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BOSSENBROEK, Byron Justin, 1939-
INTERACTIONS AND REACTIONS OF PARALLEL
ACETYLENES.

The Ohio State University, Ph.D., 1967
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan
INTERACTIONS AND REACTIONS
OF PARALLEL ACETYLENES

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

By

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* * * * * *

The Ohio State University
1967

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ACKNOWLEDGMENTS

The author wishes to express his appreciation to Professor Harold Shechter for suggesting this problem and for his continuing guidance and interest. His assistance in preparing this dissertation is gratefully acknowledged. The author wishes to acknowledge the help of his colleagues through discussion and suggestion. The Petroleum Research Foundation and the Du Pont Company are acknowledged for their financial support during the course of this research. Finally, the author wishes to thank his wife, Joann, and his son, Daniel, for their understanding and patience during many absences from home.
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INTRODUCTION

The major portion of the present research involves preparation and study of 1,8-bis(phenylethynyl)naphthalene (I). The spectral and chemical properties of I have been investigated to determine under which conditions, if any, a stable cyclobutadiene system might be formed (Equation 1).

\[
\begin{align*}
\text{C} & \quad \text{C} \\
\text{N} & \quad \text{N} \\
\end{align*}
\rightarrow
\begin{align*}
\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} \\
\text{N} & \quad \text{N} & \quad \text{N} & \quad \text{N} \\
\end{align*}
\]

The ultraviolet and nuclear magnetic resonance spectra have been compared with those of 1,5-bis(phenylethynyl)naphthalene and 1,8-diphenylnaphthalene to determine if there is transannular interaction in the parallel acetylene.

A study has thus been made of irradiation or thermolysis of I and the product formed has been identified. I reacts with bromine, hydrogen bromide and iron pentacarbonyl to form stable adducts. The structures of these products have been determined. Addition of phenyl azide,
phenyl isocyanide, dimethyl acetylenedicarboxylate and sulfur to I was also attempted. Initial efforts to synthesize parallel acetylenes containing substituents such as ethoxy and methoxycarbonyl in place of phenyl in I were unsuccessful.
HISTORICAL

The first attempt to synthesize cyclobutadiene was reported by Willstatter and von Schmaedel (1). The product of dehydrobromination of 1,2-dibromocyclobutane is acetylene, not cyclobutadiene. "This observation plus the fact that conversion of two molecules of acetylene into one of cyclobutadiene would involve very little molecular reorganization suggests that in principle such dimerization is possible although such a reaction is unknown" (2). Many routes leading to possible stable cyclobutadienes have been investigated and several literature reviews are available (3). Only those attempts to prepare cyclobutadienes using acetylenes as initial materials are particularly pertinent to this dissertation.


Cram and Allinger (2) synthesized 1,7-cyclododecadiyne (II) in order to study its possible intramolecular dimerization to a tricyclic cyclobutadiene (Equation 2).

\[
\begin{array}{c}
\text{II} \\
\begin{array}{c}
\text{(CH}_2\text{)}_4 \text{C} = \text{C} \\
\text{C} = \text{C} \text{(CH}_2\text{)}_4
\end{array}
\end{array}
\]

Spectroscopic examination of II shows normal acetylenic infrared absorption at 4.5 and only end absorption in the ultraviolet, indicating that conjugation is not present. II is reduced to 1,7-cyclododecadiene and cyclododecane. Thus both spectroscopic and chemical evidence indicate that there is no real tendency for II to isomerize to a cyclobutadiene.

Synthesis of cyclooctatetraene by tetramerization of acetylene catalyzed by nickel cyanide produces little benzene despite its thermodynamic stability. Lonquet-Higgins and Orgel suggest (4) that cyclooctatetraene is formed by a bimolecular reaction in which the precursor contains cyclobutadiene complexed with nickel cyanide (Equation 3).

Sauer and Cairns have studied such a mechanism in the formation of 1,3,5-hexatrieny1 cyanide (5) from two molecules of acetylene and one of acrylonitrile in the presence of triphenylphosphine and nickel tetracarbonyl. Tracer studies have shown that when C\textsuperscript{14}-labeled acrylonitrile is condensed with acetylene, the resulting hexatrieny1 cyanide is not labeled on the terminal methylene group as would be required by following reaction path a (Equation 4) via cyclobutadiene.

Beiber suggests (6) an alternate route (b, Equation 4).
involving a cyclobutadiene intermediate and proton migration to account for the lack of C$^{14}$ in the terminal position. Sauer and Cairns argue, however, that if a cyclobutadiene intermediate is involved, two molecules of acetylene and one of dimethylacetylene should form some p-xylene along with o-xylene (Equation 5) whereas spectroscopy shows no evidence for the former isomer. Beiber again points out that if this argument is valid, some dimethycyclobutadiene must be formed and acetylene must add to its more hindered position to yield p-xylene. He concludes that neither assumption is justified and the lack of evidence for p-xylene does not rule out a cyclobutadiene intermediate.
Lagidze reported (7) that 2,5-diacetoxy-3-hexynes (7) R. M. Lagidze, from Chem. Abstr., 47, 4321 (1953); ibid., 50, 11960 (1956); ibid., 51, 3545 (1957).

(III) condense with benzene in the presence of aluminum chloride to give stable benzocyclobutadienes (IV, Equation 6). Hancock, Taber and Scheuchenpflug (8) have found that

\[
\text{AcO-CH}_2-C\equiv-C-CH_2-\text{OAc} + \text{C}_6\text{H}_5 - \xrightarrow{\text{AlCl}_3} \text{III} \rightarrow \text{IV (a)}
\]

III (a) \( R = R' = H \)

(b) \( R = R' = \text{Me} \)

(c) \( R = \text{Me}, R' = -(\text{CH}_2)\text{Me}_2- \)

\[
\text{IV (b,c)}
\]


these structural assignments are wrong; the correct structures (IV a,b,c) are shown below.
Buchi, Perry and Robb have studied irradiation of diphenylacetylene (V) in hexane (9). The product mixture consists of starting material (94%) and small amounts of hexaphenylbenzene (VII), octaphenylcubane (VIII), 1,2,3-triphenylcubane (IX) and 1,2,3-triphenylazulene (X) (Equation 7). To account for these products, tetraphenyl-

cyclobutadiene (VI) was proposed as a reaction intermediate.
Muller, Saurbier and Heiss attempted to prepare a stable substituted cyclobutadiene by irradiation of $\omega$-bis(phenylethynyl)benzene (10). The product isolated is a dark blue-green diazulene (XII, Equation 8).

The mechanism suggested involves a cyclobutadiene intermediate which undergoes bond redistribution and product formation in a manner similar to that proposed for conversion of VI to X.

The work of Watts, Fitzpatrick and Pettit (11) is of
some interest relative to the mechanism schemes suggested for cyclobutadiene intermediates proposed in previous studies. Decomposition of cyclobutadiene iron tricarbonyl by ceric ion in the presence of substituted acetylenes yields "Dewar benzene" derivatives which isomerize to substituted benzenes when heated (Equation 9). These investigators also trapped cyclobutadiene at low temperatures and showed that while it is extremely reactive it does possess a finite lifetime.

Molecular orbital calculations by Dewar and Gleicher (12) lead to the postulate that cyclobutadiene is a singlet in the ground state. Thus cyclobutadiene should be a typical cyclic polyene with essentially localized single and double bonds. The calculated resonance energy is nearly zero and the high reactivity can be justified.
on the basis of ring strain and ideal geometry for Diels-Alder reactions.

More recently Dessy and Kandil observed that irradiation of 2,2-bis(phenylethynyl)biphenyl (XIII) (13) yields a product which may be a tetrahedrane (XIV) or a cyclobutadiene derivative (XV, Equation 10). X-ray studies to determine the structure of the product are still in progress. This reaction and its product(s) are discussed in the succeeding section of this dissertation.

RESULTS AND DISCUSSION

The present investigation involves preparation of 1,8-diethynlnaphthalene derivatives leading to possible formation of stable cyclobutadiene systems (Equation 11).

\[ \text{(11)} \]

![Chemical structure](image)

Study has also been made of the chemistry of such parallel diacetylenes.

Stephens and Castro have described a synthesis of diarylacetylenes (14) by refluxing aryl iodides with copper ary lacetylides in pyridine under nitrogen (Equation 12).


\[ \emptyset - I + Cu-C=C - \emptyset \xrightarrow{C_5H_5N} \emptyset - C=C - \emptyset + CuI \text{ (12)} \]

The possible extension of this method to the present research made the facile preparation of large amounts of 1,8-diiodonaphthalene (XVI) desirable.
Preparation of Iodonaphthalenes.

Two methods for preparing XVI have been reported and both were used in this research. Hodgson and Whitehurst prepared XVI (15) in 38% yield on small scale in a single operation by addition of 1,8-naphthalenediamine (XVII) in concentrated sulfuric acid to sodium nitrite in glacial acetic acid at 0° to give the bis-diazonium salt (Equation 13). Decomposition of the salt in aqueous potassium iodide yields XVI. Early efforts to repeat this work gave poor results. Yields of crude product were low (12-15%) and 1,5-diiodonaphthalene (XVIII) and 1-iodonaphthalene (XIX) were formed along with XVI. Laborious chromatography and recrystallization were required to achieve separation of XVI.

Attempts to remove 1,5-naphthalenediamine from commercial XVII by column chromatography were unsuccessful. Recrystallization of commercial XVII from 30% ethanol-water yields reasonably pure starting material. When the

\[
\begin{align*}
\text{NH}_2 & \quad \text{NH}_2 \\
\text{H}_2\text{SO}_4 & \quad \text{HNO}_2 \\
\text{XVII} & \quad \text{N}_2 \quad \text{N}_2
\end{align*}
\]

\[
\xrightarrow{2\text{HSO}_4^- \quad \text{KI}}
\]

\[
\text{XVI}
\]

\[
(13)
\]
diazotization is conducted at -3 to -4° and the bis-
diazonium salt is heated to 80° in excess aqueous potassium
iodide, crude yields of up to 32% of XVI are obtained.
Recrystallization from Skelly Solve B to remove XIX gives
XVI in a final yield of 25%.

XVII in tetrahydrofuran could not be diazotized
effectively with isoamyl nitrite using the procedure of
Logullo and Friedman (16).


Preparation of XVI from XVII in two laboratory oper-
atations has been described by Scholl, et al (17) (Equation 14).

(17) R. Scholl, Chr. Seer and R. Weitzenbock, Ber.,
43, 2202 (1910).

\[
\begin{align*}
\text{XVII} \quad \text{HNO}_2 \quad \text{HCl} & \quad \text{N}_2\text{Cl} \quad \text{NH}_2 \\
\text{XX} & \quad \text{I} \quad \text{NH}_2 \cdot \text{HCl} \\
\text{XVI} \quad \text{KI} & \quad \text{I} \quad \text{N}_2\text{Cl} \\
\end{align*}
\]
Reaction of XVII with one equivalent of nitrous acid in dilute hydrochloric acid results primarily in diazotization of only one of the amine groups. Treatment of 1-naphthylamine-8-diazonium chloride with hydriodic acid yields 1-iodo-8-naphthylamine which was isolated as the hydrochloride salt (XX). Diazotization of XX and reaction with aqueous potassium iodide results in XVI. The second step in this sequence gave acceptable yields (67%) without complication; the yield in the first step for formation of 1-iodo-8-naphthylamine, however, was less than 25%.

Alternate routes to XX were also investigated. The disodium salt of 1,8-naphthalic acid was refluxed with aqueous mercuric acetate to form 1-(acetoxymercuri)-8-naphthoic acid which is converted by sodium hypoiodite and subsequent acidification to 1-iodo-8-naphthoic acid (XXI, Equation 15). The best yield obtained from this reaction was 46% of XXI containing some mercuric oxide.

XXI was converted to XX in good yield (90%) by the Schmidt reaction (Equation 16). Sodium azide was added to a suspension of powdered XXI in 88% sulfuric acid at 10° and the mixture allowed to warm to room temperature.
1-Iodo-8-naphthylamine was isolated as its hydrochloride (XX).

