicarbonate. Upon drying and concentrating the solution, the resulting yellow oil was purified by column chromatography on silica gel with 20% benzene-hexane as eluent. The products were obtained:

1) [methoxy(2-methoxy-1-naphthyl)methyl]trimethylsilane (0.21 g, 55%) as a white solid, mp 75.5-77.5°C (pentane); IR (KBr, cm\textsuperscript{-1}) 3040, 2940, 2920, 2820, 2800, 1615, 1585, 1505, 1460, 1370, 1320, 1245, 1075, 1025, 945, 875, 850, 810, 755; NMR (CDCl\textsubscript{3}, \textdelta, CH\textsubscript{2}Cl\textsubscript{2} was added as an internal standard) 0.02(s, 9H, -Si(CH\textsubscript{3})\textsubscript{3}), 3.24 (s, 3H, -OCH\textsubscript{3}), 3.88(s, 3H, -OCH\textsubscript{3}), 5.18(s, 1H, -CH=OCH\textsubscript{3}), 7.2-7.5(m, 3H, H-3, 5 and 6 of naphthyl ring), 7.65-7.85(m, 2H, H-4 and 5 of naphthyl ring), 8.65-8.75(m, 1H, H-8 of naphthyl ring); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, \textdelta, 75.43 MHz) -2.18(Si(CH\textsubscript{3})\textsubscript{3}), 56.32 and 59.19 (OCH\textsubscript{3}), 74.10 (CH), and 6 aromatic C-H signals at 112.92 (C\textsubscript{3} of naphthyl ring), 123.41, 125.42, 126.40, 128.02, 128.17 and 4
quaternary aromatic signals at 122.11, 129.61, 133.10 and 154.28 (C₉ of naphthyl ring); exact mass: calcd. 274.1390, obsd. 274.1398.

Anal. Calcd. for C₁₆H₂₂O₂Si: C, 70.02; H, 8.08.

Found: C, 69.68; H, 8.17.

The yield of 238 was 86% based on recovered starting material.

2) 2-methoxy-1-methoxymethylnaphthalene, the starting material (0.10 g, 36%), as a colorless oil and identified by comparison with an authentic sample.

Pyrolysis of [Methoxy(2-methoxy-1-naphthyl)methyl]trimethylsilane (238). Pyrolysis of [methoxy(2-methoxy-1-naphthyl)methyl]trimethylsilane (0.26 g, 0.95 mmol) by slow distillation through a quartz tube at 610°C (0.05-0.10 mm) gave a pale yellow oil. Preparative thin-layer chromatography on silica gel with hexane:benzene (5:1) yielded three compounds:

1) naphtho[2,1-b]furan (243, 0.05 g, 31%), as a light yellow oil purified by preparative VPC (10 ft x ½ in 5% SE-30 on chromosorb P, isothermal at 160°C) followed by sublimation at 35-40°C and 0.02 mm, white crystals, mp 51-54°C (lit88 mp 61-62°C); ¹H NMR (CDCl₃, δ, 200 MHz) 7.265[d, 1H, H-1 β-hydrogen on furanyl ring], J=2 Hz], 7.763[d, 1H, H-2 (α-hydrogen on furanyl ring), J=2 Hz], 7.36-7.64 (m, 2H, H-7 and H-8 on naphthyl), 7.70 (d, 2H, H-4 and H-5, J=5 Hz, appears as a singlet at 90 MHz), 7.94 (d, 1H, H-6, J=8 Hz), 8.14 (d, 1H, H-9, J=8 Hz); mass
spectrum (70eV) m/e (relative intensity) 169(15), 168(100, M⁺), 140 (18), 139(27); exact mass: calcd. 168.0575; obsd. 168.0580. The ¹H NMR and mass spectra of 243 agree with those previously reported. ²⁸

2) 1,2-dihydronaphtho[2,1-b]furan (244, 0.10 g, 64%) as a colorless liquid; IR (neat, cm⁻¹) 1245, 1050, 970, 805; ¹H NMR (CDCl₃, δ, 90 MHz, CH₂Cl₂ was used as an internal standard) 3.46 [t, 2H, H-1 (β-hydrogens on furanyl ring), J=9 Hz], 4.78 [t, 2H, H-2 (α-hydrogens), J=9 Hz], 7.1-7.9 (m, 6H, aromatic); mass spectrum (70eV) m/e (relative intensity) 171(14), 170(100, M⁺), 169(58), 142(13), 141(30), 139(13), 115(21); exact mass: calcd. 170.0732; obsd. 170.0737. The ¹H NMR and IR spectra agree with those for 244 in the literature. ²⁹

3) [methoxy(2-methoxy-1-naphthyl)methyl] trimethylsilane (238, 0.01 g, 3%) identified by comparison with authentic sample.

6-Methyl-1-naphthalenemethanol (249). 6-Methyl-1-naphthoic acid (5.3 g, 28 mmol) was refluxed with borane-dimethyl sulfide (35 mL, 2.0 M, 70 mmol) in anhydrous tetrahydrofuran (125 mL) and trimethylborate (10 mL) under argon for 6.5 hr. Methanol (50 mL) was cautiously added to the cooled solution and the mixture concentrated after bubbling ceased. After dissolving the residue in diethyl ether (100 mL) the resulting solution was washed with water and with saturated aqueous sodium bicarbonate and then dried. Removal of solvent left 6-methyl-1-
naphthalenemethanol as a white solid (4.8 g, 100%), mp 77-78\(^\circ\)C (pentane/benzene), lit\(^\circ\) mp 79-80\(^\circ\)C; \(^1\)H NMR (CDCl\(_3\), \(\delta\)) 2.48(s, 3H, \(-CH_3\)), 5.00 (s, 2H, \(-CH_2OH\)); mass spectrum m/e 172 (M\(^+\)).

\(\text{1-Methoxymethyl-6-methylnaphthalene (250).}\) After sodium hydride (0.33 g, 50% mineral oil dispersion, 6.8 mmol) had been washed with dry hexane (2 x 10 mL), 6-methyl-1-naphthalenemethanol (0.81 g, 4.7 mmol) in dry dichloromethane (25 mL) was added dropwise. The mixture was stirred 2 hr at room temperature and then dimethyl sulfate (0.50 mL, 5.2 mmol) was added. After stirring overnight, the solution was washed with water and dried over magnesium sulfate. Concentration of the mixture left a yellow oil which was chromatographed on silica gel with benzene:hexane (1:5) as eluent to give 1-methoxymethyl-6-methylnaphthalene as a colorless liquid (0.70 g, 78%); \(^1\)H NMR (CDCl\(_3\), \(\delta\)) 2.50(s, 3H, \(CH_3\)), 3.40(s, 3H, \(-OCH_3\)), 4.81(s, 2H, \(CH_2OCH_3\)), 7.2-7.8(m, 5H, naphthyl), 7.9-8.1 (d, 1H, H-8 of naphthyl, J=9 Hz).

\([\text{Methoxy(6-methyl-1-naphthyl)methyl]trimethylsilane (247).}\) 1-Methoxymethyl-6-methylnaphthalene (3.6 g, 19 mmol) and tetramethylethylenediamine (3.1 mL, 21 mmol) in anhydrous diethyl ether (125 mL) was cooled to -78\(^\circ\)C under argon and a 2.0 M \(t\)-butyllithium in pentane solution (10 mL, 20 mmol) was added dropwise. After 30 min at -78\(^\circ\)C, the red-black mixture was treated with chlorotrimethylsilane (2.5 mL, 20 mmol), allowed
to warm to room temperature and then stirred 1 hr. The resulting
colorless solution and white precipitate were washed with water and
with saturated aqueous sodium bicarbonate and dried over magnesium
sulfate. Concentration of the mixture left [methoxy(6-methyl-1-naph-
thyl)methyl]trimethylsilane as a light yellow oil (4.9 g, 100%); IR
neat film, cm⁻¹) 3040, 2960, 2820, 1255, 1090, 880, 870, 845, 820, 805,
750; ¹H NMR (CDCl₃, δ, CH₂Cl₂ was added as an internal standard)
-0.08(s, 9H, -Si(CH₃)₃), 2.41(s, 3H, CH₃), 3.19(s, 3H, -OCH₃), 4.67(s,
1H, -CH-OCH₃), 7.1-7.6(m, 5H, naphthyl), 7.8-8.0(d, 1H, H-8 of naphthyl
ring, J=9 Hz); exact mass: calcd. 258.1440, obsd. 258.1446. An analy­
tical sample was prepared as a colorless liquid by molecular distilla-
tion at 66-68°C/0.07 mm.

Anal. Calcd. for C₁₆H₂₂OSi: C, 74.36; H, 8.58.
Found: C, 74.40; H, 8.48.

Pyrolysis of [Methoxy(6-methyl-1-naphthyl)methyl]trimethylsilane (247);
3-Methyl-1H-cyclobuta[de]naphthalene (252) and 2-Methyl-1H-cyclobuta[de]-
naphthalene (253). Volatilization of [methoxy(6-methyl-1-naphthyl)-methyl]trimethylsilane (0.83 g, 3.22 mmol) through a quartz-tube heated
to 510°C under vacuum (0.1-0.2 mm) gave a dark red-black pyrolysate.
Preparative thin-layer chromatography with hexane yielded two fractions:
1) a mixture (0.16 g, relative ratio by VPC 14: 1.7:1) of 3-methyl-1H-
cyclobuta[de]naphthalene (252, 22%), 2-methyl-1H-cyclobuta[de]naph-
thalene (253, 3%) and 1,6-dimethylnaphthalene (251, 2%). Yields
were determined by VPC using 1,6-dimethylnaphthalene as an internal
standard and separation of 251, 252 and 253, was achieved via VPC
The physical and spectral characteristics of the products were:

a) 3-methyl-1H-cyclobuta[de]naphthalene, colorless liquid; IR (neat film, cm⁻¹) 3020, 2910, 1600, 845, 765, 755; ¹H NMR (CDCl₃, δ, 300 MHz) 2.553 (s, 3H, -CH₃), 4.761 (s, 2H, -CH₂-), 6.966 (s, 1H, H-2 of naphthyl), 7.041 (d, 1H, H-7), 7.348-7.482 (m, 3H, naphthyl); ¹³C NMR (CDCl₃, δ, 75.43 MHz) 23.662 (CH₃), 47.103 (-CH₂-), 116.274 (C-2 of naphthyl), 119.143 (C-7), 120.148, 120.590 (C-4 and C-5), 125.371 (C-9), 130.570 (C-6), 140.920 (C-3), 141.040, 141.236 (C-1a and C-7a), and 144.920 (C-8); UV (λ, ε, hexane) 322nm (380), 312 (332), 305 (462), 274 (3,570), 228 (56,100); exact mass: calcd. 154.0782; obsd. 154.0787.

Anal. Calcd. for C₁₂H₁₀: C, 93.46; H, 6.54.

