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ALKYLIDENETRIPHENYLPHOSPHORANES AND
DIETHYL ALKYLPHOSPHONATE ANIONS:
SYNTHETIC APPROACHES TO
PHENANTHRO[9]CYCLOPROPENES

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
1965

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furan

10-(p-Bromobenzylidene)-9-phenanthrone

10-Benzylidene-4-nitro-9-phenanthrone

Attempted preparation of 10-diphenylmethylen-
9-phenanthrone

10-Diphenylmethylen-4-nitro-9-phenanthrone

10-(a-Cyanobenzylidene)-4-nitro-9-phenan-
throne

3-Methoxy-4'-nitro-3-phenylphenanthro[9]valerolac-
tone

10-Fluorenylidene-9-phenanthrone

10-(a-Carboethoxymethylene)-9-phenanthrone

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INTRODUCTION AND HISTORICAL

The present investigation involves study of the reactions of phenanthrenequinone with various alkylidenetriphenylphosphoranes (Equation 1) and with diethyl alkylphosphonate anions and possible syntheses of phenanthro[1]-cyclopropenes from the resulting intermediates (Equation 2) via their diazo compounds.

The reaction between an aldehyde or a ketone and an alkylidenetriphenylphosphorane is popularly known as the
Wittig Reaction (1,2). The synthetic method is illustrated by the formation of styrene from benzaldehyde and methylene-triphenylphosphorane (Equation 3).

\[
\begin{align*}
\text{H} & \quad \text{C}=\text{O} \quad \varphi_3 - \text{P} = \text{CH}_2 \\
\rightarrow & \\
\text{H} & \quad \text{C}=\text{CH}_2
\end{align*}
\]

(3)

The Wittig Reaction is believed to involve an intermediate dipolar adduct (betaine) which decomposes to an unsaturated product and triphenylphosphine oxide (1,2) (Equation 4).

\[
\begin{align*}
\text{R} - \text{C} - & \text{R} + \varphi_3 - \text{P} = \text{CH}_2 \\
\rightarrow & \\
\text{R} & \quad \text{C} - \text{C} - \text{R} \\
\text{o} & \quad \text{p} \varphi_3
\end{align*}
\]

(4)

The effects of electron-donating and electron-withdrawing groups on reaction of various arylaldehydes with
alkyldienetriphenylphosphoranes have been studied (3).


p- and m-Nitrobenzaldehydes react faster and give higher yields with fluorenyldienetriphenylphosphorane than does benzaldehyde. Benzaldehyde in turn reacts more rapidly and in higher yield with the ylide than do p- or m-toluinaldehydes. Kinetic experiments have shown that p-nitrobenzaldehyde reacts $1.5 \times 10^3$ times faster with carbomethoxymethylenetriphenylphosphorane than does p-methoxybenzaldehyde. p-Nitrobenzaldehyde was also shown to react $1.1 \times 10^2$ times faster with carbomethoxymethylenetriphenylphosphorane than does benzaldehyde. The mechanism of the Wittig Reaction (4) is believed to involve rate determining and


reversible betaine formation followed by rapid decomposition of betaine to olefin and triphenylphosphine oxide.
Phosphoranes vary greatly in their stabilities. Relatively stabilized Wittig reagents are those which have an unsaturated electronegative group such as carbomethoxy or nitrile, etc., on the ylide carbon. Such triphenylphosphoranes may be isolated and are insensitive to moisture or air. Unstable ylides are generated in situ and must be protected. Reagents such as diphenylmethylenetriphenylphosphorane are intermediate in stability since they may be isolated, but react slowly in aqueous or oxygenic environments.

An excellent supplement to the Wittig Reaction is the olefin synthesis from aldehydes or ketones via phosphonate carbanions (5). The method is illustrated by the formation of carbomethoxymethylene cyclohexane from cyclohexanone and carboethoxymethylenediethylphosphonate anion (Equation 5). This reaction has advantages over the Wittig Reaction in that diethyl alkylphosphonates are cheaper than triphenylphosphoranes and the phosphonate anion-olefin synthesis is conducted under milder conditions. However, simple
diethyl alkylphosphonate anions which do not contain a stabilizing group undergo rapid self-condensation at the elevated temperatures necessary for their preparation. The mechanism for the phosphonate anion-olefin synthesis is similar to that for the Wittig Reaction.

Although many studies of reactions of carbonyl compounds and substituted alkylidenetriphenylphosphoranes have been recorded, few reports exist which are concerned with dicarbonyl compounds. α-Phthalaldehyde (6) reacts with

\[
\begin{align*}
\text{(6) G. Wittig, Angew. Chem., 68, 505 (1956).}
\end{align*}
\]

bifunctional triphenylphosphoranes, \( \phi_3 \text{P=CH-(CH}_2\text{)}_n \text{CH=P}\phi_3 \) to yield benzocycloheptadiene (n=1) and benzocyclooctatriene (n=2). Benzocyclobutenequinone (7) and α-carbobemethoxymethylenetriphenylphosphorane give

\[
\begin{align*}
\end{align*}
\]
2-α-carbomethoxymethylenebenzocyclobutenone (I) and 1,2-dicarbomethoxymethylenebenzocyclobutene (II). Attempts to isolate methylenebenzocyclobutenone and 1,2-dimethylenebenzocyclobutene from benzocyclobutenequinone and methylenetriphenylphosphorane were unsuccessful.