Dessy and Kandil prepared 1-bromo-8-iodonaphthalene in 28% yield (18) by refluxing 1-bromo-8-naphthoic acid with iodine and mercuric oxide in cyclohexane. An attempt to prepare XVI from XXI under similar conditions (Equation 17) gave a yield of only 15%.

\[ \text{CO}_2\text{H} \quad \xrightarrow{1) \text{HN}_3} \quad \text{CO}_2\text{H} \]
\[ \quad \xrightarrow{2) \text{NaOH}} \quad \xrightarrow{3) \text{HCl}} \quad \text{HgO} \quad \text{XXI} \quad \text{XX} \]

1,5-Diodonaphthalene was prepared in 71% yield in a single operation from commercially available 1,5-naphthalenediamine using the procedure of Hodgson and Whitehurst (14) involving bis-diazotization and subsequent reaction with iodide ion. This reaction provides much better results
for the 1,5-diiodide than the 1,8-diiodide. Steric interaction of the iodine atoms in 1,8-diiodonaphthalene must be extensive; 1-iodo-8-naphthylamine, however, by diazotization and reaction with potassium iodide, can be readily converted to XVI. Thus steric factors in 1,8-diiodonaphthalene do not explain the difficulty in its preparation from 1,8-naphthalenediamine. Diazotization of XVII by excess nitrous acid in concentrated sulfuric acid produces in part the 1,8-bis-diazenonium ion (XXII). Comparison of XXII with the 1,5-bis-diazenonium ion (XXIII) shows that the positive charges in XXII are much closer than in XXIII. It is suggested that the charge repulsion in XXII leads to difficulty in its formation and results in its instability.

Preparation of Copper Acetylides.

The copper salts of phenylacetylene, ethoxyacetylene, methyl propiolate, 1-phenyl-2-propyne-1-ol and 2-methyl-3-butyne-2-ol were prepared by adapting the procedure of Stephens and Castro (13). Phenylacetylene in 95% ethanol was added to a rapidly stirred solution of cuprous chloride
in concentrated aqueous ammonium carbonate (Equation 18).

\[ \text{C}_6\text{H}_{10}=\text{C}-\text{H} + \text{CuCl} (\text{NH}_4)_2\text{CO}_3 \rightarrow \text{C}_6\text{H}_{10}=\text{C}-\text{Cu} \]  (18)

Bright yellow (phenylethynyl)copper (XXIV, 74%), after washing and drying, is stable to air and heat. Methyl propiolate treated similarly gives orange [(methoxycarbonyl)ethynyl] copper in nearly 80% yield.

Preparation of (ethoxyethynyl)copper (XXV) is greatly influenced by oxygen and the normal procedure gives yields of less than 40%. When the reaction is conducted under nitrogen, the yield of XXV is considerably increased.

Substituted acetylenes containing a hydroxyl group gave poor results in efforts to prepare their copper salts. Cuprous 1-phenyl-2-propyne-1-ol and cuprous 2-methyl-3-butyne-2-ol (XXVI) are sensitive to oxidation. Preparation of XXVI is accompanied by oxidative coupling of the salt even under nitrogen and 2,7-dimethyl-3,5-octadiyne-2,7-diol (XXVII) is the major product (Equation 19) (19).

\[
\begin{align*}
2 \text{Cu-\text{C}=\text{C}-\text{C}-\text{CH}_3} & \overset{\text{O}_2}{\rightarrow} \text{CH}_3\text{-C}=\text{C}-\text{C}=\text{C}-\text{C}=\text{C}-\text{C}-\text{CH}_3 \\
\text{XXVI} & \quad \text{XXVII}
\end{align*}
\]
Y. S. Zal'kind and M. A. Aizikovich, J. Gen. Chem. (U.S.S.R.), 7, 227 (1937) described a similar general method for preparing tertiary diacetylene glycols. Thus 2-methyl-3-butyne-2-ol yields XXVII quantitatively when treated with aqueous cuprous chloride and ammonium chloride.

Preparation of Ethynylnapthalenes.

The next objective in the present research was preparation of 1,8-bis(phenylethynyl)naphthalene (I) by reaction of (phenylethynyl)copper (XXIV) with 1,8-diido-naphthalene (XVI). XXIV (2 equivalents) and XVI (1 equivalent) react at 25-30° under nitrogen to give, after chromatography, light yellow needles of I (72%), m.p. 105-106° (Equation 20).

\[
\text{XXIV} + 2 \text{Cu-C≡C-∅} \xrightarrow{\text{C}_2\text{H}_5\text{N}} \text{I}
\]

In previous reactions of aryl iodides with copper acetylides, the reagents were refluxed in pyridine for 6 to 24 hours. As will be discussed later, I would not have survived if reflux temperatures had been necessary for reaction of XVI and XXIV to occur. The structure of I was initially assigned on the following basis: (1)
elemental analysis and molecular weight agree almost exactly with theory, (2) infrared absorption (Fig. 1) at 4.48\(\mu\) (C=C), (3) ultraviolet absorption maxima (Fig. 13): 209 (\(\epsilon 47,800\)), 243 (66,300), 265 (26,800), 344 (29,300) and 356\(\mu\) (26,800) and (4) nuclear magnetic resonance (Fig. 19): 87.20 (m,12H) and 7.75 (m,4H) (20).

(20) The 4 protons centered at 8 7.75 are those ortho and para to the ethynyl groups on the naphthalene ring. \(\alpha\)-Naphthyl protons are normally centered at 8 7.73 and \(\beta\)-naphthyl protons at 8 7.37. Electron withdrawal by the ethynyl groups deshields the ortho protons resulting in a shift from 8 7.37 to 8 7.75.

I is slightly fluorescent in ultraviolet light and reacts with 2,4,7-trinitrofluorenone in hot benzene (21).


to give a stable red-brown 1:1 molecular complex (C\(_{39}\)H\(_{21}\)N\(_{3}\)O\(_{7}\)), m.p. 149-150\(^{\circ}\).

1,5-Bis(phenylethynyl)naphthalene (XXVIII) was synthesized and its spectral properties were compared with those of I to determine if there was evidence for interaction of the acetylene groups in I. Initial efforts to prepare XXVIII by refluxing 1,5-diiodonaphthalene (XVIII, 1 equivalent) and XXIV (2 equivalents) in pyridine under nitrogen yielded only diphenylbutadiyne (XXIX) and unreacted XVIII. The presence of even a small amount of oxygen in the system makes oxidative coupling of XXIV the
preferred process. When greater precautions are taken to exclude oxygen from the system, XXVIII is obtained in low yield (10%) along with 75% of XXIX (Equation 21). XXVIII was isolated as white cubic crystals, m.p. 198-199°, which produce a blue fluorescence in ultraviolet light. The structure of XXVIII is assigned on the basis of elemental analysis, molecular weight, infrared absorption (Fig. 2): 4.47μ(C=C); ultraviolet absorption maxima (Fig. 14): 207 (46,600), 240 (70,400), 263 (44,000), 341 (33,200) and 355μ(26,900) and nuclear magnetic resonance (Fig. 20): δ7.53 (m,14H) and 8.47 (d,2H) (22). XXVIII forms a red-

(22) Electron withdrawal through space by the ethynyl groups deshields the para protons resulting in a downfield shift to δ8.47.

brown trinitrofluorenone complex (21), m.p. 180-181° which analyses correctly for C_{52}H_{26}N_{6}O_{14}: a molecular complex
composed of one molecule of XXVIII and 2 molecules of 2,4,7-trinitrofluorenone.

The ultraviolet spectra of I (Fig. 19) and XXVIII (Fig. 20) are very similar except that I absorbs at slightly longer wave lengths and absorption for its acetylene groups is less intense (626,300 for I and 44,000 for XXVII). I is slightly more colored than XXVII indicating that I may have a higher degree of conjugation. Dessy and Kandil (18) have assigned the band at 269m (tetrahydrofuran) in the spectrum of 1-(phenylethynyl)naphthalene to the acetylene group. This band appears in the spectrum of I at 265m (626,800, 95% ethanol) and at 263m (44,000, 95% ethanol) in that of XXVIII. Interaction of the adjacent acetylene groups in an excited state of I may be responsible for this decrease in the intensity of acetylene absorption.

The nuclear magnetic resonance spectrum of I was compared with those of XXVIII, 1,8-diphenynaphthalene (XXX), phenylacetylene (XXXI), diphenylbutadiyne (XXIX) and cis-stilbene. The resonance signal for the phenyl protons in XXX occurs at 66.85 (23) and is shifted


upfield from that for phenyl protons in 1,7-diphenynaphthalene (67.49) and 1-phenynaphthalene (67.38). A similar shift of the same order of magnitude is observed in the resonance signals of the aryl protons in (2.2)-paracyclo-
phane ($\delta 6.37$) (24) and $p$-xylene ($\delta 7.05$) (25a). This


(25) (a) Varian N* R, Catalogue, Varian Associates, Palo Alto, Calif, 1962, no. 203; (b) *ibid.*, no. 186; (c) *ibid.*, no. 305.

shift is produced by shielding of the phenyl protons by an adjacent parallel benzene ring.

A shift in the same direction but of smaller magnitude is observed for the phenyl protons in I. Phenyl proton resonance signals occur at $\delta 7.32$ for XXXI (25b), $\delta 7.33$ for XXIX (Fig. 25) and $\delta 7.43$ for XXVIII (Fig. 20). The signal is moved to $\delta 7.13$ for I (Fig. 19). While this shift is apparently due to the shielding of the benzene rings, the magnitude of the effect can possibly be interpreted to mean that the benzene rings in I are farther apart than those in XXX. To account for the smaller shift in I, it is suggested that the acetylene groups may possibly interact such that I has some cyclobutadiene character. The actual phenyl proton resonance signal for I ($\delta 7.13$) is similar to that for cis-stilbene ($\delta 7.18 \pm 0.03$) (25c).

It is also possible that the phenylethynyl groups are not parallel but are pushed apart for steric reasons. As a result the phenyl protons would be much less shielded. Thus the signal for phenyl protons in I ($\delta 7.13$) may indicate that the phenyl groups are farther apart than those in XXX ($\delta 6.85$) but closer than those in o-bis(phenylethynyl)-
Attempts to couple 1,8-diiodonaphthalene (XVI) with other copper acetylenes using the normal procedure were unsuccessful. [(Methoxycarbonyl)ethynyl]copper and (ethoxyethynyl)copper did not react with XVI in pyridine at room temperature. Recovery of XVI was nearly quantitative.

In the course of this investigation, it was found that (phenylethynyl)copper could be prepared conveniently from cuprous chloride and phenylacetylene in pyridine under nitrogen. In two experiments yields of up to 85% were obtained. This method was extended to the preparation of (ethoxyethynyl)copper in situ followed by refluxing with XVI for 24 hours. Chromatography on neutral alumina gave 1,8-dichloronaphthalene (XXXII, 62%) (27). Bacon and Hill (28) reported that 1-chloronaphthalene is obtained
An unidentified product was also isolated from this reaction (see Experimental Section).


Quantitatively when 1-iodonaphthalene and cuprous chloride are refluxed in pyridine. Although initial formation of (ethoxyethynyl)copper occurs, the cuprous chloride apparently present undergoes exchange with XVI to form XXXII.

Efforts to prepare 1,8-bis(3-hydroxy-3-methyl-1-butynyl)naphthalene in a similar manner yielded 2,7-dimethyl-3,5-octadiyne-2,7-diol (XXVII, 79%) and unreacted XVI. (3-Hydroxy-3-methyl-1-butynyl)copper formed in the reaction is oxidatively coupled to XXVII (Equation 19).

An investigation was made of the possible synthesis of tolanes from aryl bromides and copper acetylides. Bromobenzene and (phenylethynyl)copper in refluxing pyridine under nitrogen yields diphenylbutadiyne and bromobenzene. α-Bromonaphthalene gives similar results. Use of dimethylformamide or N-methylpyrrolidone as a solvent does not alter the results.

Reactions of 1,8-Bis(phenylethynyl)naphthalene.

The largest portion of the present research involves an investigation of the chemical reactions of 1,8-bis-(phenylethynyl)naphthalene (I). I was subjected to irradiation to determine if a stable cyclobutadiene might be formed.
Photolysis of I in Skelly Solve B at 65-70° for 24 hours followed by chromatography yields pale yellow crystals of 7-phenylbenzo[k]fluoranthene (XXXIII), m.p. 166-167°. The reaction may well be thermal rather than photochemical since it proceeds more slowly and in lower yield at 40° whereas the best yields are obtained at 130° in the absence of light.

XXXIII is not oxidized with acidic or basic potassium permanganate nor is it reduced catalytically with palladium on charcoal or platinum oxide and hydrogen under mild conditions. It does form a red-brown 1:1 molecular complex with 2,4,7-trinitrofluorenone (21), m.p. 184-185°.

A possible mechanism for formation of XXXIII is shown in Equation 22. I may cyclize to B by a dipolar process when heated; hydride transfer, either by 1-3 or successive 1-2 processes, yields the product, XXXIII. Reaction may also proceed through a diradical intermediate (Equation 23)
in which the final product is formed by transfer of hydrogen.

Another possible mechanism involves cyclobutadiene and "Dewar benzene" intermediates (Equation 24).
Buchi, et al (9) have proposed XI as an intermediate arising from a cyclobutadiene to explain formation of IX and X from irradiation of diphenylacetylene (Equation 7). Muller, et al (10) suggested a similar intermediate for conversion of o-bis(phenylethynyl)benzene to the azulene derivative XII (Equation 8).