Found: C, 93.29; H, 6.63.

b) 2-methyl-1H-cyclobuta[de]naphthalene, a colorless liquid; ¹H NMR (CDCl₃, δ, 200 MHz) 2.376 (s, 3H, -CH₃), 4.704 (s, 2H, -CH₂-), 7.02 (d, 1H, H-7 of naphthyl, J=5 Hz), 7.2-7.8 (m, 4H, naphthyl);

c) 1,6-dimethylnaphthalene, a colorless liquid; identification was based on comparison to an authentic sample by ¹H NMR and VPC.⁹¹

Identification was based on comparison to an authentic sample by ¹H NMR and VPC.

2) Original [methoxy(6-methyl-1-naphthyl)methyl]trimethylsilane (0.25 g, 28%); identified by comparison with an authentic sample by TLC and ¹H NMR.
Yields of 251, 252, and 253 based on recovered starting material were 31%, 4% and 2% respectively. 2-Methyl-1H-cyclobuta[de]naphthalene could not be cleanly separated from 1,6-dimethylnaphthalene and thus was not characterized further.

9-Bromophenanthrene (257). Bromine (29.5 mL, 0.58 mol) was added dropwise to a refluxing solution of phenanthrene (100 g, 0.56 mol) in carbon tetrachloride (200 mL). Heating was continued for 8.5 hr after which time the initial red color had dissipated and evolution of hydrogen bromide ceased. The reaction mixture was washed with water and the solvent then removed at 70°C under vacuum. The brown syrup remaining was vacuum distilled affording 9-bromophenanthrene (123 g, 85%) bp 175-190°C/1.5 mm, as a light yellow oil which could be crystallized from hot absolute ethanol, mp 57-60°C, lit mp 54-56°C.

9-Phenanthrenemethanol (258). 9-Bromophenanthrene (10.0 g, 39 mmol) in dry tetrahydrofuran (125 mL) was added dropwise over 1 hr to magnesium turnings (1.06 g, 44 mmol) in refluxing tetrahydrofuran (50 mL) under argon. The solution was refluxed until all the magnesium had dissolved (3 hr), allowed to cool to room temperature and paraformaldehyde (1.27 g, 42 mmol) was added as a neat solid in one portion. After refluxing 17 hr, the mixture was allowed to cool, poured into saturated ammonium sulfate (100 mL) and the organic layer separated, washed with saturated
sodium bicarbonate and dried over magnesium sulfate. Removal of solvent left a white solid which was recrystallized from benzene (75 mL) yielding white fluffy needles of 9-phenanthrenemethanol (4.89 g, 60%), mp 145-148° C, lit93 149-150° C.

9-Methoxymethylphenanthrene (259). Sodium hydride (6.8 g, 50% mineral oil suspension, 0.14 mol) was washed with hexane (2 x 20 mL) and a solution of 9-phenanthrenemethanol (27.7 g, 0.13 mol) in dry tetrahydrofuran (300 mL) added dropwise with mechanical stirring over 1.5 hr. After stirring 3 hr, the thick white suspension was treated with dimethyl sulfate (13.5 mL, 0.14 mol), stirred 12 hr, and then refluxed 3 hr. Water (2 mL) was cautiously added to the nearly colorless clear solution, and the organic layer washed with saturated aqueous sodium bicarbonate and brine, and then dried over magnesium sulfate. Removal of solvent left a yellow crystalline solid (29.94 g, 100%) which was homogeneous by TLC and whose spectral properties were identical to 9-methoxymethylphenanthrene. The material was usually used without further purification, although it could be recrystallized from methanol resulting in a light yellow crystals of 9-methoxymethylphenanthrene, mp 63-66° C, lit86 mp 69-70° C.
[Methoxy(9-phenanthryl)methyl]trimethylsilane (256).  9-Methoxymethylphenanthrene (34.1 g, 0.15 mol) was dissolved in a mixture of dry diethyl ether (400 mL) and dry tetramethylethylenediamine (25 mL, 0.17 mol) under argon and the solution cooled to -70°C. A 2.5 M t-butyllithium in pentane solution (70 mL, 0.18 mol) was added dropwise with mechanical stirring, over 20 min. The dark brown solution was stirred 30 min at -70°C and chlorotrimethylsilane (20 mL, 0.16 mol) then added dropwise. After stirring 30 min at -70°C the emerald green solution was allowed to warm to room temperature and stirred 3 hr. The resulting light yellow solution was washed with water and saturated sodium bicarbonate, and dried over magnesium sulfate. Removal of solvent left a white solid (43.7 g, 99%) which was homogeneous by TLC; recrystallization from hexane (75 mL) yielded white crystals of [methoxy(9-phenanthryl)methyl]trimethylsilane (33.4 g, 76%), mp 106-108°C; IR (KBr, cm⁻¹) 3060, 2980, 2820, 1600, 1450, 1250, 1085, 940, 925, 865, 845, 755; ¹H NMR (CDCl₃, δ, CH₂Cl₂ was as an internal standard) 0.05(s, 9H Si(CH₃)₃, 3.38(s, 3H, OCH₃), 4.78(s, 1H, CH), 7.5-7.8(m, 6H, aromatic), 8.0-8.2 (m, 2H, aromatic), 8.58-8.88(m, 2H, aromatic); exact mass: calcd. 294.1440; obsd. 294.1449.

Anal. Calcd. for C₁₉H₂₂O₁Si:  C, 77.50; H, 7.53.

Found:  C, 77.62; H, 7.52.
Pyrolysis of [Methoxy(9-phenanthryl)methyl]trimethylsilane (256); 4H-Cyclobuta[jk]phenanthrene (260). [Methoxy(9-phenanthryl)methyl]-trimethylsilane (0.54 g, 1.8 mmol) was dropped as a neat solid, into a quartz tube heated to 590°C at 0.1 mm. The black pyrolysate, on purification by preparative thin-layer chromatography on silica gel using hexane as eluent yielded:

1) a 9:1 mixture (by $^1H$ NMR) of 4H-cyclobuta[jk]phenanthrene (260) and 4H-cyclopenta[def]phenanthrene (261, 0.13 g, 37%). Recrystallization from pentane afforded pure 4H-cyclobuta[jk]phenanthrene as white flakes, mp 87.5-88.5°C; IR (KBr, cm$^{-1}$) 3020, 2910, 1440, 1360, 1270, 1190, 875, 850, 790, 760, 745; $^1H$ NMR (CDCl$_3$, $\delta$, 90 MHz) 4.80(s, 2H, -CH$_2$-), 7.2(d, 1H, H-3 on phenanthryl nucleus, J=2 Hz), 7.31(s, 1H, H-5), 7.5-8.2(m, 6H, aromatic), 8.35-8.50(m, 1H, H-1 or H-9); $^{13}C$ NMR (CDCl$_3$, $\delta$, 75.43 MHz) 46.56 (1C, C-4), 8 aromatic C-H signals at 117.62, 119.27, 119.56, 123.97, 125.37, 126.20, 129.93, 130.20 and 6 quaternary aromatic signals at 126.55, 129.61, 137.41, 139.08, 141.06 and 145.04; UV ($\lambda$, $\epsilon$, hexane) 345nm(1,100), 338(490), 330(720), 323(430), 314(430), 294(12,900), 282(10,200), 275(13,500), 264(shoulder, 19,500), 249(96,200), 244(shoulder, 82,400), 228(19,800), 223(17,000), 205(23,100); exact mass: calcd. 190.0782; obsd. 190.0788. An analytical sample (white crystals, mp 87.5-88.5°C) was prepared by sublimation at 55-58°C and 0.02 mm.
Anal. Calcd. for C$_{15}$H$_{10}$: C, 94.70; H, 5.30.
Found: C, 94.35; H, 5.50.

The yield of 260 was 72% based on recovered starting material.

2) [methoxy(9-phenanthryl)methyl]trimethysilane (0.26 g, 48%) as a light yellow solid whose TLC and $^1$H NMR were identical with that of an authentic sample.

Identification of 4H-cyclopenta[def]phenanthrene (261) as the minor component of the mixture obtained in the first fraction was based on comparison of the mixture's $^1$H NMR spectrum and HPLC trace (μ porasil; 1:1 methanol/water) with those of authentic 261. No change (other than relative intensities of the peaks) in the $^1$H NMR spectrum or HPLC trace was observed when authentic was added to the mixture obtained from pyrolysis.

Amounts of 256 up to 10 g could by pyrolyzed and purification of 260 accomplished by column chromatography on silica gel followed by recrystallization from pentane or methanol. Yield 4H-cyclobuta[jk]-phenanthrene and ratio of 260 to 261 varied greatly with temperature and pressure at which pyrolyses were performed (Table 13). In general purification of 260 was easier when pyrolysis was conducted at lower temperature since higher 260 to 261 ratio was obtained. The starting material could easily be recycled and thus no material was wasted.
4H-Cyclobuta[jk]phenanthrene·2,4,7-Trinitrofluoren-9-one Complex.

4H-Cyclobuta[jk]phenanthrene (0.40 g, 2.1 mmol) dissolved in hot ethanol (10 mL) was added to a hot ethanolic solution (40 mL) of 2,4,7-trinitrofluoren-9-one (0.70 g, 2.2 mmol). Benzene (30 mL) was slowly added until the boiling solution was clear. Upon cooling bright orange crystals separated from the reaction mixture and were re-crystallized from benzene to give bright orange needles of the 4H-cyclobuta[jk]phenanthrene·2,4,7-trinitrofluoren-9-one complex (0.58 g, 54%), mp 209.5-211°C.

Anal. Calcd. for C_{26}H_{15}N_{3}O_{7}: C, 66.53; H, 2.99; N, 8.32.

Found: C, 66.78; H, 3.09; N, 8.07.

Decomposition of the complex on silica gel using 1:1 benzene/hexane as eluent regenerated the initial 4H-cyclobuta[jk]phenanthrene.

4H-Cyclopenta[def]phenanthrene (261). A mixture of 4H-cyclopenta[def]phenanthrene-4-one (0.27 g, 1.3 mmol), hydrazine hydrate (0.45 mL, 9.3 mmol) and potassium hydroxide (0.30 g, 5.4 mmol) in ethylene glycol (10 mL) was warmed to 195-205°C in 3 hr. Heating was continued at these temperatures for 12 hr, during which time white crystals sublimed from the mixture. The solid was collected and chromatographed on silica gel with hexane as eluent, yielding flaky white crystals of 4H-cyclopenta[def]phenanthrene (0.08 g, 32%) mp 111-113°C, lit\textsuperscript{95} mp
114-115°C; $^1$H NMR (CDCl$_3$, $\delta$) 4.31 (s, 2H, -CH$_2$), 7.4-7.9 (m, 8H, aromatic).

4H-Cyclopenta[def]phenanthrene-4-one ( ). 4-Phenanthrenecarboxylic acid$^{96}$ (1.0 g, 4.5 mmol) was refluxed in thionyl chloride (10 mL) for 5 hr, and the thionyl chloride then removed in vacuo. The brown oil was dissolved in carbon disulfide (25 mL), added dropwise to anhydrous aluminum chloride (1.6 b, 12 mmol), and the black mixture refluxed 13 hr. The mixture was poured into ice/water (100 mL) and extracted with benzene:ether (1:1, 300 mL). The organic extract was washed with water, brine and dried over magnesium sulfate. Removal of solvent left a brown solid which was purified by column chromatography on silica gel with benzene as eluent affording 4H-cyclopenta-[def]phenanthrene-4-one, a yellow-orange solid (0.28 g, 30%), mp 160-165°C (ethanol), lit$^*$ mp 170°C; IR (KBr, cm$^{-1}$) 1715 (C=O); no O-H stretch.

1-Pyrenemethanol (266). 1-Pyrenecarboxaldehyde (10.1 g, 44 mmol) was stirred with sodium borohydride (3.3 g, 87 mmol) in dioxane (250 mL) for 13 hr. After the mixture had been concentrated, the residue was dissolved in benzene (250 mL) and acetic acid carefully added resulting in vigorous bubbling. After stirring several hr, the solution was carefully treated with water. The organic layer was removed and washed with water, saturated aqueous sodium bicarbonate, and then brine solution. The extract was dried over magnesium sulfate, filtered and concentrated, leaving 1-pyrenemethanol as yellow crystals, (9.5 g, 93%), mp 122.5-125.5°C (hexane/benzene), lit$^*$ mp 126-127°C.
1-Methoxymethylpyrene (267). Dry hydrogen chloride was bubbled through a chloroform solution (250 mL) of 1-pyrene-methanol (9.5 g, 41 mmol) for 45 min and the light yellow solution then dried over magnesium sulfate. Removal of solvent left a yellow solid (no O-H stretch in its IR spectrum) which was dissolved in dry tetrahydrofuran (300 mL).

A 25% sodium methoxide in methanol solution (100 mL) was added and the mixture stirred 24 hr at room temperature. After addition of diethyl ether (400 mL) the organic layer was washed with water, saturated aqueous sodium bicarbonate and then brine. After drying over magnesium sulfate, the solution was concentrated yielding 1-methoxymethylpyrene as a yellow solid (9.6 g, 94%), mp 53-54°C (pentane); IR (KBr, cm⁻¹) 3030, 1385, 1185, 1080, 840, 750, 705; ¹H NMR (CDCl₃, δ) 3.48(s, 3H, -OCH₃); 5.10(s, 2H, -CH₂-OCH₃), 7.87-8.42(m, 9H, aromatic); mass spectra: m/e 246 (M⁺, 59%), 215 (M⁺-OCH₃, 100%).

Anal. Calcd. for C₁₈H₁₄O: C, 87.77; H, 5.73.
Found: C, 87.90; H, 5.73.

[Methoxy(1-pyrenyl)methyl]trimethylsilane (264). An anhydrous diethyl ether solution (175 mL) of 1-methoxymethylpyrene (2.7 g, 11 mmol) and tetramethylethylenediamine (1.7 mL, 12 mmol) was cooled to -78°C under argon and a 1.9 M t-butyllithium in pentane solution (6.2 mL, 12 mmol) added dropwise. The resulting thick purple-black suspension
was stirred 40 min at -78°C and chlorotrimethylsilane (1.5 mL, 12 mmol) then added. After 15 min at -78°C, the reaction mixture was allowed to warm to room temperature, washed with water and saturated aqueous sodium bicarbonate and dried over magnesium sulfate. Concentration of the solution left a yellow solid. Recrystallization from hexane afforded [methoxy(1-pyrenyl)methyl]trimethylsilane as yellow crystals (2.7 g, 77%), mp 96.5-98.5°C; IR (KBr, cm\(^{-1}\)) 3040, 2960, 1600, 1240, 1175, 1070, 930, 870, 840, 705, 620; \(^1\)H NMR (CDCl\(_3\), \(\delta\)) \(\delta\) \(\text{CHCl}_3\) was added as an internal standard) 0.18(s, 9H, -Si(CH\(_3\))\(_3\)), 3.51(s, 3H, -OCH\(_3\)), 5.23(s, 1H, -CHOCH\(_3\)) 7.9-8.5(m 9H, aromatic); exact mass: calcd. 318.1440, obsd. 318.1449.

Found: C, 79.42; H, 7.22.

Pyrolysis of [Methoxy(1-pyrenyl)methyl]trimethylsilane (264): 3H-Cyclobuta[cd]pyrene (263). [Methoxy(1-pyrenyl)methyl]trimethylsilane (0.50 g, 1.6 mmol) was slowly distilled through the quartz pyrolysis unit (Fig. 5) heated to 520-525°C at 0.05-0.07 mm. The pyrolysate upon purification by preparative thin-layer chromatography using hexane as eluent yielded:

1) 3H-cyclobuta[cd]pyrene (263, 0.11 g, 32%) as a light yellow solid. Recrystallization from pentane gave white crystals, mp 117-118°C; IR (KBr, cm\(^{-1}\)) 3030, 2920, 1170, 860, 825, 755, 705; \(^1\)H NMR (CDCl\(_3\), \(\delta\)) \(\delta\) \(\text{CH}_2\)\(_2\)), 7.5(s, 1H, H-10 on aromatic ring), 7.62(d, 1H, H-2, J=6 Hz), 7.8-8.2(m, 6H, aromatic);
$^{13}$C NMR (CDCl$_3$, δ) 52.97 (1C, C-1), 8 aromatic C-H signals at 116.81, 121.28, 123.27, 124.77, 125.79, 126.37 (2C), 127.82, and 8 quaternary aromatic signals at 124.43, 124.97, 128.36, 131.08, 135.55, 137.10, 139.82 and 144.14; UV (λ, ε, hexane) 375nm (299), 340(36,300), 335(24,800); 324(26,100), 310(12,700), 275(41,000), 265(24,200), 254(15,200), 244(58,400), 235(shoulder, 36,000); exact mass: calcd. 214.0782; obsd. 214.0786.

**Anal.** Calcd. for C$_{17}$H$_{10}$: C, 95.30; H, 4.70.

Found: C, 94.75; H, 4.80.

Re-analysis of the product after standing open to air for one day revealed that it contained 91.51% carbon and 5.09% hydrogen, thus indicating extensive oxidation. A more satisfactory analysis could not be obtained even after repeated chromatography, recrystallization, and sublimation (100°C and 0.02mm). All analytical samples were sealed in ampules under argon. The yield of 263 based on recovered starting material was 86%.

2) Original [methoxy(1-pyrenyl)methyl]trimethylsilane (0.31 g, 62%) as a light yellow oil; identical to authentic sample by TLC and $^1$H NMR.

**3H-Cyclobuta[cd]pyrene:2,4,7-Trinitrofluoren-9-one Complex.** To a refluxing benzene solution (10 mL) of 2,4,7-trinitrofluoren-9-one (0.30 g, 0.95 mmol) was added 3H-cyclobuta[cd]pyrene (0.19 g, 0.89 mmol) in benzene (2 mL). Upon cooling the mixture dark maroon crystals separated which recrystallized from benzene as glistening,
bright maroon-purple needles (0.27 g, 57%). The 3H-cyclobuta[cd]pyrene: 2,4,7-trinitrofluoren-9-one complex turned black when heated to 190°C and charred to a black dust at 220°C with no visible sign of melting. Anal. Calcd for C₃₀H₁₅N₃O₇: C, 68.05; H, 2.86; N, 7.94. Found: C, 68.02; H, 3.10; N, 7.85.

9-Anthraldehyde p-Tosylhydrazone ( ). 9-Anthraldehyde (3.5 g, 17 mmol) was dissolved in hot ethanol (75 mL) and a solution of p-tosylhydrazide (3.1 g, 17 mmol) in hot ethanol (25 mL) added. After the mixture had been refluxed 2 hr and then cooled, yellow crystals of 9-anthraldehyde p-tosylhydrazone were obtained (5.0 g, 78%), mp 180-182°C (ethanol), lit mp 183-184°C.

Pyrolysis of the Sodium Salt of 9-Anthraldehyde p-Tosylhydrazone (271). A dry dichloromethane solution (100 mL) of 9-anthraldehyde p-tosylhydrazone (1.0 g, 2.7 mmol) was added dropwise to hexane-washed sodium hydride (0.20 g, 50% dispersion in mineral oil, 4.2 mmol) and the mixture stirred until the evolution of gas ceased (1 hr). Removal of solvent left a yellow solid which was dried in vacuo and then dropped as a neat solid via a "Normag" solid addition funnel (method 3 described above) into a quartz tube packed with quartz chips and heated to 500-520°C at 0.3-1.0 mm. The pyrolysate, collected at -78°C, was purified by preparative thin-layer chromatography on silica gel (hexane). 9-Methylandanthracene (272, 0.10 g, 20%) was the only hydrocarbon product and was identified by comparison with an authentic sample by TLC and
NMR. No attempt was made to identify the remaining black tarry residue.

Pyrolysis at higher temperature (650°C) again gave only 9-methylanthracene, however the yield was considerably lower (7%).

**Thermolysis of Sodium 9-Anthraldehyde p-Tosylhydrazonate in Chlorobenzene.** A 50% mineral oil suspension of sodium hydride (0.20 g, 4.2 mmol) was washed with hexane and 9-anthraldehyde p-tosylhydrazone (1.0 g, 2.9 mmol) in dry dichloromethane (50 mL) and dry tetrahydrofuran (10 mL) added dropwise. The yellow slurry was stirred until hydrogen evolution ceased (1 hr) and the solvent then removed in vacuo. A freshly distilled chlorobenzene (50 mL) slurry of the resulting yellow solid was refluxed under argon for 30 min. The hot solution was filtered through Celite and the chlorobenzene then removed. Column chromatography on silica gel (hexane) of the residue gave a yellow glass (0.12 g). $^1$H NMR analysis revealed that no $^1$H-cyclobuta[de]anthracene was present; only complex signals from $\delta = 4-8$ were observed and this material was not further characterized.

The remaining material, eluted from the column with ethyl acetate, was red tar consisting of many components by TLC. No further characterization was attempted.
9-Chloromethylanthracene (299). A solution of 9-anthracenemethanol (10.0 g, 48 mmol) and thionyl chloride (4.8 mL, 66 mmol) in p-dioxane (150 mL) was refluxed 10 hr. After the mixture had been cooled to room temperature, the solvent was removed under reduced pressure and the yellow green residue recrystallized from hexane/benzene yielding yellow needles of 9-chloromethylanthracene (8.1 g, 74%), mp 137-139°C, lit\textsuperscript{101} mp 137.5-138°C, 141-142.5°C.