Two intermediates of this type (XXXIV and XXXV, Equation 25) can possibly form in thermolysis or photolysis of I. XXXIV can lead to XXXIII, the observed product, but formation of a substituted azulene (XXXVI) is also possible. XXXV can give XXXVI and/or 11-phenylbenzo[j]fluoranthene (XXXVII) which is isomeric with XXXIII. Formation of an azulene as a reaction product would be evident by its deep blue or green color. Visual examination and chromatography of the reaction mixture give no evidence for the presence of an azulene in any of the thermolysis or photochemical experiments in which XXXIII is formed. Spectral data discussed below leads to the choice of XXXIII, not XXXVII, as the thermolysis product. It thus seems likely that intermediates such as XXXIV or XXXV are not formed in thermolysis or photolysis of I.

The infrared spectrum of XXXIII in solution (Fig. 6) gives no evidence for acetylene absorption. Elemental analysis and molecular weight determination indicate that XXXIII is isomeric with the starting material, I. The nuclear magnetic resonance spectrum (Fig. 21) exhibits
signals only for aromatic protons at $\delta 6.53$ (d, 1H), 7.51 (m, 14H) and 8.17 (s, 1H). The naphthyl proton in the 6 position is shielded by the electrons in the phenyl ring and gives the signal at $\delta 6.53$. The signal at $\delta 8.17$ is probably that for the proton on the 12 position. This
signal is absent in an analogous product containing bromine rather than hydrogen in that position (Fig. 23).

The identification of XXXIII is based primarily on the similarity of its ultraviolet spectrum (Fig. 15) with that of benzo[k]fluoranthenes (XXXVIII) (29) and 7,12-di-phenylbenzo[k]fluoranthenes (XXXIX) (30). The ultraviolet data are summarized in Table I.

The three compounds, XXXIII, XXXVIII and XXXIX, differ only in the number of phenyl substituents. Due to steric requirements the phenyl groups are highly twisted from the planes of the benzo-fluoranthenes nuclei in XXXIII and XXXIX. This prevents significant conjugation of the phenyl rings with the fluoranthene system and thus the spectra show only small substituent effects in that absorption is at
Table I

Ultraviolet maxima of XXXIII, XXXVIII, XXIX and XL in Ethanol

<table>
<thead>
<tr>
<th>XXXVIII</th>
<th>XXXIII</th>
<th>XXXIX</th>
<th>XL</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Chemical Structure" /></td>
<td><img src="image2.png" alt="Chemical Structure" /></td>
<td><img src="image3.png" alt="Chemical Structure" /></td>
<td><img src="image4.png" alt="Chemical Structure" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>215</th>
<th>36,200</th>
<th>216</th>
<th>42,300</th>
<th>226</th>
<th>38,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>240</td>
<td>56,200</td>
<td>246</td>
<td>42,900</td>
<td>252</td>
<td>63,000</td>
</tr>
<tr>
<td>269</td>
<td>22,900</td>
<td>270</td>
<td>17,700</td>
<td>270</td>
<td>30,200</td>
</tr>
<tr>
<td>282</td>
<td>26,200</td>
<td>286</td>
<td>18,000</td>
<td>298</td>
<td>42,600</td>
</tr>
<tr>
<td>296</td>
<td>46,700</td>
<td>298</td>
<td>31,200</td>
<td>308</td>
<td>30,200</td>
</tr>
<tr>
<td>308</td>
<td>56,200</td>
<td>309</td>
<td>38,400</td>
<td>310</td>
<td>61,500</td>
</tr>
<tr>
<td>361</td>
<td>7,240</td>
<td>364</td>
<td>5,250</td>
<td>366</td>
<td>7,940</td>
</tr>
<tr>
<td>380</td>
<td>13,200</td>
<td>384</td>
<td>8,200</td>
<td>386</td>
<td>15,100</td>
</tr>
</tbody>
</table>

slightly longer wavelengths for XXXIII and XXXIX than for XXXVIII.

1-Phenynaphthalene has an ultraviolet spectrum similar to that of naphthalene. The apparent reason for the similarity of absorption is that steric factors prevent coplanarity of the phenyl and naphthalene rings. Support for such an interpretation comes from the similarity of its ultraviolet absorption ($\lambda_{\text{max}} 225, 288$) with that of
1-cyclohexynaphthalene (λ_max 224, 283) (31). The ultra-

violet absorption of 2-phenynaphthalene (λ_max 213, 250, 286) (31) is shifted to longer wavelengths from that of 1-phenynaphthalene. This indicates that the 2-phenyl group is coplanar with the naphthalene ring and absorption occurs at longer wavelengths due to increased conjugation.

The spectral data for benzo[1]fluoranthene (XL) (29) are also included in Table I. Comparison shows that the values for XXXIII are different from those for XL especially in the region from 315 to 335 μ. The spectra for XXXIII and XXXVIII, on the other hand, are nearly superimposable. A phenyl substituent in the 11 position (XXXVII) would not change the spectrum significantly since a model shows that coplanarity is prevented by steric interaction with the 6-phenyl proton. There could be little significant conjugation of the phenyl group with the fluoranthene system in XXXVII, although there would be a small substituent effect.

Several attempts were made to effect 1,4 addition of various reagents to I under the influence of light and/or heat (Equation 26). When sulfur and I are heated under nitrogen, the only product formed is XXXIII. I does not react with dimethyl acetylenedicarboxylate, phenyl isocyan-
ide or phenyl azide when irradiated at room temperature or in refluxing benzene or Skelly Solve B or when heated with I in a steel bomb at 130° in benzene, diethyl Carbitol or diglyme. In all cases the only product formed was XXXIII and the yield depended on the temperature and reaction time.

Iron pentacarbonyl does not react with I at room temperature or in refluxing diglyme. When these reactants are heated in diglyme in a steel bomb at 130° for 24 hours, the main product is XXXIII (80%). A small amount (5%) of a light tan solid was isolated and identified as acecyclopreneiron tricarbonyl (XLI, Equation 27), m.p. 204-205° (27)

\[
\begin{align*}
\text{XXXII} & \quad \text{Fe(CO)}_3 \\
\end{align*}
\]

after crystallization from acetone. The solid turns black on standing and chromatography of this residue yields blue-black crystals of acecycloprene. Identification as acecycloprene was verified by mixed melting point, thin layer chromatography and infrared absorption. XLI gave a fair elemental analysis; it is unstable and difficult to recrystallize. Its molecular weight (492) agrees very well with
theory (496).

The infrared spectrum of XLI (Fig. 7, KBr wafer) exhibits absorption at 4.37, 5.02 and 5.05 μ; normal carbon-yl absorption occurs at 6.13 μ. The spectrum was compared with those of 2,5-diphenylcyclopentadienoneiron tricarbonyl (XLII) and hexatrienyliiron tricarbonyl (XLIII). Metal tricarbonyl absorption for XLII occurs at 4.78, 4.93 and 4.97 μ (nujol) (32) and at 4.88, 5.03, 5.07 μ (film) for


XLIII (33a). Iron tetracarbonyl complexes show a minimum of 4 bands for metal carbonyl absorption (33b). The first band always appears at a wavelength of 4.75 μ or less. XLI has only 3 such bands with the first appearing at 4.37 μ. Therefore XLI has a tricarbonyl rather than a tetracarbonyl structure.

Schrauzer suggested (34) a mechanism for formation of tetracycloneiron tricarbonyl from diphenylacetylene (V) and iron tetracarbonyl (Equation 28). The mechanism for formation of XLI in the present study is probably similar but involves loss of carbon monoxide.

(34) G. N. Shrauzer, Chem. and Ind., 1403 (1958).
Assong and Kharasch reported (35) the formation of 3,4,5,6-tetraphenyl-1-cyclohexene (X) in 25% yield from diphenylacetylene in the presence of 2,4-dinitrobenzenesulfenyl chloride and aluminum chloride. In a similar experiment in the present study I was treated with a catalytic amount of aluminum chloride in ethylene dichloride. Rapid reaction occurred to give XXXIII (16%) and a dark green solid (4%) which may be the substituted azulene XXXVI. Because of the small amount of material available and the low yield, its identity could not be established. A possible mechanism for acid catalyzed conversion of I to XXXIII is shown in Equation 29.

Treatment of I with one equivalent of bromine at room temperature in chloroform yields white crystals, m.p. 148-149°. The elemental analysis of the product corresponds to C_{26}H_{16}Br_{2}; a dibromo adduct of I. The mass spectrograph indicates a molecular weight of 488. The 6 structures shown below excluding possible stereochemistry were con-
sidered in determining the identity of the adduct. The spectral and chemical properties of the product indicate that 1,2-bis(α-bromobenzylidene)acenaphthene (II) is the correct structure.

The infrared spectrum of the adduct (Fig. 8) shows no acetylene absorption. 1,8-Bis(phenylethynyl)naphthalene exhibits acetylene absorption at 4.43 μ, 1,5-bis(phenylethynyl)naphthalene at 4.47 μ and 1-nitro-8-(phenylethynyl)naphthalene at 4.46 μ (Figs. 1, 2 and 3). On this basis
Possible Structures for Dibromo Adduct

Structure XLIV was determined to be incorrect.

The dibromo adduct gives a negative alcoholic silver nitrate test even when heated. 3,4-Dibromotetraphenylcyclobutene (36) and 3,4-dibromo-1,2-diphenylcyclobutene (37) give immediate precipitates with silver nitrate at room temperature. Structures XLV and XLVI are therefore


The ultraviolet spectrum of IL (Fig. 17) has been compared with those of acenaphthenequinone (L) (31), acenaphthylene (LI) (31), phenalenone (LII) (38), peri-cycloheptanaphthalene (LIII) (39) and peri-cycloheptacene (39) R. D. Campbell and N. H. Cromwell, J. Am. Chem. Soc. 79, 3456 (1957). cycloheptanaphthalene (LIII) (39) and peri-cycloheptacene (39) V. Boekelheide and G. K. Vick, J. Am. Chem. Soc., 78, 653 (1956).

structures and spectral data for these compounds are shown in Table II. The absorption maxima of IL are quite close to those of L and LI. Structures XLV and XLVI, both of which might be expected to exhibit ultraviolet absorption similar to that of LI, are eliminated on the basis of chemical evidence.

Structure XLVII is similar to phenalenone (LII) which is yellow and shows absorption at longer wavelengths than does the dibromo adduct which is nearly white. Phenalenone is not oxidized with 50% excess refluxing sodium dichromate dihydrate in glacial acetic acid. Oxidation of IL to yield acenaphthenequinone is discussed below. Thus, on the basis of color and spectral and chemical properties, structure XLVII is eliminated.

XLVIII is a substituted peri-cycloheptanaphthalene and should be highly colored since LIII, the parent compound,
Table II
Ultraviolet maxima of IL, L, LI, LII, LIII, and LIV

<table>
<thead>
<tr>
<th></th>
<th>IL</th>
<th>L</th>
<th>LI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Br 0&lt;sup&gt;&lt;/sup&gt;-C C-Br</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>IL</td>
<td>L</td>
<td>LI</td>
</tr>
<tr>
<td></td>
<td>210 41,800</td>
<td>211 19,300</td>
<td>207 9,700</td>
</tr>
<tr>
<td></td>
<td>239 65,900</td>
<td>225 28,200</td>
<td>228 46,800</td>
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<tr>
<td></td>
<td>328 13,000</td>
<td>329 7,570</td>
<td>323 9,540</td>
</tr>
<tr>
<td></td>
<td>338 7,400</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>LII</th>
<th>LIII</th>
<th>LIV</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LII</td>
<td>LIII</td>
<td>LIV</td>
</tr>
<tr>
<td></td>
<td>218 19,100</td>
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<td></td>
<td>260 9,500</td>
<td>340 10,000</td>
<td>310 50,100</td>
</tr>
<tr>
<td></td>
<td>340 7,500</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>355 11,500</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>380 9,000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

and LIV are deep red. Since the dibromo adduct is white, it appears unlikely that XLVIII is the correct structure even though the spectra of IL and LIII are somewhat similar.