9-Methoxymethylanthracene (274). To a solution of 9-chloromethylanthracene (6.6 g, 29 mmol) in freshly distilled dry tetrahydrofuran (150 mL) was added 25% sodium methoxide in methanol solution (42 mL, 180 mmol). After stirring 24 hr, the solution was diluted with diethyl ether (500 mL), washed with water and with saturated sodium bicarbonate solution and then dried over magnesium sulfate. Removal of solvent left a brown solid which was recrystallized from hexane yielding yellow needles of 9-methoxymethylanthracene (5.4 g, 84%), mp 89-90.5°C, lit\textsuperscript{101} mp 90-91°C.
[9,10-Dihydro-10-(methoxymethylene)-9-anthryl]trimethylsilane (276).

A mixture of 9-methoxymethylanthracene (1.1 g, 5.0 mmol), dry diethyl ether (120 mL) and dry tetramethylethylenediamine (0.80 mL, 5.3 mmol) was cooled to -78°C under argon. A 2.2 M tert-butyllithium in pentane solution (2.6 mL, 5.7 mmol) was added dropwise with stirring to the yellow suspension resulting in a dark green-black solution. After stirring 30 min at -78°C, the mixture was treated with dry chlorotrimethylsilane (0.69 mL, 5.5 mmol) and allowed to warm to room temperature. After 3 hr the solution was colorless and contained a white precipitate. The mixture was washed with water and with saturated sodium bicarbonate and then dried over magnesium sulfate. Removal of solvent left a yellow oil. Flash chromatography with hexane as eluent gave two products:

1) 9-neopentylanthracene (277, 0.20 g, 16%), mp 108-110°C, lit mp 104-105°C; 1H NMR (CDCl$_3$, $\delta$) 0.96 (s, 9H, C(CH$_3$)$_3$), 3.64 (s, 2H, -CH$_2$); exact mass: calcd. 248.1565; obsd. 248.1569.

2) [9,10-dihydro-10-(methoxymethylene-9-anthryl]trimethylsilane as white needles (276, 0.59 g, 40%), mp 110-112°C (hexane); IR (KBr, cm$^{-1}$) 3150, 3110, 2950, 2920, 2880, 2860, 1635 (C=CHOCH$_3$), 1475, 1445, 1250, 1230, 1140, 1085, 850, 835, 775; 1H NMR (CDCl$_3$, $\delta$, CH$_2$Cl$_2$ was added as an internal standard) -0.05 (s, 9H, -Si(CH$_3$)$_3$), 3.55 (s, 1H, -CH$_2$), 3.83 (s, 3H, -OCH$_3$), 6.55 (s, 1H, vinyl CH), 7.0-7.5 (m, 7H, aromatic), 7.8-8.0 (m, 1H, hydrogen on C-4, peri position cis to OCH$_3$); $^{13}$C NMR (CDCl$_3$, $\delta$, 20.11 MHz) -2.28 (3C, Si(CH$_3$)$_3$), 43.21 (C-9), 60.73 (-OCH$_3$), 116.27 (C-10), 144.92 (C=CHOCH$_3$),
8 aromatic CH signals at 122.83, 124.48, 125.16, 125.45, 125.98, 126.58, 126.86, 128.17, and 4 quarternary aromatic signals at 131.52, 133.80, 137.35 and 137.98; UV (λ, ε, hexane) 311 nm (4,800), 272(12,600), 242(shoulder, 12,250), 223(29,000), 208 (39,800); exact mass: calcd. 294.1440; obsd. 294.1447.

Anal. Calcd. for C_{19}H_{22}OSi: C, 77.49; H, 7.53.

Found: C, 77.47; H, 7.18.

Hydrolysis of [9,10-Dihydro-10-(methoxymethylene)-9-anthryl]trimethylsilane (276) on Silica Gel. [9,10-Dihydro-10-(methoxymethylene)-9-anthryl]trimethylsilane (276) in hexane (4 mL) was stirred over silica gel, open to the air for 20 hr. After filtration, the silica gel was washed with benzene and diethyl ether and the filtrate concentrated to a yellow solid. $^1$H NMR analysis of this material (CH$_2$Cl$_2$ was added as internal standard) showed it to be a mixture of starting 276 (43%) and 9-anthraldehyde (27%, 47% based on recovered 276).

9,10-Dihydro-9-(methoxymethylene)-10-d-anthracene (294). Upon cooling a yellow suspension of 9-methoxymethylanthracene (0.30 g, 1.4 mmol) in dry diethyl ether (30 mL) and dry tetramethylethylenediamine (0.22 mL, 1.5 mmol) to $-78^\circ$C under argon, a 2.2 M $t$-butyllithium in pentane solution (0.75 mL, 1.6 mmol) was added dropwise. After 3 min at $-78^\circ$C, the blue-black mixture was quenched with deuterium oxide (2 mL). The resulting clear light orange solution was allowed to warm to room temperature, washed with water and with saturated sodium
bicarbonate, and dried over magnesium sulfate. Removal of solvent left a yellow paste. Column chromatography with 20% benzene/hexane as eluent yielded three products:

1) 9-neopentylanthracene as a white solid (277, 0.059 g, 18%), mp 108-110°C; identical to an authentic sample,

2) 9,10-dihydro-9-(methoxymethylene)-10-methylanthracene (294, 0.050 g, (17%) as a yellow oil; $^1$H NMR (CDCl$_3$, $\delta$), 3.52(s, 1H, CH), 3.83(s, 3H, OCH$_3$), 6.70(s, 1H, vinyl CH), 7.0-7.4(m, 7H, aromatic), 7.8-8.0 (m, 1H, hydrogen on C$_1$, peri position cis to $-OCH_3$); mass spectrum: m/e 223 (M$^+$); 95% D incorporation by $^1$H NMR. Satisfactory analysis could not be obtained because 294 was extremely unstable.

3) 9-anthraldehyde as a yellow solid (281, 0.109 g, 39%) containing 64% deuterium at the 10 position of the anthracene nucleus as shown by $^1$H NMR and mass spectra.

9,10-Dihydro-9-(methoxymethylene)-10-methylanthracene (295). A 2.0 M t-butyllithium in pentane solution (1.3 mL, 2.5 mmol) was added dropwise to a yellow suspension of 9-methoxymethylanthracene (0.50 g, 2.3 mmol) in dry diethyl ether (60 mL) add dry tetramethylethylenediamine (0.4 mL, 2.7 mmol) cooled to -78°C under argon. After stirring 15 min the dark purple-black solution was treated with dimethyl sulfate (0.35 mL, 3.7 mmol), allowed to warm to room temperature and then refluxed 24 hr. The mossy green mixture was then washed with water and with saturated sodium bicarbonate and dried over magnesium sulfate. Removal of solvent left a yellow oil which was
purified by flash chromatography with 5% ethyl acetate/hexane as eluent.
Two products were obtained:

1) 9-neopentylanthracene as white crystals (277, 0.11 g, 20%), as identified earlier.

2) 9,10-dihydro-9-methoxymethyl-10-methylanthracene (295, 0.40 g, 75% as light yellow crystals, mp 123-126°C; IR (KBr, cm⁻¹) 2920, 1640 (C=CHOCH₃), 1475, 1450, 1230(C-O), 1130, 1085, 780, 760; ¹H NMR (CDCl₃, δ, 200.13 MHz) 1.36(d, 3H, CH₃, J=6.8 Hz), 3.86(s, 3H, -OCH₃), 4.02(q, 1H, CH, J=6.8 Hz), 6.76(s, 1H; -CH=OCH₃), 7.2-7.7(m, 6H, aromatic), 7.7-7.9(m, 1H, hydrogen on C-1, peri position trans to OCH₃), 7.95-7.99(m, 1H, hydrogen on C-8, peri position cis to OCH₃); ¹³C NMR (CDCl₃, δ, 20.1 MHz), 25.97 (CH₃), 41.99(CH), 60.93(OCH₃), 113.75(C-9), 145.89(=CH=OCH₃), 8 aromatic CH signals at 122.83, 125.69, 126.08, 126.23, 126.57, 126.71, 217.00, 128.12 and 4 quaternary aromatic signals at 132.20, 134.67, 140.36, 141.08; exact mass: calcd. 236.1201; obsd. 236.1195.

Found: C, 86.46; H, 6.59.

9,10-Dihydro-10-(methoxymethylene)-9-anthryl Phenyl Ketone (296a). A 2.1 M t-butyllithium in pentane solution (1.2 mL, 2.6 mmol) was added dropwise to a yellow suspension of 9-methoxymethylanthracene (0.52 g, 2.4 mmol), dry diethyl ether (60 mL) and dry tetramethylethyldiamine (0.45 mL, 3.0 mmol) cooled to -78°C under argon. After stirring 15 min at -78°C,
the dark purple solution was treated with freshly distilled benzoyl chloride (0.35 mL, 3.0 mmol) and the resulting mossy green mixture allowed to warm to room temperature. The now bright yellow solution containing a white precipitate was washed with water and with saturated sodium bicarbonate, dried (MgSO₄) and concentrated. Careful column chromatography of the yellow oily residue on silica gel with 50% benzene/hexane as eluent gave two products:

1) 9-neopentylanthracene (277, 0.15 g, 25%), identical with an authentic sample.

2) 9,10-dihydro-10-(methoxymethylene)-9-anthryl phenyl ketone (296a) as a yellow gum (0.35 g, 45%); IR (KBr, cm⁻¹) 3060, 3030, 1680 (C=O), 1635(CHOCH₃), 1475, 1445, 1235, 1200, 1135, 1090, 770, 700, 635; ¹H NMR (CDCl₃, δ) 3.80(s, 3H, OCH₃), 5.90(s, 1H, -CHC(0)-), 6.80(s, 1H, vinylic CH), 7.0–7.6(m, 10H, aromatic), 7.9–8.3[m, 3H, hydrogens on C-1, C-8(peri position to C=0) and C-4(peri to OCH₃)]; ¹³C NMR (CDCl₃, δ, 20.1 MHz) 54.86(C-9), 61.05(-OCH₃), 113.97(C-10), 146.56 (=CHOCH₃), 197.47(C=0) and 11 aromatic C-H signals at 123.07, 125.86, 126.29, 126.89, 127.50, 127.68, 127.99, 128.47, 128.72, 129.14, 132.72, and 4 quaternary aromatic signals (5th is buried) at 132.36, 133.33, 135.76 and 136.48; exact mass: calcd. 326.1307; obsd. 326.1299. Satisfactory analysis could not be obtained for 296a because of its instability.
9,10-Dihydro-10-(methoxymethylene)-α-methyl-9-anthracenemethanol (296b).

9-Methoxymethylantracene (0.51 g, 2.3 mmol) in dry diethyl ether (60 mL) and dry tetramethylethylenediamine (0.40 mL, 2.7 mmol) was cooled to -78°C under argon. To the resulting yellow suspension was added, dropwise, a 2.1 M t-butyllithium in pentane solution (1.4 mL, 2.8 mmol). Upon stirring the dark blue-purple solution for 25 min at -78°C, freshly distilled acetaldehyde (0.40 mL, 7.0 mmol) was added. In 5 min the mixture became a clear light orange and was then warmed to room temperature, washed with water and with saturated sodium bicarbonate, and dried over magnesium sulfate. Removal of solvent left a yellow oil. Flash chromatography on silica gel with 10% ethyl acetate/hexane as eluent gave two products:

1) 9-neopentylanthracene (277, 0.13 g, 23%), as identified earlier,

2) 9,10-dihydro-10-(methoxymethylene)-α-methyl-9-anthracenemethanol as a yellow gum (296b, 0.32 g, 53%); IR (KBr, cm⁻¹) 3540(free OH), 3400 (broad, OH), 3050, 3020, 2960, 2920, 2890, 1640(=O CH₃), 1475, 1450, 1235, 1135, 1085, 780, 750; ¹H NMR (CDCl₃, δ) 1.05(d, 3H, CH₃, J = 6 Hz), 1.62 (broad s, 1H, OH), 3.7-3.9(s superimposed on m, 5H, -OCH₃, -CHOH, CH), 6.85(s, 1H, vinylic CH), 7.1-7.5(m, 7H, aromatic), 7.9-8.1 (m, 1H, hydrogen on C-4, peri position to OCH₃); ¹³C NMR (CDCl₃, δ, 20.1 MHz) 20.20(CH₃), 55.93(CHCH(CH₃)OH), 61.03 (OCH₃), 71.71(CH(CH₃)OH), 114.28 (C-10), 146.04(COHCH₃), 8 aromatic C-H signals at 123.17, 125.74, 126.32(2C), 127.10, 128.12, 128.70, 129.14 and 4 quaternary aromatic signals at 133.27, 135.35, 135.69,
135.99; the sample decomposed during data acquisition (evidenced by color change and TLC) and several extra signals were present in the $^{13}$C NMR spectrum; exact mass: calcd. 266.1307; obsd. 266.1317.

**Anal.** Calcd for C$_{18}$H$_{16}$O$_2$: C, 81.17; H, 6.81.

Found: C, 80.25; H, 6.61.

A better analysis for 296b could not be obtained. The product could be recrystallized from hexane at $-78\degree$C, but would turn to a paste after 5-10 min at room temperature. Crystalline material was homogeneous by TLC but the resulting paste showed traced of other compounds.

9,10-Dihydro-10-(methoxymethylene)-a-phenyl-9-anthracenemethanol (296c).

To a yellow suspension of 9-methoxymethylanthracene (0.41 g, 2.3 mmol) in dry diethyl ether (60 mL) and dry tetra-methylethylenediamine (0.40 mL, 2.7 mmol) at $-78\degree$C under argon was added dropwise a 2.0 M t-butyllttithium in pentane solution (1.3 mL, 2.6 mmol). The resulting dark blue-purple mixture was stirred 10 min at $-78\degree$C followed by addition of freshly distilled benzaldehyde (0.30 mL, 2.9 mmol) and the mixture was allowed to warm to room temperature. The light orange solution was washed with water and with saturated sodium bicarbonate and dried over magnesium sulfate. Removal of solvent left a yellow oil.

Flash chromatography on silica gel with 10% ethyl acetate/hexane afforded two products:

1) 9-neopentylanthracene (277, 0.16 g, 28%), identical with an authentic sample,
2) 9,10-dihydro-10-(methoxymethylene)-α-phenyl-9-anthracenemethanol as a yellow foam (296c, 0.29 g, 39%); IR (KBr, cm⁻¹) 3540 (free OH), 3420 (OH), 3060, 3030, 2930, 2840, 1640 (C CHOCH₃), 1480, 1450, 1240, 1135, 1090, 775, 705; ¹H NMR (CDCl₃, δ) 2.1 (broad s, 1H, OH), 3.75 (s, 3H, OCH₃), 4.10 (d, 1H, A of AB pattern, J = 7.5 Hz), 4.60 (d, 1H, B of AB, J = 7.5 Hz), 6.50 (s, 1H, vinylic CH), 6.7-7.3 (m, 12H, aromatic), 7.8-8.0 (d, 1H, hydrogen on C-4, peri position cis to OCH₃); ¹³C NMR (CDCl₃, δ, 20.1 MHz) 56.22 (CHOH), 113.70 (C-10), 145.99 (CHOCH₃), 11 aromatic CH signals at 122.93, 125.60, 125.79, 126.18, 127.10 (2C), 127.54 (2C), 127.68, 128.90, 129.20 and 4 quaternary aromatic signals (5ᵗʰ is buried) at 133.61, 134.63, 136.18, 141.28; exact mass: calcd. 328.1463; obsd. 328.1470.

Satisfactory analysis of 296c could not be obtained because of its instability. Several attempts at recrystallization failed.

9,10-Dihydro-10-(methoxymethylene)-α,α-dimethyl-9-anthracenemethanol (296d). A dry diethyl ether suspension (60 mL) of 9-methoxymethylanthracene (0.52 g, 2.34 mmol) and dry tetramethylethylenediamine (0.40 mL, 2.7 mmol) was cooled to -78°C under argon and a 2.0 M t-butyllithium in pentane solution (1.3 mL, 2.7 mmol) added dropwise. The resulting blue-black solution was stirred 20 min at -78°C. Acetone (0.22 mL, 3.0 mmol) was added and the reaction mixture was allowed to warm to room temperature. The solution was washed with
water and saturated sodium bicarbonate, dried (MgSO₄) and concentrated to a yellow oil. Preparative thin-layer chromatography with 10% diethyl ether/benzene eluent gave two products:

1) 9-neopentylanthracene (277, 0.21 g, 36%), as identified earlier.

2) 9,10-dihydro-10-(methoxymethylene)-α,α-dimethyl-9-anthracenemethanol (296d, 0.36 g, 55%) as a yellow paste; IR (KBr, cm⁻¹) 3550 (free OH), 3440 (OH), 3060, 3020, 2960, 2920, 1680, 1475, 1445, 1235, 1130, 1085, 775;¹H NMR (CDCl₃, δ) 1.12 (s, 6H, CH₃), 1.65 (broad s, 1H, OH), 3.83 (s, 3H, OCH₃), 3.98 (s, 1H, CH), 6.85 (s, 1H, vinylic CH), 7.1-7.5 (m, 7H, aromatic), 7.9-8.1 (m, 1H, hydrogen on C-4, peri position cis to OCH₃);¹³C NMR (CDCl₃, δ, 50.3 MHz) 27.12 and 27.21 (CH₃, split into doublet by adjacent asymmetric center), 58.56 (C-9), 60.95 (OCH₃), 76.22 (COH), 115.99 (C-10), 145.66 (CHOCH₃), 8 aromatic CH signals at 123.05, 125.39, 125.98, 126.38, 126.89, 128.31, 129.71, 130.11 and 4 quaternary aromatic signals at 134.12, 135.03, 135.59, and 136.55.

Further analysis of the product was prevented by its instability. The¹³C NMR spectrum showed the presence of decomposition products formed during accumulation of data.

Methyl 9-Anthrylmethyl Sulfide (298). Sodium hydride (50% mineral oil suspension, 1.9 g, 39 mmol) was washed with hexane (2 x 10 mL) under argon and suspended in dry tetrahydrofuran (25 mL). Methanethiol (3.0 g, 60 mmol) was then introduced via distillation and the grey-white suspension was stirred 15 min. A tetrahydrofuran solution of
9-chloromethylanthracene (7.5 g, 33 mmol) was added dropwise (45 min) and the subsequent mixture was stirred 3 hr. The solution was washed with water and with saturated sodium bicarbonate and then dried over magnesium sulfate. Removal of solvent left a yellow solid which was recrystallized from methanol (200 mL) yielding methyl 9-anthrylmethyl sulfide as yellow needles (6.1 g, 77%), mp 112-114°C, lit\textsuperscript{102} mp 110-112°C.

**Attempted Deprotonation of Methyl 9-Anthrylmethyl Sulfide.** A summary of the bases, solvents, and temperatures used in attempted deprotonation of methyl 9-anthrylmethyl sulfide is shown in Table 23. In all cases 1 equiv of base and 1 equiv of tetramethylethylenediamine were used and either methanol-\textsuperscript{0-d} or chlorotrimethylsilane was used to trap the suspected anion. No deuterated starting material or trimethylsilylated products were ever observed. With the exception of \textit{t}-butyllithium or \textit{n}-butyllithium (see later Experimental), the bases used gave complex mixtures of products or starting material.

**Reaction of Methyl 9-Anthrylmethyl Sulfide with \textit{n}-Butyllithium; 9-\textit{n}-Pentylanthracene (300).** To an anhydrous diethyl ether solution (60 mL) of methyl 9-anthrylmethyl sulfide (0.20 g, 0.84 mmol) and anhydrous tetramethylethylenediamine (0.18 mL, 0.98 mmol) was added a 1.6 M solution of \textit{n}-butyllithium in hexane (0.61 mL, 0.98 mmol). After the resulting black solution had been stirred 30 min at 0°C, chlorotrimethylsilane (0.17 mL, 1.4 mmol) was added resulting in an immediate color
TABLE 23

Conditions Used in the Attempted Deprotonation of Methyl 9-Anthrylmethyl Sulfide (298).

<table>
<thead>
<tr>
<th>Base</th>
<th>Time (min)</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Trapping Agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-BuLi</td>
<td>15</td>
<td>Et₂O/TMEDA</td>
<td>-78</td>
<td>TMSCl&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>LDA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15</td>
<td>Et₂O/TMEDA</td>
<td>-78</td>
<td>TMSCl</td>
</tr>
<tr>
<td>LDA</td>
<td>10</td>
<td>Et₂O/TMEDA</td>
<td>0</td>
<td>TMSCl</td>
</tr>
<tr>
<td>LDA</td>
<td>45</td>
<td>Et₂O/TMEDA</td>
<td>25</td>
<td>TMSCl</td>
</tr>
<tr>
<td>t-BuLi</td>
<td>90</td>
<td>Et₂O/TMEDA</td>
<td>-78</td>
<td>CH₃OD</td>
</tr>
<tr>
<td>CH₃Li</td>
<td>30</td>
<td>THF/TMEDA</td>
<td>-78</td>
<td>CH₃OD</td>
</tr>
<tr>
<td>CH₃Li</td>
<td>30</td>
<td>THF/TMEDA</td>
<td>0</td>
<td>CH₃OD</td>
</tr>
<tr>
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<td>60</td>
<td>THF</td>
<td>-78</td>
<td>CH₃OD</td>
</tr>
</tbody>
</table>

<sup>a</sup> TMSCl = Chlorotrimethylsilane

<sup>b</sup> LDA = Lithium Di-isopropylamide

<sup>c</sup> LiTMP = Lithium Tetramethylpiperidide
discharge. The reaction mixture was washed with water and saturated aqueous sodium bicarbonate, dried ($\text{MgSO}_4$) and concentrated. The yellow oil obtained gave, after chromatography on silica gel (hexane), 9-n-pentylanthracene (300, 0.06 g, 29%) as a light yellow gum; $^1$H NMR ($\text{CDCl}_3$, 6) 1.00(t, 3H, $\text{CH}_3$, $J = 6$ Hz), 1.3-2.0(m, 6H, $-(\text{CH}_2)_3-$), 3.65 (t, 2H, $-\text{CH}_2\text{Ar}$, $J = 9$ Hz), 7.4-7.7(m, 4H, aromatic, H-2,3,6,7), 7.9-8.1(m, 2H, aromatic, H-4,5), 8.3-8.5(m, 3H, aromatic, H-1,8,10); the spectrum of 300 corresponds to that reported.