The dibromo adduct was oxidized with excess (30%)
refluxing sodium dichromate dihydrate in glacial acetic acid. The infrared spectrum of the crude product corresponds to a mixture of naphthalic anhydride (C=O at 5.62 μ and 5.73 μ), acenaphthenequinone (5.75 μ) and benzoic acid (5.89 μ). The acenaphthenequinone (~25%) was separated by column chromatography and its identity confirmed by its mixed melting point, infrared absorption and retention time on a vapor phase chromatograph. IL would be expected to yield acenaphthenequinone on oxidation (Equation 30).

\[
\begin{align*}
\text{IL} & \xrightarrow{\text{Na}_2\text{Cr}_2\text{O}_7, 2 \text{H}_2\text{O}} \text{O} & \text{O} \\
& \text{O} & \text{O} \\
& + \text{O} & \text{O} \\
& + \text{C} & \text{Br} \\
& + \text{Br} & \text{CO}_2\text{H}
\end{align*}
\]

There are three possible isomers of IL (a,b,c). In each of the isomers the exocyclic double bonds are highly twisted. ILc is definitely ruled out on the basis of the nuclear magnetic resonance spectrum (Fig. 22) which shows that the phenyl protons are not shielded by an adjacent
Benzene ring. There is no spectral evidence which confirms or excludes ILa or ILb. However, both the proposed mechanism for formation of IL and its facile loss of hydrogen bromide which are discussed below suggest that ILa is the correct structure.

1,2-Bis(methylene)acenaphthenes are colored compounds.

Maxim prepared (40) a series of such compounds (LV, $R=H, Et, i-Pr, \emptyset$) which range in color from yellow-orange to red-orange. Acenaphthenequinone itself is light yellow whereas IL is almost white. It is suggested that the twisting of the exocyclic double bonds in IL accounts for its lack of color. This twisting also suppresses conjugation with the result that the ultraviolet absorption spectrum of IL is similar to those of acenaphthylene and 7,8-dibromoacenaphthylene. The alkyl or aryl groups in LV can be trans-trans as shown and the size of the cis-cis protons does not require that the double bonds be twisted. Thus these compounds are highly colored since the exocyclic

double bonds are not distorted.

IL readily loses hydrogen bromide under the influence of heat or light. Irradiation (3500 and 5250 Å) of IL in Skelly Solve B followed by chromatography yields fine light yellow needles of 7-bromo-12-phenylbenzo[k]fluoranthene (LVI, 78%), m.p. 137-138°. A possible mechanism for formation of LVI is shown in Equation 31. The elemental analysis is correct for C_{26}H_{15}Br showing loss of hydrogen bromide from IL. IL in 95% ethanol also loses
hydrogen bromide to give LVI when exposed to laboratory light for several weeks.

Both LVI and XXXIII are light yellow. The ultraviolet absorption of LVI [Fig. 16: 216 (ε 31,800), 248 (43,900), 271 (12,900), 288 (11,500), 299 (28,700), 311 (37,200) and 387μ (6,400)] is similar to that for XXXIII (Fig. 15). The nuclear magnetic resonance spectrum (Fig. 23) shows doublets at δ 6.40, 8.48 and 3.78 and a multiplet at δ 7.40 (1:1:1:12). The doublet at δ 6.40 is assigned to the proton in the 1 position, being shielded by the phenyl ring on the 12 position (see diagram, p. 30). The doublets at δ 8.48 and 8.78 are assigned to protons which are deshielded by the bromine. 1-Bromonaphthalene and 2,3-dibromonaphthalene show similar deshielding effects. In each case only 2 protons are affected leading to the assumption that the deshielding takes place through space rather than by electron withdrawal through bonds. Thus it is suggested that the protons in LVI which are deshielded by bromine are those in the 6 and 8 positions.

The structure of LVI is confirmed upon its reaction with magnesium followed by hydrolysis to give XXXIII in near quantitative yield (Equation 32).

Debromination of IL by zinc dust or copper bronze in benzene was unsuccessful. Stirring the reactants at room temperature yields only starting materials, whereas 5 to 7 hours of reflux again results in loss of hydrogen bromide.
to yield LVI (Equation 31). Refluxing IL in benzene without zinc or copper also produces LVI.

Treatment of dibromide IL with excess (4.5 equivalents) n-butyllithium gives a red solution which becomes light brown after 4 hours. Acidification and chromatography yields I (18%), XXXIII (12%) and LVI (53%). Reasonable mechanisms for formation of I, LVI and XXXIII from IL are illustrated in Equations 33, 34 and 35. XXXIII may also be derived from I on standing by the mechanism shown in Equation 22 or from LVI by exchange with n-butyllithium and acidification (Equation 36).

Reaction of IL with excess magnesium (4 equivalents) in anhydrous ether at room temperature was followed by hydrolysis. Analysis by thin layer chromatography indicates that the major product is I along with a smaller amount of XXXIII (Equation 37). Trace amounts of LVI were also present. Thus reaction of IL with magnesium yields the same products as reaction with butyllithium. The
reaction with magnesium produces only traces of LVI because it will react with magnesium to yield XXXIII on acidification (Equation 32). XXXIII may also be formed from I on
standing (Equation 22).

A proposed mechanism for bromination of I to give IL is shown in Equation 38. Electrophilic attack by reagent bromine possibly leads to the bridged structure LVII which reacts with bromine and/or bromide ion to give IL. The overall reaction and its mechanism differ from that described by Whitlock and Sandvick (41) for bromination.

of o-bis(phenylethynyl)benzene (Equation 39) to give 3-bromo-1-(α-bromobenzylidene)-2-phenylindene by a falling domino process.

Treatment of I in benzene with excess gaseous hydrogen
bromide at room temperature results in formation of a white crystalline compound, m.p. 160-160.5°, in 65% yield which corresponds to C_{26}H_{18}Br_{2} (LVIII), an adduct of I with two equivalents of hydrogen bromide. Molecular weight determination by osmometry (494) agrees well with theory (490). The infrared spectrum of the adduct (Fig. 10) exhibits no acetylene absorption indicating that both acetylene groups have been affected by reaction with hydrogen bromide. The ultraviolet absorption spectrum in hexane [Fig. 18: 210 (ε38,200), 222 (43,500) and 279mμ (23,400)] is similar to that for alkyl substituted naphthalenes and shows no extended conjugation. The dihydrobromide adduct gives a complicated nuclear magnetic resonance spectrum [Fig. 24: δ6.93 (m,9H), 7.19 (s,1H), 7.30 (s,2H), 7.50 (m,4H) and 7.95 (m,2H)] consisting of 5 singlets and multiplets which lie totally in the aromatic region. The absence of benzylic protons eliminates structures LIX and LX.

![Structures LIX and LX](image)

The main signal for phenyl protons occurs at δ6.94 suggesting that the phenyl groups are shielded. It is thus appar-
ent that the phenyl groups are relatively close.

LVIII gives a negative alcoholic silver nitrate test at room temperature. It does lose hydrogen bromide when heated to melting and will give a positive silver nitrate test in hot alcohol. Irradiation of LVIII at 40° results in loss of 2 equivalents of hydrogen bromide to yield XXXIII (Equation 40).

\[ C_{26}H_{18}Br_2 \xrightarrow{h\nu} \xrightarrow{-2HBr} LVII \rightarrow XXXIII \]

Attempts to remove one equivalent of hydrogen bromide from the dihydrobromide by stirring with 1 or 2 equivalents of potassium t-butoxide in benzene were unsuccessful. At room temperature there was no reaction and at 50° LVIII was partially converted to XXXIII (Equation 40).

Neglecting geometrical isomers there are 4 possible basic structural types which can be derived from addition of 2 equivalents of hydrogen bromide to I. In the structures shown (LVIII a,b,c,d) all the phenyl groups are cis to the naphthalene rings. The phenyl groups in each structure can also be trans to the naphthalene ring giving 4 more
isomers. Placing one phenyl cis and the other trans gives rise to 2 more isomers for each of LVIII a and b and 1 more for each of LVIII c and d or a total of 14 geometrical isomers for LVIII.

In all of the isomers the substituted phenylethylene groups are twisted out of the plane of the naphthalene ring and are approximately perpendicular to it. This twisting can place the phenyl rings side by side which accounts for the shielding indicated in the nuclear magnetic resonance spectrum. Each of the isomers will explain the chemical and spectral data but the positions of the protons and bromines on the ethylene groups cannot be established on the basis of the available evidence.
Photolysis of 1-Nitro-8-(phenylethynyl)naphthalene.

Pfeiffer has reported (42) preparation of 2-phenyl-

(42) P. Pfeiffer, Ann., 411, 72 (1916).

isatogen by thermolysis or photolysis of (o-nitrophenyl) phenylacetylene in pyridine (Equation 41). In the present investigation, 1-nitro-8-(phenylethynyl)naphthalene (LXI) was prepared for possible conversion to a 6 membered analog of an isatogen (LXII, Equation 42). Diazotization of 1-

\[
\begin{align*}
\text{NO}_2 & \quad \text{hν or \[ \quad \text{C}_5\text{H}_5\text{N} \\
\text{C}={\text{C}}_{-\varnothing} & \quad \text{C}={\text{C}}_{-\varnothing}
\end{align*}
\]

nitro-8-naphthylamine in dilute hydrochloric acid and reaction of the diazonium salt with aqueous potassium iodide yields 1-iodo-8-nitronaphthalene (LXIII, 44\%, Equation 43). LXIII and (phenylethynyl)copper were stirred in pyridine for 24 hours to give LXI in low yield. LXI was
identified by its elemental analysis and infrared absorption (Fig. 3): 4.46 (C=C) and 6.55 and 7.36 \( \gamma \) (NO\(_2\)).

Irradiation of LXI in pyridine at 40° for 24 hours did not give the expected product (LXII). The starting material was recovered nearly quantitatively along with a small amount of intractable material. Irradiation of LXI in refluxing pyridine for 7 hours gave the same results except that more tar was produced. The infrared absorption of the intractable product showed no evidence for a carbonyl function which would be expected for LXII.

**Thermolysis of Dilithium Acenaphthenquinone bis-p-tosylhydrazone.**

Salts of \( p \)-tosylhydrazones can be thermolyzed to diazo compounds which can frequently be isolated (43). Acenaph-

---

(44) W. J. Link, Ph. D. Dissertation, The Ohio State University, 1960.

diazo compound \((\text{LXV})\) could give acenaphthyne which could dimerize to \(7,8,15,16\text{-tetradecahydrocyclodeca [1,2,3d,e:6,7,8d,e}^*] \text{dinaphthalene (LXVI, Equation 44). LXIV in dry tetrahydrofuran was treated with a 15\% excess of 2 equivalents of \(\text{n-butyllithium to yield the bright yellow dili-thium salt (LXVII, 91\%, Equation 45). The infrared spect-

\[
\begin{align*}
\text{LXIV} & \xrightarrow{2 \text{ BuLi}} \text{LXVII} \\
\end{align*}
\]

rum of the salt (Fig. 12) showed that N-H absorption had disappeared. The salt contained some residual tetrahydrofuran which could be removed by heating to 135\(^\circ\) (0.5mm.).
At 137-138° (0.5 mm.) the salt decomposed but no volatile products were obtained. Thin layer chromatography of the involatile product revealed the presence of acenaphthenequinone; the major product was an unidentifiable tar (45).

(45) K. Rasheed, Tetrahedron, 22, 2957 (1966) describes attempts to form acenaphthyne by oxidation of acenaphthenequinone-bis-hydrazone with mercuric oxide and manganese dioxide. The only identifiable product is acenaphthylene in low yield.

Preparation and isolation of bis-diazoacenaphthenequinone (LXV) appears to be impossible under the conditions employed to decompose the dilithium salt. The presence of acenaphthenequinone in the reaction product indicates, however, that acenaphthyne may have been formed and reacted with oxygen in the system (Equation 46).

\[
\text{LXV} \xrightarrow{-2N_2} \quad \text{O}_2 \quad \xrightarrow{0} \quad \text{product}
\]
ADDENDUM

During the present research Dessy and Kandil (13) reported that irradiation of 2,2'-bis(phenylethynyl)biphenyl (XIII) gives a light yellow isomeric product (LXVIII), m.p. 235-236°. The product was believed to be a tetrahedrane (XIV) or a cyclobutadiene (XV) (Equation 10).

XIII and I are analogous compounds in that they have interacting phenylethynyl groups; the acetylene groups are approximately parallel in I and are crossed in XIII. It is reasonable, however, to expect that the same mechanism is involved for photolysis of I and XIII. Extension of the mechanism for photolysis of I to photolysis of XIII led to the prediction in July, 1966, that 9-phenyldibenz[a,c]-anthracene (LXIX), not XIV or XV, is the product (Equation 46).

Previously, Bergmann and Berlin had independently synthesized LXIX (62), white, m.p. 227°. No ultraviolet absorption data was reported. However, ultraviolet data for the parent, dibenz[a,c]anthracene [241 (ε37,100), 248 (41,600), 265 (53,600), 275 (102,000), 286 (107,000), 321

(7,750) and 333 m\(\mu\) (6,300)] (63) are in good agreement with


those reported for LXVIII: 242 (\(\epsilon_{26,500}\)), 250 (27,300), 262 (27,800), 281 (51,900), 291 (64,600), 328 (5,700) and 343 m\(\mu\) (5,100). The absorption maxima for LXVIII are at longer wavelengths than those for dibenz[\(a,c\)]anthracene.

The 9-phenyl group is expected to move the absorption maxima to longer wavelengths in this manner. Thus it is
concluded that LXVIII and LXIX are identical.

After this dissertation had been completed and approved, White and Sieber reported that irradiation of XIII indeed yields LAIX, 80%, m.p. 230-231° (64) which is identical with LAVIII. Thus the earlier independent prediction of the present author has been confirmed.

EXPERIMENTAL

General Information

**Melting Points.** Melting points were determined with a Thomas Hoover capillary melting point apparatus and are uncorrected.

**Elemental Analyses.** Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee and Micro-Analysis, Inc., Wilmington, Delaware.

**Infrared Spectra.** Infrared spectra were obtained with a Perkin-Elmer 137 Sodium Chloride Spectrophotometer. Spectra of solid samples were run in potassium bromide wafers or in solution in carbon tetrachloride or chloroform.

**Ultraviolet Spectra.** Ultraviolet spectra were measured on a Perkin-Elmer 202 Spectrophotometer. The solvent used was 95% ethanol.

**Nuclear Magnetic Resonance Spectra.** Nuclear magnetic resonance spectra were determined with a Varian A-60 instrument using carbon tetrachloride or deuterated chloroform as the solvent. Tetramethylsilane was used as an internal standard.

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Molecular Weights. Molecular weights were determined with a Microlab, Inc. vapor pressure osmometer using chloroform as the solvent.

Chromatography. Column chromatography was frequently used in the separation and purification of products. The alumina was Woelm Alumina – activity grade 1. The silica gel was Baker Analyzed reagent grade.

Thin layer plates, used for the examination of reaction mixtures, were prepared with Silica Gel G (Acc. to Stahl). A slurry of silica gel (10 parts by weight) in water (30 parts) and methanol (1 part) was sprayed on carefully cleaned microscope slides. The slides were ready for use after drying in an oven. The slides were developed in a wide mouth bottle containing iodine crystals. In many cases an ultraviolet lamp was used to locate the spots making development with iodine vapors unnecessary.

Solvents. Solvents used for chromatography and recrystallization were dried and purified by passing them through a short column of neutral alumina.
Preparation of Intermediates

Phenyl azide. Diazotization of phenyl hydrazine yielded phenyl azide (46).


Phenyl isocyanide. Using the procedure for o-tolyl isocyanide, phenyl isocyanide was prepared from formanilide (47).


Formanilide. Aniline reacted with formic acid to yield formanilide (48).

(48) G. Tobias, Ber., 15, 2443 (1882).

Acyclone. Condensation of dibenzyl ketone withacenaphthenequinone yielded acyclone (49).


8-Nitro-1-naphthylamine. Nitration of 1-naphthylamine yielded 8-nitro-1-naphthylamine (50).

p-Toluenesulfonylhydrazine. p-Toluenesulfonyl chloride reacted with hydrazine to give p-toluenesulfonylhydrazine (51).

Experiments

Preparation of 1-Iodo-8-naphthoic Acid.

1,8-Naphthalic anhydride (160 g., 0.906 mole) and sodium hydroxide (110 g., 2.74 moles) were dissolved in water (3 l.) and filtered while hot. Red mercuric oxide (294 g., 1.356 moles) in water (800 ml.) and glacial acetic acid (522 ml.) and then additional glacial acetic acid (240 ml.) were added to the alkaline solution of 1,8-naphthalic anhydride. The stirred mixture was refluxed for 96 hours, cooled to room temperature and filtered. The tan solid produced, after being washed with water, was dissolved in aqueous sodium hydroxide (72 g., 1.8 moles in 2 l. of water) and filtered while hot. A solution of iodine (230 g., 0.91 mole) and sodium hydroxide (76.8 g., 1.92 moles) in water (1 l.) was added to the filtrate and the mixture heated to boiling. Sodium thiosulfate (400 g., 2.53 moles) was added to the cooled, stirred solution followed by concentrated hydrochloric acid (424 ml.). The resulting solid contained large amounts of mercuric oxide and was extracted twice with aqueous sodium bicarbonate. Treatment of the combined extracts with concentrated hydrochloric acid gave 1-iodo-8-naphthoic acid (126 g., 0.423 mole, 46.5%), m.p. 158-161°, lit. (52) 164-165°.

(52) A. Corbellini and V. Fossati, Rend. ist. lombardo sci., 69, 264 (1936).
The product was used without further purification. A small amount of the acid, recrystallized from toluene, melted at 163-165°.

Preparation of 1-Iodo-6-naphthylamine Hydrochloride.

**Method A.**

Sodium azide \((2.5 \text{ g.}, 0.0385 \text{ mole})\) was added to a stirred suspension of powdered 1-iodo-6-naphthoic acid \((10 \text{ g.}, 0.0334 \text{ mole})\) in concentrated sulfuric acid \((160 \text{ ml.})\) and water \((40 \text{ ml.})\) at 5°. The system was closed to the atmosphere and attached to a gas collection apparatus. The stirred mixture was allowed to warm to room temperature; the gas collected \((1440 \text{ ml.}, 1355 \text{ ml. at standard conditions})\) indicated 89% completion of the reaction. The mixture was poured onto ice \((500 \text{ g.})\) and made basic with concentrated aqueous sodium hydroxide. The aqueous solution was extracted with ether until the extracts were colorless. The combined extracts were washed with water, dried over potassium carbonate and filtered. Treatment of the filtrate with gaseous hydrogen chloride gave a fluffy tan precipitate which on filtration and drying yielded 1-iodo-6-naphthylamine hydrochloride \((8.65 \text{ g.}, 0.0283 \text{ mole, 85%}), \text{ m.p. 192-195°, lit. (17) 186-189°.}\)

**Method B (17).**

1,8-Naphthalenediamine \((15 \text{ g.}, 0.095 \text{ mole})\) was dissolved in warm water \((200 \text{ ml.})\) and concentrated hydro-
chloric acid (36 ml.). The filtered solution was added to water (1500 ml.) and ice (300 g.) and cooled to 5°. Sodium nitrite (6.7 g., 0.097 mole) in water (50 ml.) was added dropwise at 0-5°. After standing 2 hours the solid was filtered with suction and added to hydriodic acid (113 g., 47%). Copper bronze (1 g.) was added and the mixture heated on a steam bath until nitrogen evolution ceased. The black solid was filtered, dried and powdered, and treated with sufficient cold 10% sodium hydroxide to make the mixture basic. The black solid was filtered, dried and extracted with ether. The combined ether extracts were dried over potassium carbonate and treated with gaseous hydrogen chloride to give a fluffy tan precipitate. Filtering and drying yielded 1-iodo-o-naphthylamine hydrochloride (6.75 g., 0.022 mole, 23%), m.p. 188-189°.

Diazotization of a more concentrated solution (15 g. of 1,8-naphthalenediamine in 1 l. of water and 36 ml. of concentrated hydrochloric acid) gave 7.75 g. of iodoamine (26.4%, yield). Replacement of hydriodic acid with aqueous potassium iodide lowered the yield to 11%. An attempt to decompose the diazonium salt under reduced pressure at room temperature resulted in a yield of only 3.5%.

Preparation of Iodonaphthalenes.

1,8-Diiodonaphthalene.

Method A.

A solution of 1-iodo-o-naphthylamine hydrochloride
(16.8 g., 0.0552 mole) in water (150 ml.) and concentrated hydrochloric acid (15 ml.) was cooled to 0°. Sodium nitrite (3.87 g., 0.0561 mole) in water (50 ml.) was added dropwise in 30 minutes to the stirred solution at 0-5°. After stirring 1 hour at 0-5°, the mixture was filtered directly into a stirred solution of potassium iodide (150 g., 0.9 mole) in water (200 ml.). After the mixture had been stirred under reduced pressure overnight, the solid formed was filtered and dried. Extraction of the dry solid with Skelly Solve B have a dark red solution which was concentrated and chromatographed on basic alumina. The yellow solid obtained was crystallized from methanol-Skelly Solve B to yield 1,6-diiodonaphthalene (14.0 g., 0.0368 mole, 67%), m.p. 109-110°, lit. (15) 109°. Anal. Calcd. for C_{10}H_{5}I_{2}: C, 31.61; H, 1.59

Found: C, 31.63; H, 1.81

Method B (53).

(53) This method was adapted from H. H. Hodgson and J. S. Whitehurst, J. Chem. Soc., 60 (1947).

A solution of 1,6-naphthalenediamine (54) (6.0 g.,

(54) Commercial 1,6-naphthalenediamine, m.p. 58-61°, was powdered and extracted with 30% ethanol at room temperature. After filtering the mixture to remove insoluble material, the ethanol was removed under reduced pressure. Filtering and drying yielded light pink needles of the diamine, m.p. 64-65°, lit. (55) 66°. Repeated extraction gave about 60% recovery.
0.036 mole) in glacial acetic acid (50 ml.) was added drop-wise to a stirred solution of sodium nitrite (6.0 g., 0.087 mole) in concentrated sulfuric acid (50 ml.) in 45 minutes at -8 to -4°. After 30 minutes the dark viscous mixture was poured onto ice (100 g.) and urea (1 g.) was added to destroy excess nitrous acid. The black mixture was filtered into a stirred solution of potassium iodide (200 g., 1.2 moles) in water (200 ml.) and heated with steam until nitrogen was no longer evolved. After cooling, the solid formed was filtered, dried, powdered and extracted with ether. The ether extracts were dried over magnesium sulfate and concentrated to give a black tar. The residue was taken up in warm carbon tetrachloride and chromatographed on neutral alumina to give a yellow-brown oily solid (4.6 g.). Recrystallization from Skelly Solve B yielded light yellow crystals of 1,8-diiodonaphthalene (3.45 g., 0.0091 mole, 24%), m.p. 107-108°.

Method C (56).

(56) This method is adapted from the procedure of R. E. Dessy and S. A. Kandil, J. Org. Chem., 30, 3859, (1965) for preparing 1-bromo-8-iodonaphthalene from 1-bromo-8-naphthoic acid.

A stirred solution of 1-iodo-8-naphthoic acid (10.0 g.,
0.0336 mole), red mercuric oxide (10.0 g., 0.0461 mole) and iodine (10.0 g., 0.0394 mole) in cyclohexane (250 ml.) was protected from light and refluxed overnight. After cooling the solids were filtered and the solvent evaporated. The residue was dissolved in ether and washed with aqueous sodium bisulfite and then aqueous sodium bicarbonate until carbon dioxide was no longer evolved. The ether solution was dried with anhydrous magnesium sulfate, decolorized with charcoal and evaporated. The residue (4.16 g.) was dissolved in Skelly Solve B and chromatographed on basic alumina. Evaporation of the solvent yielded 1,8-diiodonaphthalene (1.9 g., 0.005 mole, 14.9%), m.p. 108-109°.

Method D (57).

(57) This method of diazotization is adapted from L. Friedman and F. M. Logullo, J. Am. Chem. Soc., 85, 1549 (1963).

1,8-Naphthalenediamine (5.0 g., 0.0316 mole) in tetrahydrofuran (150 ml.) containing a catalytic amount of trichloroacetic acid (0.1 g.) was treated with isopentyl nitrite (7.4 g., 0.0632 mole) at 0°. Addition of the mixture to potassium iodide (15.0 g., 0.0905 mole) in methanol (200 ml.) and water (10 ml.) gave a dark brown oil. Chromatography and repeated attempts at crystallization failed to yield the desired product. It is apparent that 1,8-diamino-
naphthalene cannot be diazotized under these conditions.

1,5-Diiodonaphthalene (53).

1,5-Naphthalenediamine (12.0 g., 0.076 mole) in glacial acetic acid (100 ml.) was added dropwise to a stirred solution of sodium nitrite (12.0 g., 0.174 mole) in concentrated sulfuric acid (100 ml.) at 0-5°. After stirring 15 minutes, the mixture was poured onto ice (100 g.) and urea (1 g.) was added to destroy excess nitrous acid. The mixture was added to potassium iodide (400 g., 2.4 moles) in water (400 ml.) and stirred overnight at reduced pressure. The solid was filtered, dried and extracted with carbon tetrachloride. The combined extracts were decolorized with charcoal and concentrated. Chromatography on neutral alumina yielded pale yellow needles of 1,5-diiodonaphthalene (20.6 g., 0.542 mole, 71%), m.p. 148.5-149°, lit. (15) 147°.

Anal. Calcd. for C_{10}H_{6}I_{2}: C, 31.61; H, 1.59

Found: C, 31.69; H, 1.60

1-Iodo-8-nitronaphthalene.