9-Anthrylmethyltrimethylsilane (301).

**Method A**: Reaction of Methyl 9-Anthrylmethyl Sulfide with t-Butyllithium. Methyl 9-anthrylmethyl sulfide (6.1 g, 25 mmol) was dissolved in dry diethyl ether (150 mL) and the solution cooled to -78°C under argon. To the resulting yellow suspension was added, dropwise, a 2.0 M solution of t-butyllithium in pentane (14 mL, 28 mmol). The dark blue-green solution formed was then stirred 40 min at -78°C. Chlorotrimethylsilane (3.6 mL, 29 mmol) was added and the mixture stirred 1 hr at -78°C after which time a clear yellow solution remained. After warming to room temperature, the mixture was washed with water and with saturated sodium bicarbonate and then dried over magnesium sulfate. Removal of solvent left a yellow solid which was chromatographed on silica gel with hexane. Recrystallization of the light yellow solid product (6.0 g, 91%) from hexane yielded colorless crystals of 9-anthrylmethyltrimethylsilane, mp 66-68°C; IR (KBr, cm$^{-1}$)
3180, 3140, 2940, 1620, 1450, 1410, 1345, 1250, 1150, 890, 865, 840, 770, 730, 670; $^1$H NMR (CDCl$_3$, $\delta$, CH$_2$Cl$_2$ was added as an internal standard) 0.02(s, 9H, Si(CH$_3$)$_3$), 3.18(s, 2H, CH$_2$), 7.38-7.60(m, 4H, H-2,3,6 and 7 of anthryl), 7.90-8.30(m, 5H, H-1,4,5,8 and 9); $^{13}$C NMR (CDCl$_3$, $\delta$, 20.1 MHz) -0.38(Si(CH$_3$)$_3$), 18.93(CH$_2$), 5 aromatic CH signals at 123.65(1C), 124.47(2C), 124.72(2C), 125.45(2C), 129.14(2C and one quaternary carbon), 2 apparent aromatic quaternary carbons at 131.76, 134.18; UV (λ, ε, hexane) 397(8,500), 392(shoulder, 5,300), 376(9,000), 356(5,300), 340(2,600), 326(shoulder, 1,200), 260(177,000), 251(81,000), 217(14,400); exact mass: calcd. 264.1334; obsd. 264.1344.

Anal. Calcd for C$_{18}$H$_{17}$Si: C, 81.75; H, 7.62.
Found: C, 82.02; H, 7.57.

Method B: Reductive Silylation of 9-Anthrylmethyloxytrimethylsilane. To an anhydrous diethyl ether solution of 9-anthracenemethanol (1.1 g, 5.0 mmol) and triethylamine (1.2 mL, 8.3 mmol) was added chlorotrimethylsilane (1.0 mL, 7.9 mmol). The mixture was refluxed 8 hr, allowed to cool to room temperature, filtered through Celite and concentrated. The yellow solid, on chromatography on a short column of silica gel (benzene), yielded 9-anthrylmethyloxytrimethylsilane (304, 1.3 g, 94%) as a yellow solid, mp 74-75°C; IR (KBr, cm$^{-1}$) 3050, 2960, 2980, 1260, 1250, 1070, 1030, 895, 880, 845; $^1$H NMR (CDCl$_3$, $\delta$) 0.16 (s, 9H, Si(CH$_3$)$_3$), 5.58(s, 2H, CH$_2$), 7.3-7.6(m, 4H, H-2,3,6,7 of anthryl), 7.9-8.1(m, 2H, H-4,5), 8.3-8.5(m, 3H, H-1, 8,10); exact mass: calcd. 280.1283; obsd. 280.1291.

9-Anthrylmethyloxytrimethylsilane (1.2 g, 4.4 mmol) was dissolved in anhydrous tetrahydrofuran (50 mL) and chlorotrimethylsilane (1.5 mL,
12 mmol) and lithium metal (0.10 g, 14 mmol) were added. The initial dark green solution became brown-orange after stirring overnight and was then poured into diethyl ether (150 mL), filtered, washed with water and aqueous saturated ammonium sulfate and dried over magnesium sulfate. The yellow oil obtained from concentration of the solution was chromatographed on silica gel (hexane) to give 9-anthrylmethyltrimethylsilane as a yellow solid (0.88 g, 63%), mp 64-67°C (hexane).

α-d-9-Anthrylmethyltrimethylsilane (301). A dry tetrahydrofuran solution (60 mL) of 9-anthrylmethyltrimethylsilane (0.23 g, 0.87 mmol) and dry tetra-ethylenediamine (0.30 mL, 2.0 mmol) was cooled to 0°C under argon and a 1.6M solution of n-butyllithium in hexane (0.65 mL, 1.0 mmol) was added. After the dark emerald green solution had been stirred 30 min at 0°C, methanol-0-d was added and the colorless reaction mixture was washed with water and saturated aqueous sodium bicarbonate and dried over magnesium sulfate. Removal of solvent gave 9-anthrylmethyltrimethylsilane in quantitative yield containing 70% deuterium at the benzylic position as shown by 1H NMR and mass spectral analysis.

Reaction of 9-Anthryl(lithio)methyltrimethylsilane with Dimethyl Disulfide: [9-Anthryl(methylthio)methyl]trimethylsilane (307). 9-Anthrylmethyltrimethylsilane (0.50 g, 1.9 mmol) was dissolved in a mixture of dry tetrahydrofuran (50 mL) and dry tetramethylethylenediamine (0.32 mL, 2.1 mmol) under argon. Addition of 1.6 M
n-butyllithium in hexane (1.3 mL, 2.1 mmol) gave a dark green solution. After 30 min dimethyl disulfide (0.21 mL, 2.3 mmol) was added resulting in a clear red-orange solution. After stirring 1 hr, the clear yellow mixture was poured into diethyl ether (100 mL) and washed with water and saturated sodium bicarbonate and dried over magnesium sulfate. Removal of solvent left a yellow oil which was chromatographed on silica gel with hexane eluent yielding:

1) 9-anthrylmethyltrimethylsilane (301, 0.20 g, 40%), identical with an authentic sample,

2) [9-anthryl(methylthio)methyl]trimethylsilane (307, 0.34 g, 58%), mp 100-102°C (hexane); IR (KBr, cm\(^{-1}\)) 3160, 2970, 2930, 1630, 1525, 1455, 1410, 1335, 1255, 1095, 900, 850, 750, 735; \(^1\)H NMR (CDCl\(_3\), \(\delta\), CH\(_2\)Cl\(_2\) was added as an internal standard) 0.10(s, 9H, Si(CH\(_3\))\(_3\)), 1.84 (s, 3H, SCH\(_3\)), 4.80(s, 1H, CH), 7.3-8.9(m, 9H, aromatic); \(^13\)C NMR (CDCl\(_3\), \(\delta\), 20.1 MHz) -0.43(Si(CH\(_3\))\(_3\)), 17.28(SCH\(_3\)), 33.64(CH), 9 aromatic CH absorptions at 123.45, 123.79, 124.47, 125.11, 125.79, 126.27, 127.44, 129.14 and 129.72 and 5 quaternary aromatic signals at 129.81, 130.98, 131.47, 132.05, and 134.14; UV (\(\lambda,\epsilon\), hexane) 396(10,200), 390 (shoulder, 6,200), 375(10,200), 356(6,200), 340 (2,700), 325(1,200), 259(140,000), 252(shoulder, 69,500), 216 (13,300); exact mass: calcd. 310.1211; obsd. 310.1220.

Analytical. Calcd for C\(_{19}\)H\(_{22}\)SSi: C, 73.49; H, 7.14; S, 10.32. Found: C, 73.58; H, 7.06; S, 10.04.

The yield of 307 was 97% based on recovered starting material.
Reaction of 9-Anthryl(lithio)methyltrimethylsilane with Chlorotrimethylsilane; [9,10-Dihydro-10-(trimethylsilylmethylene)-9-anthryl]trimethylsilane (308). 9-Anthrylmethyltrimethylsilane (0.30 g, 1.1 mmol) and tetramethylethylenediamine (0.37 mL, 2.5 mmol) were cooled to 0°C in anhydrous diethyl ether and a 1.6 M solution of n-butyllithium in hexane (0.83 mL, 1.3 mmol) was added. The dark green solution was stirred 30 min at 0°C and chlorotrimethylsilane (0.20 mL, 1.6 mmol) was added. After 15 min at 0°C, the clear, colorless solution was washed with water and saturated aqueous sodium bicarbonate and dried over magnesium sulfate. A light yellow oil (0.31 g) was obtained upon removal of solvent and 1H NMR analysis (CDCl₃, 90 MHz) indicated a clean 1:2 mixture of starting material (29%) and a compound with signals at δ -0.05 (s, 9H), 0.20 (s, 9H), 3.64 (s, 1H), 6.10 (s, 1H), and 7.1-8.3 (m, 8H). On the basis of 1H NMR, the reaction product was assigned as [9,10-dihydro-(trimethylsilylmethylene)-9-anthryl]trimethylsilane (308, 55%). Separation of 301 and 308 could not be achieved. The mixture could not be crystallized and chromatography resulted in hydrolysis of 308 to 9-anthrylmethyltrimethylsilane.

Attempted Reaction of 9-Anthryl(lithio)methyltrimethylsilane with Benzoyl Peroxide. A solution of 9-anthrylmethyltrimethylsilane (0.28 g, 1.1 mmol) and tetramethylethylenediamine (0.30 mL, 2.0 mmol) in anhydrous tetrahydrofuran (50 mL) was treated with a 1.6 M solution of
n-butyllithium in hexane (0.84 mL, 1.3 mmol). The dark green mixture was stirred 50 min at room temperature and benzoyl peroxide (0.31 g, 1.3 mmol) in tetrahydrofuran (15 mL) then added. The green color was immediately discharged and the solution was washed with water and saturated aqueous sodium bicarbonate and dried over magnesium sulfate. Starting 9-anthrylmethyltrimethylsilane was the only material present when the solvent was removed.