Sodium nitrite (0.85 g., 0.0123 mole) in water (50 ml.) was added dropwise at 0° to a stirred solution of 1-nitro-8-naphthylamine (2.3 g., 0.0122 mole) in 10% hydrochloric acid (50 ml.). After stirring 1 hour the mixture was filtered with suction into a stirred solution of potassium iodide (50 g., 0.3 mole) in water (100 ml.). The solid formed was filtered, dried and extracted with Skelly Solve
B. Chromatography on neutral alumina yielded 1-iodo-8-nitronaphthalene (1.6 g., 0.0053 mole, 44%), m.p. 78-80°, lit. (58) 80°.


Preparation of Copper Acetylides.

Attempts to prepare copper salts of mono-substituted acetylenes by adapting the procedure of Stephens and Castro (14) met with varying success.

(Phenylethynyl)copper.

Cuprous chloride (54.4 g., 0.55 mole) and ammonium carbonate (70.0 g., 0.73 mole) were dissolved in water (200 ml.). Concentrated ammonium hydroxide was added to dissolve the white precipitate which formed on the surface. The dark blue solution was stirred rapidly while phenylacetylene (25.5 g., 0.25 mole) in 95% ethanol (75 ml.) was added. After stirring 15 minutes the yellow-green product was filtered and the large lumps broken up in a mortar containing 5% ammonium hydroxide. The solid was filtered and washed with 5% ammonium hydroxide until the washings were colorless and then successively with water, absolute ethanol and ether. Air drying yielded (phenylethynyl)-copper (30.3 g., 0.18 mole, 74%) as a bright yellow amorphous solid.
[(Methoxycarbonyl)ethynyl]copper.
Methyl propiolate (3.61 g., 0.043 mole) when similarly treated with ammoniacal cuprous chloride (4.68 g., 0.0453 mole) yielded [(methoxycarbonyl)ethynyl]copper (5.0 g., 0.0341 mole, 79%) as an orange solid.

(Ethoxyethynyl)copper.
Ethoxyacetylene (3.33 g., 0.0475 mole) reacted with cuprous chloride (21.3 g., 0.215 mole) to yield dark orange (ethoxyethynyl)copper (4.0 g., 0.0302 mole, 63.6%). The yield was greatly enhanced by preparing the salt in a nitrogen atmosphere using solvents which had been boiled to expel oxygen and then cooled under nitrogen.

(3-Hydroxy-3-phenyl-1-propynyl)copper.
1-Phenyl-2-propyne-1-ol (10.0 g., 0.0757 mole) when treated with cuprous chloride (37.5 g., 0.379 mole) gave a reddish brown solid (11.54 g., 0.0594 mole, 78.5%) which turned black on standing. Analysis for carbon was 11% low suggesting the presence of cuprous oxide.

(3-Hydroxy-3-methyl-1-butynyl)copper.
2-Methyl-3-butyne-2-ol (1.0 g., 0.0119 mole) was treated with cuprous chloride (3.56 g., 0.036 mole) under nitrogen in oxygen free solvents. The red-brown solid (0.14 g., 0.00956 mole, 8%) turned black on standing. Evaporation of the ethanol and ether washings gave a light yellow solid. Recrystallization from Skelly Solve B yielded pure white needles of 2,7-dimethyl-3,5-octadiyne-
2,7-diol (0.81 g., 0.0046, 77%), m.p. 131-132°, lit. (19) 132-132.5°. Infrared absorption: 3.12 (-OH), 4.63 (-C=C-) and 7.25 and 7.36 μ [(CH₃)₂C].

Anal. Calcd. for C₁₀H₁₄O₂: C, 72.26; H, 8.49
Found: C, 72.19; H, 8.32

**Coupling Reactions of Iodonaphthalenes with Copper Acetylides.**

**1,8-Bis(phenylethynyl)naphthalene.**

(Phenylethynyl)copper (8.7 g., 0.0529 mole) and 1,8-diodonaphthalene (10.0 g., 0.0263 mole) were dissolved in dry pyridine (250 ml.) and protected from light. The system was purged with nitrogen and the mixture stirred at room temperature for 24 hours. Removal of the solvent under reduced pressure gave a tan solid which was stirred with ether (200 ml.) and filtered. The filtrate was evaporated and the residue dissolved in Skelly Solve B. Chromatography on basic alumina gave 1,8-bis(phenylethynyl)naphthalene (6.16 g., 0.0188 mole, 72%) as a light yellow solid. Several recrystallizations from Skelly Solve B gave nearly white crystals, m.p. 105-106°. Infrared absorption (Fig. 1): 4.48 μ (C=C); ultraviolet absorption (Fig. 13): 209 (ε 48,400), 243 (66,900), 265 (26,800) 344 (29,300) and 356 μ (26,800); nuclear magnetic resonance (Fig. 19): δ 7.20 (m, 12H) and 7.75 (m, 4H).
Anal. Calcd. for $C_{26}H_{16}$: C, 95.09; H, 4.91
mol. wt. 328

Found: C, 94.78; H, 4.85
mol. wt. 328

2,4,7-Trinitrofluorenone (192 mg., 0.61 mmole) and
1,8-bis(phenylethynyl)naphthalene (200 mg., 0.61 mmole)
were dissolved separately in warm benzene (15 ml.) and the
two hot solutions mixed (21). A dark red color appeared
immediately and cooling yielded red-brown needles. Recrys­
tallization from absolute ethanol gave the trinitrofluoren­
one complex as fine red-brown needles, m.p. 149-150°.

Anal. Calcd. for $C_{39}H_{21}N_3O_7$: C, 72.78; H, 3.29;
N, 6.53

Found: C, 72.59; H, 3.30;
N, 6.69

1,5-Bis(phenylethynyl)naphthalene.

Pure dry nitrogen was bubbled through a solution of
1,5-diodonaphthalene (5.0 g., 0.01315 mole) in dry pyridine
(100 ml.) and a solution of (phenylethynyl)copper (4.35 g.,
0.0265 mole) in dry pyridine (100 ml.) for 18 hours. The
mixtures were combined with a large syringe and stirred at
room temperature under nitrogen. After 2 days the copper
salt was still visible and the mixture was heated at 110°
for 12 hours. Most of the pyridine was removed under
reduced pressure and the residue extracted with ether. The
combined ether extracts were washed with dilute hydrochloric
acid and water and dried over magnesium sulfate. Concentration gave a brown oily solid which was dissolved in Skelly Solve B and chromatographed on silica gel. The first two fractions gave diphenylbutadiyne (1.99 g., 0.00985 mole; 75%) m.p. 85-86°, lit. (59) 88°. The next five fractions gave a white to light yellow solid which produced a blue fluorescence in ultraviolet light. Decolorization and recrystallization from Skelly Solve B yielded white crystals of 1,5-bis(phenylethynyl)naphthalene (0.42 g., 0.00128 mole, 9.8%), m.p. 198-199°. Infrared absorption (Fig. 2): 4.47 μ (C≡C); ultraviolet absorption (Fig. 14): 207 (ε 46,600), 240 (70,400), 263 (44,000), 341 (33,200) and 355 μ (26,900); nuclear magnetic resonance (Fig. 20): δ 7.53 (m, 14H) and δ 8.47 (d, 2H).

Anal. Calcd. for C_{26}H_{16}: C, 95.09; H, 4.91
mol. wt. 328

Found: C, 94.91; H, 5.02
mol. wt. 337

Reaction of the product with a molecular equivalent of 2,4,7-trinitrofluorenone in hot benzene (21) gave a trinitrofluorenone complex as fine red-brown needles, m.p. 180-181° after two recrystallizations from absolute ethanol. The analysis indicated that the complex was composed of 1 molecule of 1,5-bis(phenylethynyl)naphthalene and 2 mole-
cules of trinitrofluorenone.

**Anal.** Calcd. for $C_{52}H_{26}N_6O_{14}$: C, 65.14; H, 2.73; N, 8.76

Found: C, 64.79; H, 2.59; N, 8.40

1-Nitro-8-(phenylethynyl)naphthalene.

1-Iodo-8-nitronaphthalene (1.6 g., 0.00535 mole) and (phenylethynyl)copper (0.88 g., 0.00535 mole) were stirred in dry pyridine (100 ml.) under nitrogen for 24 hours. The solvent was removed under reduced pressure and the residue extracted with ether. Concentration gave an oil which was crystallized twice from methanol to yield a light brown solid, m.p. 118-120°. The solid was dissolved in carbon tetrachloride and decolorized with silica gel. Recrystallization from 95% ethanol gave yellow crystals of 1-nitro-8-(phenylethynyl)naphthalene (0.24 g., 0.000915 mole, 17%), m.p. 120.5-121.5°. Infrared absorption (Fig. 3): 4.46 (C=O) and 6.55 and 7.36 μ (NO$_2$).

**Anal.** Calcd. for $C_{16}H_{11}NO_2$: C, 79.11; H, 4.06; N, 5.13

Found: C, 79.16; H, 4.19; N, 5.13

Attempted Preparation of 1,8-Bis[(methoxycarbonyl)ethynyl]naphthalene.

A solution of 1,8-diodonaphthalene (2.15 g., 0.00565 mole) and [(methoxycarbonyl)ethynyl]copper (1.66 g., 0.0113 mole) in dry pyridine (100 ml.) was stirred under nitrogen at room temperature for 22 hours. Removal of the solvent and extraction of the solid residue with ether gave only 1,8-diodonaphthalene. Recovery was nearly quantitative.
When the reaction mixture was refluxed for 20 hours at 120° and worked up, a brown oil was obtained. Chromatography on neutral alumina with Skelly Solve B gave a quantitative recovery of 1,8-diiodonaphthalene and then a yellow oily solid (25 mg.). The infrared spectrum of the solid showed characteristic absorption for carbonyl and acetylene groups but no evidence for aromaticity. It is possible that this product is dimethyl 2,4-hexadiyne-1,6-dicarboxylate formed by oxidative coupling of the copper salt. This compound is not reported in the literature and investigation of its identity was terminated.

**Attempted Preparation of 1,8-Bis(ethoxyethynyl)naphthalene.**

A. (Ethoxyethynyl)copper (1.05 g., 0.0079 mole) and 1,8-diiodonaphthalene (1.5 g., 0.00395 mole) were stirred in dry pyridine (80 ml.) under nitrogen for 5 days at room temperature. The usual workup yielded 1,8-diiodonaphthalene nearly quantitatively.

B. Nitrogen was bubbled through dry pyridine (100 ml.) to remove oxygen. Cuprous chloride (1.8 g., 0.018 mole) and ammonium carbonate (0.9 g., 0.0091 mole) were introduced and the mixture stirred overnight under nitrogen. Ethoxyacetylene (1.25 g., 0.018 mole in hexane) was added and the solution stirred for 5 hours during which time the dark orange copper salt appeared. 1,8-Diiodonaphthalene (2.5 g., 0.066 mole) was added and the mixture refluxed at 125° for 24
hours. Removal of the pyridine gave an oily solid which was stirred with carbon tetrachloride and filtered. Chromatography of the concentrated filtrate on neutral alumina gave two bands. Removal of the first band with carbon tetrachloride yielded white plates of 1,8-dichloronaphthalene (0.8 g., 0.041 mole, 62%), m.p. 87-88°, lit. (60)


88.5-89°. The infrared spectrum of 1,8-dichloronaphthalene (Fig. 4) is similar to that of 1,8-diiodonaphthalene (Fig. 5).

**Anal.** Calcd. for C_{10}H_{6}Cl_{2}: C, 60.95; H, 3.07

mol. wt. 197

Found: C, 60.93; H, 3.43

mol. wt. 205

The second band was removed with ether to give a yellow oil. Crystallization from carbon tetrachloride yielded yellow needles (0.25 g.), m.p. 146-147°. The infrared spectrum showed strong bonds at 3.24, 6.03, 6.11, 6.42, 6.96, 7.64, 8.45, 9.44, 12.65, 13.77 and 14.68μ. Nuclear magnetic resonance occurred at 5 1.47 (t,3H), 4.12 (q,2H), 6.1 (s,1H), 6.7 (m,1H) and 7.2 (m,2H): The compound gave a positive test with alcoholic silver nitrate. The mass spectrogram showed no peaks higher than 315.
Anal.  Found :  C, 43.64, 43.27, 42.77  
H, 4.65, 3.33, 3.18  
I, 36.80  
mol. wt. 366,351

**Attempted Preparation of 1,8-Bis(3-hydroxy-3-methyl-1-butynyl)naphthalene.**

Cuprous chloride (0.52 g., 0.00526 mole) in pyridine (50 ml.) was stirred under nitrogen until dissolved. A solution of 2-methyl-3-butyn-2-ol (0.44 g., 0.00526 mole) in ethanol (15 ml.) was added dropwise. After 90 minutes, 1,8-diiodonaphthalene (1 g., 0.00263 mole) in pyridine (20 ml.) was added and the mixture stirred in the dark for 18 hours at room temperature. Removal of the solvent gave a green residue which was extracted with ether. Concentration gave a brown oil which yielded crystals on standing. Recrystallization from Skelly Solve B yielded fine white needles of 2,7-dimethyl-3,5-octadiyne-2,7-diol (0.35 g., 0.0021 mole, 79%), m.p. 131-132°. The uncrystallized portion of the product was a mixture of 1,8-diiodonaphthalene and 2,7-dimethyl-3,5-octadiyne-2,7-diol.

**Attempted Coupling of Aryl Bromides with (Phenylethynyl)copper.**

A mixture of bromobenzene (4.71 g., 0.03 mole) and (phenylethynyl)copper (5.0 g., 0.03 mole) in dry pyridine (100 ml.) was purged with nitrogen. After refluxing the mixture for 120 hours under nitrogen, its color changed
from bright yellow to reddish brown. The cooled mixture was diluted with water (300 ml.) and filtered to give unreacted (phenylethynyl)copper (1.2 g., 0.0072 mole, 24%). The filtrate was extracted with ether and the combined extracts washed with 10% hydrochloric acid and water, dried and decolorized. Concentration followed by dilution with ethanol and cooling yielded colorless needles of diphenylbutadiyne, m.p. 86.5-87°, lit. (59) 88°. Further concentration and cooling of the ethanol solution gave two additional crops of crystals for a total yield of 1.63 g. (53%). The residue, after removal of the ethanol, was shown to be impure bromobenzene by its infrared spectrum.

Identical amounts of the same starting materials were refluxed under nitrogen in N,N-dimethylformamide (200 ml.) for 20 hours and in N-methylpyrrolidone (200 ml.) for 4 hours. Both mixtures took on a reddish brown color and when worked up gave diphenylbutadiyne (0.68 g., 22% and 0.9 g., 29% respectively). Bromobenzene and (phenylethynyl)copper were also recovered in both cases.

In a similar experiment, 1-bromo-naphthalene (6.3 g., 0.03 mole) and (phenylethynyl)copper (5.0 g., 0.03 mole) were refluxed under nitrogen in pyridine (175 ml.) for 48 hours. Dilution with water and filtering gave nearly quantitative recovery of (phenylethynyl)copper.
Reactions of 1,8-Bis(phenylethynyl)naphthalene.

Photolysis.

A solution of 1,8-bis(phenylethynyl)naphthalene (1 g., 0.00305 mole) in Skelly Solve B (300 ml.) was placed in a quartz tube and irradiated externally at reflux temperature for 24 hours. The light source was a medium pressure mercury vapor lamp. A small amount of insoluble tar formed on the sides of the tube. The light brown solution was concentrated and chromatographed on neutral alumina with Skelly Solve B. Crystallization yielded pale yellow cubic crystals of 7-phenylbenzo[k]fluoranthene (0.59 g., 0.0018 mole, 59%) m.p. 162-163°. In solution, the product gave a blue fluorescence in ultraviolet light. It was insoluble in concentrated sulfuric acid.

External irradiation at room temperature gave the same product but much more slowly. Thus 1,8-bis(phenylethynyl)naphthalene (2.0 g., 0.0061 mole) after 24 hours gave a light yellow mixture of starting material and 7-phenylbenzo[k]fluoranthene (1.6 g., m.p. 93-98°). Further irradiation at room temperature for 24 hours yielded impure 7-phenylbenzo[k]fluoranthene (1.23 g., 0.00375 mole, 61.5%), m.p. 154-156°. In subsequent experiments it was found that heating 1,8-bis(phenylethynyl)naphthalene (2.0 g., 0.0061 mole) in diglyme at 130° for 24 hours in the dark yielded 7-phenylbenzo[k]fluoranthene (1.59 g., 0.00485 mole, 79.5%), m.p. 166-167°.
The infrared absorption of the fluoranthene is shown in Fig. 6. Ultraviolet absorption (Fig. 15): 216 (ε31,400), 250 (46,400), 270 (15,300), 286 (13,000), 298 (32,800), 309 (48,100), 364 (3,300) and 384 μμ (8,700); nuclear magnetic resonance (Fig. 21): δ6.53 (d,1H), 7.51 (m,14H) and 8.17 (s,1H).

Anal. Calcd. for C_{26}H_{16}: C, 95.09; H, 4.91
mol. wt. 328
Found: C, 94.94; H, 5.05
mol. wt. 312

7-Phenylbenzo[k]fluoranthene (0.328 g., 0.001 mole) in 95% ethanol (250 ml.) was shaken with 10% palladium on charcoal under hydrogen (18 p.s.i.) for 6 hours. Starting material was recovered quantitatively. The experiment was repeated with platinum oxide under hydrogen (20 p.s.i.) for 24 hours with the same results.

Powdered 7-phenylbenzo[k]fluoranthene (0.328 g., 0.001 mole) and potassium permanganate (0.632 g., 0.004 mole) were refluxed in water (50 ml.) and 10% aqueous sodium hydroxide (10 ml.) for 24 hours. Starting material was recovered quantitatively. Refluxing the same materials under acidic conditions for 24 hours gave the same results.

Reaction of the product with a molecular equivalent of 2,4,7-trinitrofluorenone in hot benzene (21) gave the trinitrofluorenone complex as fine maroon needles, m.p. 184–185° after two recrystallizations from absolute ethanol.
Reaction with Iron Pentacarbonyl.

1,8-Bis(phenylethynyl)naphthalene (1.0 g., 0.00305 mole) was stirred in iron pentacarbonyl (15 ml., 21.8 g., 0.111 mole) for 48 hours at room temperature. The solid was filtered, dissolved in acetone and filtered of insoluble material. Concentration gave light green prisms of impure 1,8-bis(phenylethynyl)naphthalene (1 g.) m.p. 160-162°.

Iron pentacarbonyl (0.45 g., 0.0023 mole) and 1,8-bis-(phenylethynyl)naphthalene (0.5 g., 0.00152 mole) were refluxed in diglyme (40 ml.) for 16 hours. Removal of the solvent gave a dark oil (0.55 g.) which was chromatographed on silica gel to remove tars and then on neutral alumina to yield 7-phenylbenzo[k]fluoranthene (0.4 g., 0.00122 mole, 80%) and a black oil (0.06 g.).

Iron pentacarbonyl (1.8 g., 0.0092 mole), 1,8-bis-(phenylethynyl)naphthalene (2.0 g., 0.0061 mole) and diglyme (40 ml.) were placed in a steel bomb and heated in an oil bath at 130° for 24 hours. The mixture was cooled and the solvent removed at 28-30° (2 mm.). Extraction of the residue with Skelly Solve B and chromatography with neutral alumina yielded 7-phenylbenzo[k]fluoranthene (1.59 g., 0.00485 mole, 79.5%), m.p. 166-167°. Recrystallization
of the insoluble portion of the residue from acetone yielded a light tan solid identified as acecycloneiron tricarbonyl (150 mg., 0.3 mmole, 5%), m.p. 204-205°.
Infrared absorption (Fig. 7): 4.87, 5.02 and 5.05 \( \mu \) \([\text{Fe(CO)}_3]\) and 6.13 \( \mu \) (C=O).

**Anal.** Calcd. for \( C_{30}H_{16}FeO_4 \): C, 72.60; H, 3.25; Fe 11.25

mol. wt 496

Found: C, 71.21 and 71.27;

H, 3.80 and 3.89;

Fe, 8.86 and 9.16

mol. wt. 492

On standing in air, the compound turned black. This residue was chromatographed on neutral alumina with carbon tetrachloride to yield blue-black crystals of acecyclone. Identification was confirmed by comparison with an authentic sample on thin layer chromatography and mixed melting point. The infrared absorption spectrum could be superimposed on a spectrum of an authentic sample.

**Attempted Additions to 1,8-Bis(phenylethynyl)naphthalene.**

**Dimethyl Acetylenedicarboxylate.**

1,8-Bis(phenylethynyl)naphthalene (1.0 g., 0.00305 mole) and dimethyl acetylenedicarboxylate (4.35 g., 0.0305 mole) were dissolved in benzene (30 ml.). Stirring at room temperature for 14 hours produced no reaction. Irradiation for 8 hours at room temperature or refluxing for 6 hours
at 80-85° yielded only starting materials and small amounts of 7-phenylbenzo[k]fluoranthene detectable by its blue fluorescence in ultraviolet light.

Identical amounts of the starting materials were placed in a steel bomb with benzene (50 ml.) and heated at 130° for 24 hours. The solvent and excess dimethyl acetylene dikarbonylate were removed under vacuum. Chromatography of the residue on neutral alumina with Skelly Solve B yielded 7-phenylbenzo[k]fluoranthene (0.7 g., 0.00214 mole, 70%).

Phenyl Azide.

A solution of phenyl azide (3.63 g., 0.0305 mole) and 1,8-bis(phenylethynyl)naphthalene (1.0 g., 0.00305 mole) in Skelly Solve B (300 ml.) was irradiated in a quartz tube at room temperature for 5 hours. Removal of the solvent gave a brown oil which was chromatographed on silica gel with benzene to yield a trace of 7-phenylbenzo[k]fluoranthene and 1,8-bis(phenylethynyl)naphthalene (0.9 g., 0.00274 mole, 90%). Irradiation of the same ratio of starting materials in refluxing Skelly Solve B for 24 hours yielded 7-phenylbenzo[k]fluoranthene (16%) and 1,8-bis(phenylethynyl)naphthalene (75%).

Heating an identical mixture in diglyme (40 ml.) in a steel bomb for 24 hours at 125° yielded 93% of 7-phenylbenzo[k]fluoranthene. Examination with thin layer chromatography gave no evidence for the formation of additional
products.

**Phenyl Isocyanide.**

Phenyl isocyanide (7.0 g., 0.068 mole) and 1,8-bis-(phenylethynyl)naphthalene (2.0 g., 0.0061 mole) in Skelly Solve B (300 ml.) were irradiated in a quartz tube for 24 hours at room temperature. Removal of the solvent and distillation gave phenyl isocyanide (4.5 g., 0.0436 mole, 64%), m.p. 41-43° (6 mm.). Analysis with thin layer chromatography showed that the residue was mainly 1,8-bis-(phenylethynyl)naphthalene with small amounts of phenyl isocyanide, 7-phenylbenzo[k]fluoranthene and tar.

An identical mixture in diethyl Carbitol (100 ml.) was heated in a steel bomb at 120-130° for 24 hours. The mixture was poured into water and extracted with Skelly Solve B. Removal of the solvent and distillation gave a mixture of phenyl isocyanide and diethyl Carbitol. Analysis with thin layer chromatography showed the residue was mainly 7-phenylbenzo[k]fluoranthene along with small amounts of 1,8-bis(phenylethynyl)naphthalene, solvent and tar.

**Sulfur.**

1,8-Bis(phenylethynyl)naphthalene (1.0 g., 0.00305 mole) and sulfur (0.195 g., 0.0061 mole) were heated under nitrogen for 1 hour at 140-145°. The reaction mixture was dissolved in benzene, filtered and examined with thin layer chromatography. 7-Phenylbenzo[k]fluoranthene in good yield and tar were the only products other than starting materials.
**Reaction with Aluminum Chloride.**

A catalytic amount (70 mg.) of aluminum chloride was added to a solution of 1,8-bis(phenylethynyl)naphthalene (250 mg., 0.76 mmole) in ethylene dichloride (25 ml.). The solution immediately became dark brown. After stirring one hour, the mixture was filtered and concentrated to give a dark red oil. Chromatography on silica gel with Skelly Solve B yielded 7-phenylbenzo[k]fluoranthene (40 mg., 0.12 mmole, 16%), a red oil (150 mg.) and a dark green solid (10 mg.). Due to the lack of meaningful spectral data and the small amount of material available, the investigation of these unknowns was terminated.

**Bromination.**

A solution of 1,8-bis(phenylethynyl)naphthalene (3.0 g., 0.00915 mole) in chloroform (100 ml.) was stirred at room temperature while bromine (1.46 g., 0.00915 mole) in chloroform (25 ml.) was added in 20 minutes. The solution turned dark red immediately; stirring was continued for 15 hours. Concentration gave a dark red oil which was taken up in Skelly Solve B. On standing a dark solid formed which was dissolved in carbon tetrachloride and chromatographed on silica gel to give a light brown solid. Several recrystallizations from 95% ethanol gave white crystals of 1,2-bis-(α-bromobenzylidene)acenaphthene (1.5 g., 0.0031 mole, 34%), m.p. 148-149°. Its infrared absorption (Fig. 8) is similar to that of 1,8-bis(phenylethynyl)naphthalene (Fig. 1) except
that acetylene absorption is absent. Ultraviolet absorption (Fig. 17): 210 (ε 41,300), 239 (65,900) and 328 mλ (13,000); nuclear magnetic resonance (Fig. 22): δ 7.20 (m, 12H) and 7.75 (m, 4H). The product gave a negative test with alcoholic silver nitrate.