**Attempted Reaction of 9-Anthryl(lithio)methyltrimethylsilane with t-Butyl Peroxybenzoate.** To a dry tetrahydrofuran solution (50 mL) of 9-anthrylmethyltrimethylsilane (0.25 g, 0.95 mmol) and dry tetramethylethylenediamine (0.28 mL, 1.9 mmol) was added a 1.6 M solution of n-butyllithium in hexane (0.65 mL, 1.0 mmol). After the dark green solution had been stirred 30 min and cooled to 0°C, t-butyl peroxybenzoate (0.20 mL, 1.0 mmol) was added. The solution immediately cleared to a light yellow and allowed to warm to room temperature. The mixture was washed with water and with saturated aqueous sodium bicarbonate and then dried over magnesium sulfate. Removal of solvent and chromatography of the residue on silica gel (hexane) gave only starting material (0.22 g, 88% recovery).

**Attempted Reaction of 9-Anthryl(lithio)methyltrimethylsilane with N-Bromosuccinimide.** A 1.6 M solution of n-butyllithium in hexane (0.95 mL, 1.5 mmol) was added to 9-anthrylmethyltrimethylsilane (0.21 g, 0.80 mmol) and dry tetramethylethylenediamine (0.14 mL, 0.9 mmol) in anhydrous tetrahydrofuran (50 mL). After 40 min, N-bromosuccinimide (0.26 g, 1.5 mmol) was added to the green solution and the color
disappeared. The reaction mixture was washed with water and saturated aqueous sodium bicarbonate and then dried over magnesium sulfate. The residue obtained from removal of solvent was chromatographed on silica gel (hexane). Starting silane (0.10 g, 48%) and intractables were obtained.

**Attempted Reaction of 9-Anthryl(lithio)methyltrimethylsilane with N-Chlorodiethylamine.** To an anhydrous diethyl ether solution (50 mL) of 9-anthrylmethyltrimethylsilane (0.27 g, 1.0 mmol) and tetramethylethenediamine (0.30 mL, 2.0 mmol) was added a 1.6 M solution of n-butyl-lithium in hexane (0.80 mL, 1.2 mmol). After 30 min, N-chlorodiethylamine (0.20 mL, 1.3 mmol) was added to the green solution and the color was immediately discharged. The reaction mixture was washed with water and saturated sodium bicarbonate and dried over magnesium sulfate. Removal of solvent yielded a yellow oil. Column chromatography on silica gel (hexane) gave only starting material (0.17 g, 63% recovery) and intractables.

Repeating the experiment with N-chlorosuccinimide again resulted in major recovery of starting material.

**Attempted Peroxyester Reaction of 9-Anthrylmethyltrimethylsilane with t-Butyl Peroxybenzoate.** To a refluxing benzene solution (100 mL) of 9-anthrylmethyltrimethylsilane (0.30 g, 1.1 mmol) and suspended copper (I) bromide (30 mg) was added t-butyl peroxybenzoate (0.23 mL, 1.2 mmol) in benzene (25 mL) over 2 hr. After then refluxing the mixture 2 hr, the aqua-blue solution was cooled, washed with water and aqueous sodium bicarbonate and dried over magnesium sulfate. Removal of solvent left a
yellow oil which was a complex mixture of compounds (at least six by TLC) of which 9-anthrylmethyltrimethylsilane was major. No attempt was made at separation or further identification of the mixture.

**Attempted Bromination of 9-Anthrylmethyltrimethylsilane with N-Bromosuccinimide.**

**Method A:** 9-Anthrylmethyltrimethylsilane (0.10 g, 0.40 mmol), N-bromosuccinimide (0.08 g, 0.50 mmol) and benzoyl peroxide (10 mg) were refluxed in carbon tetrachloride (15 mL) for 14 hr. The reaction mixture was then filtered and concentrated to a brown semi-solid. TLC and $^1$H NMR revealed a complex mixture of products with no one major component. Further attempts at separation or identification were not made.

**Method B:** A carbon tetrachloride solution (50 mL) of 9-anthrylmethyltrimethylsilane (0.20 g, 0.80 mmol) and N-bromosuccinimide (0.13 g, 0.80 mmol) was photolyzed with a 100W light bulb for 30 hr. Filtration and concentration of the mixture afforded a brown tar. $^1$H NMR indicated a complicated mixture of products and starting material (although only a minor component). Further characterization was not attempted.

Shorter reaction times for both Methods A and B gave mainly recovered starting material.

**Attempted Chlorination of 9-Anthrylmethyltrimethylsilane with t-Butyl Hypochlorite.** A carbon tetrachloride (25 mL) solution of 9-anthrylmethyltrimethylsilane (0.28 g, 1.1 mmol), t-butyl hypochlorite (0.15 mL, 1.3 mmol) and azoisobutyronitrile (10 mg) was refluxed 2 hr, filtered and concentrated. $^1$H NMR analysis did not reveal any
absorptions which could be attributed to the expected product.

**Attempted Methanolsysis of [9-Anthryl(methylthio)methyl]trimethylsilane (307).** Mercuric acetate (0.06 g, 0.2 mmol) and [9-anthryl-(methylthio)methyl]trimethylsilane (0.06 g, 0.2 mmol) were stirred in methanol (15 mL) for 24 hr and the mixture then refluxed 24 hr. Analysis of the reaction mixture by TLC indicated only starting material was present.

**Attempted Reaction of α-Lithio-methoxymethyltrimethylsilane (313) with 9-Anthrone.** Methoxymethyltrimethylsilane (0.27 g, 2.3 mmol) in dry tetrahydrofuran (50 mL) and tetramethylethylenediamine (0.66 mL, 4.4 mmol) was cooled to -78°C under argon and an alkoxide-free solution of s-butyllithium in cyclohexane (1.4 M, 1.8 mL, 2.6 mmol) added. Upon warming the reaction mixture to -33°C in a nitromethane/dry ice slush bath, 9-anthrone (0.47 g, 2.4 mmol) in dry tetrahydrofuran (10 mL) was added dropwise. After 30 min at -33°C, the bright yellow mixture was poured into diethyl ether and the mixture was washed with saturated aqueous ammonium sulfate and water and dried over magnesium sulfate. The residue obtained after removal of solvent was found to be mainly 9-anthrone by TLC and 1H NMR analysis.

**Attempted Reaction of α-Lithio-methoxymethyltrimethylsilane with Anthracene.** A dry tetrahydrofuran solution (50 mL) of methoxymethyltrimethylsilane (0.23 g, 1.9 mmol) and dry tetramethylethylenediamine (0.35 mL, 2.3 mmol) was cooled to -78°C under argon and an alkoxide-free 1.4 M solution of s-butyllithium in cyclohexane (1.9 mL, 2.6 mmol) was added. The light yellow solution was allowed to warm to -40°C and
anthracene (0.36 g, 2.0 mmol) in dry tetrahydrofuran (20 mL) added. After the resulting brown-red solution had been stirred 1 hr at room temperature and diethyl ether was added, the mixture was washed with saturated aqueous ammonium sulfate and water. After drying the mixture over magnesium sulfate, the solvent was removed leaving a yellow solid. $^1$H NMR analysis of the product showed no trimethylsilyl signals; anthracene was the major component.

Attempted Reaction of $\alpha$-Lithio-methoxymethyltrimethylsilane with 9-Bromoanthracene. To an anhydrous tetrahydrofuran solution (50 mL) of methoxymethyltrimethylsilane (0.32 g, 2.7 mmol) and dry tetramethyl-ethylenediamine (0.41 mL, 2.7 mmol) cooled to -78°C under argon was added an alkoxide-free 1.4 M solution of $\alpha$-butyllithium in cyclohexane (2.7 mL, 3.8 mmol). After 30 min at -78°C, the solution was warmed to -25°C and 9-bromoanthracene (0.70 g, 2.7 mmol) in dry tetrahydrofuran (10 mL) was added. The resulting dark brown solution was refluxed 5 hr, cooled, washed with saturated aqueous ammonium sulfate and dried over magnesium sulfate. 9-Bromoanthracene was the major component of the residue obtained upon removal of solvent.

$P$-(9-Anthrylmethoxymethyl)-$NN'$-$N$-$N'$-tetramethylphosphonic Diamide (316). Hexamethyldisilane (0.47 mL, 2.3 mmol) was cleaved to trimethylsilyllithium with methyllithium (2 mL, 1.6 M in diethyl ether, 3 mmol) in hexamethylphosphoramide (15 mL) at 0°C. The resulting blood-red solution was cooled to -78°C and dry tetrahydrofuran (10 mL) added followed by
dropwise addition of 9-anthraldehyde (0.43 g, 2.1 mmol) in tetrahydrofuran (30 mL). After 45 min at -78°C, the dark green solution was warmed to -45°C, dimethyl sulfate (0.9 mL, 9.5 mmol) was added and the mixture was then allowed to warm to room temperature overnight. After addition of diethyl ether, the mixture was washed with water and saturated aqueous sodium bicarbonate and then dried over magnesium sulfate. The solution was concentrated to a yellow oil which was chromatographed on silica gel. Elution with benzene gave 9-anthraldehyde (0.09 g, 21%) as a yellow solid. Elution with diethyl ether: chloroform (1:1) yielded \( P-(9\text{-anthrylmethoxymethyl})-N,N,N',N'-\text{tetramethylphosphonic diamide} \) (316, 0.55 g, 74%) as a yellow oil which slowly crystallized, mp 144-147°C; IR (KBr, cm\(^{-1}\)) 3060, 2930, 2820, 1455, 1310, 1200, 1095, 1000, 985, 790, 740; \(^1\)H NMR (CDCl\(_3\), \( \delta \)) 2.20 (d, 6H, N(CH\(_3\))\(_2\), \( J_{\text{PNCH}} = 9 \text{ Hz} \)), 2.70 (d, 6H, N(CH\(_2\))\(_2\), \( J_{\text{PNCH}} = 9 \text{ Hz} \)), 3.25 (s, 3H, OCH\(_3\)), 6.37 (d, 1H, CHOCH\(_3\), \( J_{\text{PCH}} = 15 \text{ Hz} \)), 7.42-7.70 (m, 4H, aromatic) 7.92-8.10 (m, 2H, aromatic), 8.27-8.51 (m, 2H, aromatic), 9.20-9.38 (m, 1H, aromatic); \(^{13}\)C NMR (acetone-d\(_6\), \( \delta \), 75.43 MHz) 36.47 (d, N(CH\(_3\))\(_2\), \( J_{\text{PN}} = 3 \text{ Hz} \)), 36.70 (d, N(CH\(_3\))\(_2\), \( J_{\text{PN}} = 3 \text{ Hz} \)), 57.29 (d, OCH\(_3\), \( J_{\text{PCO}} = 15 \text{ Hz} \)), 78.16 (d, CH, \( J_{\text{PC}} = 137 \text{ Hz} \)), 9 aromatic CH signals (aromatic carbons are nonequivalent because of the asymmetric center) at 125.05, 125.54 (2C), 126.00, 126.81, 129.18, 129.44 (2C), 130.19 and 4 aromatic quaternary signals (one is hidden) at 128.02, 132.00, 132.36, and 132.68; \(^{31}\)P NMR (CHCl\(_3\), \( \delta \), 36.43 MHz, (CH\(_3\))\(_3\)PO was used as an external standard) 29.67 (s, proton decoupled); UV (\( \lambda \), \( \epsilon \), methanol) 390(9,800), 370 (10,200), 353(6,800), 336(3,100), 320 (shoulder, 1,300), 255(142,000), 249 (shoulder, 76,700), 223(11,800); exact mass: calcd. 356.1654; 356.1672.
The yield of 316 was 94% based on recovered 9-anthraldehyde.