**Anal.** Calcd. for C_{26}H_{16}Br_{2}: C, 63.96; H, 3.30; Br, 32.73

**Found:** C, 63.66; H, 3.39; Br, 32.78

**Reaction with Hydrogen Bromide.**

1,8-Bis(phenylethynyl)naphthalene (750 mg., 2.28 mmole) was dissolved in benzene (100 ml.) and cooled to 10°. Gaseous hydrogen bromide was bubbled through the solution for 30 minutes with no apparent reaction. Addition of hydrogen bromide for 1 hour at room temperature caused the solution to turn dark red. After the mixture had been stirred overnight at room temperature, nitrogen was bubbled through the solution to remove residual hydrogen bromide. Concentration gave a dark red residue which was dissolved in carbon tetrachloride and chromatographed on a large column of silica gel. Four fractions were collected and analyzed by thin layer chromatography. The first two fractions were 7-phenylbenzo[k]fluorantherene (50 mg., 0.152 mmole, 6.7%). The third and fourth fractions were combined and crystallized from Skelly Solve B to yield fine white needles (750 mg., 1.43 mmole, 63%), m.p. 160-160.5°, which analyzed correctly for C_{26}H_{18}Br_{2}. Thus, 1,8-bis(phenylethynyl)naphthalene had undergone addition of 2 equivalents of
hydrogen bromide. The spectral properties of the adduct are: infrared absorption (Fig. 10); ultraviolet absorption (hexane, Fig. 18): 210 (ε 38,300), 222 (43,500) and 279 mμ (23,400); nuclear magnetic resonance (Fig. 24): δ 6.93 (m, 9H), 7.19 (s, 1H), 7.30 (s, 2H), 7.50 (m, 4H) and 7.95 (m, 2H).

Anal. Calcd. for C₂₆H₁₈Br₂: C, 63.70; H, 3.70;
Br, 32.60
mol. wt. 490

Found: C, 63.78; H, 3.92;
Br, 31.54
mol. wt. 494

The dihydrobromide lost hydrogen bromide when heated to its melting point and gave a positive alcoholic silver nitrate test when warmed but not at room temperature. Irradiation of the product (100 mg., 0.204 mmole) in Skelly Solve B (150 ml.) for 24 hours at 40° yielded 7-phenylbenzo[k]fluoranthene (39 mg., 0.119 mmole, 58%).

The dihydrobromide adduct (100 mg., 0.204 mmole) was stirred in dry benzene with commercial potassium t-butoxide (24 mg., 0.214 mmole) for 24 hours at room temperature. Examination by thin layer chromatography showed no change. Additional potassium t-butoxide (24 mg., 0.214 mmole) was introduced; after stirring the mixture 3 days at room temperature no change had occurred. The mixture was heated at 50° for 3 hours and examination by thin layer chroma-
Photolysis

A solution of 1,2-bis(α-bromobenzylidene)acenaphthene (200 mg., 0.41 mmole) in Skelly Solve B (100 ml.) was placed in a quartz tube and irradiated for 16 hours at 40°. The light source had peak intensities at 3500 Å and 5250 Å. Concentration yielded a red oil which on chromatography on neutral alumina with Skelly Solve B gave two bands. The first band was removed with 5% ether-Skelly Solve B to give a yellow solid. Recrystallization from Skelly Solve F-95% ethanol yielded fine pale yellow needles of 7-bromo-12-phenylbenzo[k]fluoranthene (132 mg., 0.32 mmole, 78%), m.p. 137-138°; ultraviolet absorption (Fig. 16): 216 (ε 31,800), 248 (43,900), 271 (12,900), 283 (11,500), 299 (28,700), 311 (37,200) and 337 mμ (6,400); infrared absorption (Fig. 9) and nuclear magnetic resonance (Fig. 23): δ 6.40 (d, 1H), 7.40 (m, 12H), 8.48 (d, 1H) and 8.78 (d, 1H).

Anal. Calcd. for C_{26}H_{15}Br: C, 76.67; H, 3.71; Br, 19.62
Found: C, 76.66; H, 3.59; Br, 19.47

The second band was removed with 50% ether-Skelly Solve B to give a bright orange solid (20 mg.), m.p. 200-220°. No meaningful spectral data could be obtained and investigation of the product was terminated.
Debromination.

A. 1,2-Bis(α-bromobenzylidene)acenaphthene (200 mg., 0.41 mmole) showed no change when stirred in benzene (25 ml.) at room temperature with zinc dust or copper bronze. Refluxing these materials in benzene for 5 to 7 hours yielded mainly starting material and small amounts of 7-bromo-12-phenylbenzo[k]fluoranthene. Similar results were obtained on refluxing 1,2-bis(α-bromobenzylidene)acenaphthene in benzene without zinc or copper.

B. Reaction of 1,2-bis(α-bromobenzylidene)acenaphthene (100 mg., 0.305 mmole) with magnesium (30 mg., 1.23 mmole) under anhydrous conditions (see previous experiment) was followed by hydrolysis. The oil obtained on work up was analyzed by thin layer chromatography. The main product was 1,8-bis(phenylethynyl)naphthalene with a small amount of 7-phenylbenzo[k]fluoranthene and traces of 7-bromo-12-phenylbenzo[k]fluoranthene and starting material.

C. 1,2-Bis(α-bromobenzylidene)acenaphthene (250 mg., 0.51 mmole) was dissolved in dry ether (50 ml.) and cooled to 0°. n-Butyllithium (0.53 mmole) in pentane was added through a syringe. After the mixture had been stirred overnight at room temperature, no change was apparent on examination with thin layer chromatography. A large excess of n-butyllithium (2.4 mmole) was added; the solution became dark immediately. After 4 hours the color changed to light brown and the reaction mixture was poured onto ice and dilute
sulfuric acid. The ether layer was separated, dried over magnesium sulfate and concentrated to give a brown oil. Chromatography on silica gel with Skelly Solve B yielded 7-phenylbenzo[k]fluoranthene (20 mg., 0.061 mmole, 12%), 1,8-bis(phenylethynyl)naphthalene (30 mg., 0.092 mmole, 18%) and 7-bromo-12-phenylbenzo[k]fluoranthene (110 mg., 0.27 mmole, 53%).

**Attempted reduction.**

1,2-Bis(α-bromobenzylidene)acenaphthene (100 mg., 0.205 mmole) in ethyl acetate (150 ml.) with a catalytic amount of 5% platinum on charcoal was shaken under hydrogen (30 p.s.i.) for 12 hours. Filtration and removal of the solvent gave an oily solid which was shown to be starting material by thin layer chromatography.

**Oxidation.**

Oxidation of 1,2-bis(α-bromobenzylidene)acenaphthene (25 mg., 0.051 mmole) was attempted in glacial acetic acid (15 ml.) with sodium dichromate dihydrate (26 mg., 0.087 mmole). No change was observed after stirring the mixture for 8 hours at room temperature. After having been refluxed for 2 hours, the mixture was poured onto ice and extracted with ether; the combined extracts were dried and concentrated. The infrared spectrum, which showed carbonyl absorption at 5.62, 5.75 and 5.89 μ, was compared with the spectra of naphthalic anhydride (C=O at 5.62 and 5.73), acenaphthenonequinone (C=O at 5.75) and benzoic acid (C=O at
Theacenaphthenequinone was separated by silica gel chromatography and identification confirmed by its mixed melting point. Its retention time on the gas chromatograph was the same as an authentic sample using a 5' x 1/8' column containing 5% S.E. 30 on 60/80 Chromosorb W.

**Debromination of 7-Bromo-12-phenylbenzo[k]fluoranthene.**

A solution of 7-bromo-12-phenylbenzo[k]fluoranthene (10 mg., 0.0246 mmole) in anhydrous ether (20 ml.) was added to dry magnesium (10 mg., 0.41 mmole). One drop of 1,2-dibromoethane was added to assure initiation of the reaction. The mixture was stirred at room temperature under dry nitrogen for 24 hours and poured onto ice and dilute sulfuric acid. The ether layer was separated, dried over potassium carbonate and concentrated. Using thin layer chromatography the products were identified as 7-phenylbenzo[k]fluoranthene in good yield and a small amount of starting material.

**Irradiation of 1-Nitro-8-(phenylethynyl)naphthalene.**

1-Nitro-8-(phenylethynyl)naphthalene (150 mg., 0.55 mmole) in pyridine (50 ml.) was irradiated (2537 Å) at 40° for 24 hours. The solution was poured into water and extracted with ether. The combined extracts were washed with 5% hydrochloric acid and water and dried over magnesium sulfate. Concentration yielded an oily solid which had the same infrared absorption as the starting material. Thin layer chromatography showed the presence of a small amount
of tar.

The solid was redissolved, irradiated in refluxing pyridine for 7 hours, and worked up in the same manner. Thin layer chromatography showed large amounts of tar and a small amount of starting material. Infrared absorption showed no evidence for a carbonyl group.

Acenaphthenequinone p-tosylhydrazones.

Preparation of Acenaphthenequinone mono-p-tosylhydrazone.

Acenaphthenequinone (10 g., 0.055 mole) was stirred in anhydrous methanol and brought to reflux. Powdered p-tosylhydrazine (11.0 g., 0.059 mole) was added with stirring. After 1.5 minutes at reflux the reactants had dissolved and the product began to precipitate. The mixture was cooled in an ice bath, filtered and washed with cold methanol. Air drying yielded acenaphthenequinone mono-p-tosylhydrazone as a light yellow powder (18.3 g., 0.052 mole, 95%) m.p. 177-178°, lit. (61) 179° dec., darkens 175°.


Preparation of Acenaphthenequinone bis-p-tosylhydrazone.

Acenaphthenequinone mono-p-tosylhydrazone (9 g., 0.0257 mole) was stirred in refluxing n-propanol (125 ml.) while powdered p-tosylhydrazine (5.15 g., 0.0277 mole) was added. The stirred mixture was refluxed for 30 minutes and cooled
to room temperature. Filtration and drying gave 6.5 g. of crude product. Recrystallization from chloroform-ethanol yielded acenaphthenequinone bis-\( p \)-tosylhydrazone as fine light tan needles (4.0 g., 0.0077 mole, 30\%), darkens slightly 195°, m.p. 200° dec., lit. (44) 190-195° dec. Infrared absorption (Fig. 11): 2.96 (N-H), 6.27 and 6.73 (C=\( N \)) and 7.52 and 8.57 (SO\(_2\)).

**Preparation of Dilithium Acenaphthenequinone bis-\( p \)-tosylhydrazone.**

Dry acenaphthenequinone bis-\( p \)-tosylhydrazone (4.0 g., 0.0077 mole) was stirred overnight in dry tetrahydrofuran (100 ml.) under dry nitrogen. Addition of n-butyllithium (0.0177 mole) in pentane by a syringe caused formation of a dark green color which disappeared with stirring. During the addition of butyllithium, undissolved tosylhydrazone disappeared and a bright yellow solid was formed. Stirring was continued for 30 minutes and dry pentane (100 ml.) was added. After 10 minutes the mixture was filtered under dry nitrogen and washed with dry tetrahydrofuran and dry pentane. After drying overnight in a vacuum desiccator the dilithium acenaphthenequinone bis-\( p \)-tosylhydrazone weighed 4.4 g. (107\%). The infrared spectrum (Fig. 12) showed no N-H absorption but indicated that the product was contaminated by tetrahydrofuran. The contaminant could be removed only by heating the dilithium salt to 135° at 0.5 mm. pressure. The actual yield was about 3.75 g. (91\%).
Pyrolysis of Dilithium Acenaphthenequinone bis-p-tosylhydrazone.

Dilithium acenaphthenequinone bis-p-tosylhydrazone (1 g.) was placed in a 100 ml. round bottom flask attached to a vacuum system containing two small traps immersed in dry ice-iso-propanol. The flask was heated slowly at 0.5 mm.; at 110° the pressure increased to 0.7 mm. After holding the temperature at 135° for several minutes the pressure returned to 0.5 mm. The volatile liquid (0.15 g.) collected in the first trap was identified as tetrahydrofuran by its infrared absorption. Further heating at 0.5 mm. produced rapid decomposition of the dilithium salt at 137-138°. Since none of the decomposition products reached the traps, the contents of the flask were extracted with ether leaving a dark grey residue. Concentration of the extracts gave a brown oil which was analyzed with thin layer chromatography. The principle product was tar with very small amounts of two other products, one of which was acenaphthenequinone. This reaction was not investigated further.
Figure 1

Figure 2

Figure 3
Figure 22
Figure 24
Figure 25