Pyrolysis of [9,10-Dihydro-10-(methoxymethylene)-9-anthryl]trimethylsilane (276). Volatilization of [9,10-dihydro-10-(methoxymethylene)-9-anthryl]trimethylsilane (0.37 g, 1.26 mmol) at 0.05-0.1 mm through a quartz tube at 600-650°C gave a black pyrolysate which was collected in a U-tube trap cooled to -78°C. Preparative thin-layer chromatography on silica gel with 10:1 hexane/benzene gave two fractions:
1) a mixture of anthracene and 9-methylanthracene and
2) a mixture of 9-methoxymethylanthracene and 9-anthraldehyde.
Identification was based on $^1$H NMR and absolute yields were not determined because of the trivial nature of the products.

Pyrolysis of 9-Anthryl(methylthio)methyl trimethylsilane (307). [9-Anthryl(methylthio)methyl]trimethylsilane (0.52 g, 1.67 mmol) was dropped as a neat solid (method 3 described above) into a quartz tube packed with quartz chips and heated to 650°C at 0.05-0.1 mm. Chromatography of the pyrolysate on silica gel (hexane) afforded a complex mixture of products as indicated by TLC and $^1$H NMR. No evidence for $^1$H-cyclobuta[de]anthracene was found and no attempt at further separation or identification of products was made.
Anthracene-1-carboxylic Acid (325). A dark red solution of benzan-throne (323, 50 g, 0.22 mol) in hot concentrated sulfuric acid (600 mL) was added dropwise to boiling water (3 L) and solid chromium trioxide (200 g, 2 mol) added simultaneously. The additions required 3 hr. After refluxing an additional 5 hr, the purple-black solution was cooled to 5°C and isopropyl alcohol (150 mL) was added to decompose the excess oxidant. Red-black crystals separated from the solution which were collected by filtration, washed with water and dissolved in hot aqueous ammonium hydroxide (1 L). The warm solution was filtered and 9,10-anthraquinone-1-carboxylic acid reprecipitated by addition of concentrated hydrochloric acid (500 mL). The tan-brown solid was collected, washed with water and dissolved in concentrated aqueous ammonium hydroxide (350 mL) and water (100 mL). Zinc dust (54 g, 0.83 mol) was added and the mixture refluxed until the initial deep red color was discharged (2 hr) and a light green solution containing a white precipitate remained. Filtration followed by acidification of the filtrate (HCl) afforded anthracene-1-carboxylic acid (325) as a bright yellow solid (23 g, 47%), mp 242-245°C, lit mp 245°C.

1-Anthracenemethanol (326). Lithium aluminum hydride (5.4 g, 0.14 mol) was suspended in dry diethyl ether (500 mL) and anthracene-1-carboxylic acid (10 g, 0.045 mol) added periodically as a neat solid. After stirring 15 hr, the milky white mixture was cooled to 0°C, ethyl acetate (10 mL) added
and the mixture stirred for 1 hr. Saturated aqueous sodium sulfate (75 mL) was then added slowly. After decanting the organic layer, the remaining white slurry was extracted with diethyl ether (2 L) and the combined ethereal solutions washed with water and saturated sodium bicarbonate and dried (MgSO₄). Concentration of the solution left a tan solid which was recrystallized from benzene/hexane yielding white needles of 1-anthracenemethanol (326, 7.3 g, 78%), mp 122-123°C, lit106 mp 125-126°C.

1-Methoxymethylantracene (327). Phosphorus tribromide (1.5 mL, 9.5 mmol) was added to 1-anthracenemethanol (2.0 g, 9.6 mmol) dissolved in cold (0-5°C) chloroform (150 mL) and pyridine (0.85 mL, 11 mmol). The reaction mixture was stirred 45 min at 0-5°C, allowed to warm to room temperature and then stirred 4 hr. After washing with water and drying over magnesium sulfate, the solution was concentrated to a yellow solid whose IR spectrum indicated the absence of a hydroxyl group. To a tetrahydrofuran (150 mL) solution of the solid was added a 25% sodium methoxide in methanol solution (30 mL, 0.13 mol) and the mixture stirred 14 hr at room temperature. The mixture was poured into diethyl ether and washed with water and saturated aqueous sodium bicarbonate and dried over magnesium sulfate. Removal of solvent yielded 1-methoxymethylantracene as yellow crystals (327, 2.0 g, 95%), mp 58-60°C (pentane), lit107 mp 60-62°C.

[Methoxy(1-anthryl)methyl]trimethylsilane (322). An anhydrous diethyl ether solution (200 mL) of 1-methoxymethylantracene (3.4 g, 15 mmol)
and dry tetramethylethylene diamine (2.4 mL, 16 mmol) was cooled under argon to -110°C and a 1.75 M t-butyllithium in pentane solution (9.0 mL, 16 mmol) added slowly. Some of the methoxymethylandanthracene crystallized on the walls of the reaction vessel, but redissolved upon addition of the t-butyllithium solution. The resulting purple-blue mixture was stirred 15 min at (-110)-(-105)°C followed by the addition of chlorotrimethylsilane (2.1 mL, 17 mmol). After having been allowed to warm to room temperature, the cloudy yellow solution was washed with water and saturated aqueous sodium bicarbonate and then dried (MgSO₄). Concentration of the solution left a yellow syrup which was chromatographed on silica gel with 20% benzene/hexane eluent affording [methoxy(1-anthryl)methyl]trimethylsilane (322) as a yellow syrup which slowly solidified (3.0 g, 68%), mp 59-61°C (methanol); IR (neat, cm⁻¹) 3050, 2950, 2890, 2810, 1250, 1080, 865, 845; ¹H NMR (CDCl₃, δ, CH₂Cl₂ was added as an internal standard) 0.04(s, 9H, Si(CH₃)₃), 3.40(s, 3H, OCH₃), 4.95(s, 1H, CHOCH₃) 7.4-7.6(m, 4H, H-2,3,6,7 of anthryl), 7.9-8.2(m, 3H, H-4,5,8 of anthryl), 8.5(s, 1H, H-10 of anthryl), 8.7(s, 1H, H-9 of anthryl); exact mass: calcd. 294.1440; obsd. 294.1447. An analytical sample was prepared by distillation at 105-107°C/0.07 mm.

Anal. Calcd for C₁₉H₂₂OSi: C, 77.50; H, 7.53.

Found: C, 77.49; H, 7.50.
Pyrolysis of [Methoxy(1-anthryl)methyl]trimethylsilane (322):

1H-Cyclobuta[de]anthracene (269). [Methoxy(1-anthryl)methyl]trimethylsilane (1.00 g, 3.44 mmol) was slowly distilled through the quartz pyrolysis unit (Fig. 5) heated to 560-570°C at 0.02-0.07 mm. Flash chromatography (silica gel) of the black pyrolysate with hexane as eluent yielded 1H-cyclobuta[de]anthracene (269) as a light yellow solid (0.34 g, 52%). Recrystallization from pentane gave light yellow crystals which rapidly turned brown when open to air. Satisfactory spectra could be obtained if the sample was handled under argon and the solvents were deoxygenated. Accurate melting point could not be determined since the sample decomposed at 60-70°C; IR (KBr, cm⁻¹) 3030, 2920, 1320, 870, 840, 760, 740, 720; ¹H NMR (CDCl₃, δ) 4.98 (s, 2H, CH₂), 6.98(d, 1H, H-2 on anthryl, J = 5 Hz), 7.3-8.0(m, 6H, aromatic), 8.1(s, 1H, H-5 on anthryl); ¹³C NMR (CDCl₃, δ) 46.34(1C, CH₂), 8 aromatic CH absorptions at 114.80(C-5), 120.88, 121.13, 123.80, 124.44, 125.32, 131.12, 131.40 and 6 aromatic quaternary carbon signals at 126.87, 128.17, 136.65, 137.26, 141.53, 144.62, UV (λ, ε, hexane) 384(5,200), 378(3,700), 364(5,300), 360(5,000), 348(4,500), 343(shoulder, 3,900), 333(3,000), 256(204,000), 250(shoulder, 126,000), 222(15,400); exact mass: calcd. 190.0782; obsd. 190.0790. Satisfactory analysis could be obtained for the 2,4,7-trinitrofluoren-9-one derivative; the complex is air and thermally stable.
1H-Cyclobuta[de]anthracene:2,4,7-Trinitrofluoren-9-one Complex.

To a boiling ethanol/benzene solution (20 mL EtOH/1 mL H2O) of 2,4,7-trinitrofluoren-9-one (0.20 g, 0.60 mmol) was added freshly chromatographed (silica gel, hexane) 1H-cyclobuta-[de]anthracene (0.12 g, 0.60 mmol) in hot ethanol (5 mL). A dark brown precipitate formed, which after cooling the mixture to room temperature, filtration and recrystallization from benzene/ethanol afforded 1H-cyclobuta-[de]-anthracene:2,4,7-trinitrofluoren-9-one complex as dark red needles (0.13 g, 41%), mp 202-204°C.


Found: C, 66.72; H, 3.06; N, 8.60.
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91. Independently synthesized from 6-methyl-1-naphthoic acid and LiAlH₄.


94. See later Experimental.


96. Generously supplied by Dr. M. Platz, The Ohio State University.


APPENDIX
Figure 9: 300 MHz $^1$H NMR Spectrum of 252.
Figure 10: 75.43 MHz $^{13}$C NMR Spectrum of 252.
Figure 11: 90 MHz $^1$H NMR Spectrum of 260.
Figure 12: 75.43 MHz $^{13}$C NMR Spectrum of 260.
Figure 13: 90 MHz $^1$H NMR Spectrum of 263.
Figure 14: 20.12 MHz $^{13}$C NMR Spectrum of 263.
Figure 15: 90 MHz $^1$H NMR Spectrum of 269.
Figure 16: 75.43 MHz $^{13}$C NMR Spectrum of 269.