During the present study, Parrick (8) reported that benzylidenetriphenylphosphorane and phenanthrenequinone gave 10-benzylidene-9-phenanthrone (III) in 46% yield even when excess triphenylphosphorane was used. Benzylidenetriphenylphosphorane gave intractable tars in reactions with 1,2-naphthoquinone, p-benzoquinone, and biacetyl; from benzil, both geometrical isomers of 1,2,3-triphenyl-2-propen-1-one are obtained.

Reactions of dicarbonyl compounds and phosphonate anions have not been previously described.

Attempts to prepare stable o-quinomethanes by other methods have usually failed. By careful selection of reaction conditions, phenanthrenequinone and various ylides or phosphonate anions might be expected to yield derivatives of 10-methylene-9-phenanthrone which will be of value in subsequent syntheses of phenanthro[4]cyclopropanes. Phenanthrenequinone and ethyl acetoacetate were reported to give 10-(α-carboethoxyacetonylidene)-9-phenanthrone (IV) (9). However, later examination (10) of the

(9B) B. Lachowicz, Monatsh., 17, 344 (1896).

Product showed that its structure was in error and that it was a cyclopentenone derivative (V).

\[
\begin{align*}
& \text{OH} \\
& \text{CO}_2\text{C}_2\text{H}_5
\end{align*}
\]

V

10-(\(\alpha\)-Benzoylmethylene)-9-phenanthrone is claimed to be an intermediate in reaction of phenanthrenequinone and acetophenone in acidic media to give 3-acetoxy-2-phenylphenanthro[\(\ell\)]furan (VI) (11).

\[
\begin{align*}
& \text{O} \\
& \text{O} \quad \text{C} - \text{CH}_3
\end{align*}
\]

VI
Preparation of 10-methylene-9-phenanthrone (12) from 9-phenanthrol, formaldehyde, and dimethylamine failed; its dimer, 3',4'-dihydrospiro[phenanthrene-9(10H), 2'-[2H]phenanthro[9,10-b]pyran]-10-one (VII) was obtained.

Syntheses of other o-quinone methides have met only with partial success. Pyrolysis of o-methoxymethylphenol gives 6-methylene-2,4-cyclohexadien-1-one (13) (Equation 6)
which is stable at -50° but trimerizes at 0°. 2-Methoxy-
methyl-2-napthol pyrolyzes to 1-methylene-2-naphthalenone
(VIII); the transient intermediate dimerizes rapidly to
IX (14). 1-Methylene-2-naphthalenone (VIII) has been

(14A) S. B. Cavitt, H. Sarrafizadeh R., and P. D.
Soc., 60, 676 (1938).

trapped by the sodium salt of malonic ester to yield X.
1-Diphenylmethylen-2-naphthalenone (15) has been prepared according to Equation 7. An alternate route has allowed synthesis of 2-diphenylmethylen-1-naphthalenone (16) (Equation 8).


Reactions of β-naphthol with carbon disulfide, base, and dimethyl sulfate or dibromoethane have afforded XI and XII (16) respectively. These compounds are the only known
stable o-quinomethides in the benzene, naphthalene, or phenanthrene series.

6-Diphenylmethylen-2,4-cyclohexadien-1-one (18) has been postulated as an intermediate in reaction of o-hydroxy-triphenylcarbinol and acetic acid which afforded 9-phenylxanthane (Equation 9).
Phenanthrocyclobutenes (XIII) and/or 9,10-dialkylidene-phenanthrenes (XIV) might be expected along with 10-methylene-9-phenanthrone derivatives from reaction of phenanthrenequinone and Wittig reagents or phosphonate anions. Phenanthrenequinone and carbomethoxymethylenetriphenylphosphorane (19) react; although no definite products were identified,

(19) R. Pohl, private communication, The Ohio State University.

\[ \text{XIII} \]

\[ \text{XIV} \]

it appeared that one of them was a lactone. Benzocyclobutene (20) has been prepared as illustrated (Equation 10). The

o-quinodimethane has been postulated as an intermediate having a high free radical index at the terminal methylene; under pyrolysis conditions intramolecular cyclization occurs rather than dimerization.

\[
\text{\begin{tikzpicture}
  \begin{scope}[scale=0.5]
    \node (a) at (0,0) {\text{SO}_2};
    \node (b) at (3,0) {+ \text{SO}_2};
    \node (c) at (1.5,0) {\text{C}};
  \end{scope}
\end{tikzpicture}}
\]

\( (10) \)

9,10-Phenanthroquinodimethane (XV) (21) has been generated in reaction of XVI and silver oxide (Equation 11). XV has also been trapped by maleic anhydride during pyrolysis of 9,10-dimethylphenanthrene-9,10-diol (22).


After successful syntheses of phenanthro[\(\ell\)]cyclobutenes were realized in the present study, it was found in this
laboratory (23) that trans-1,2-diphenylphenanthro[9]cyclo-
butene (XVII) is obtainable by a different method.

(23A) M. P. Cava and D. Mangold, private communication, The Ohio State University.
Recent studies (24) of syntheses and properties of

cyclopropenes have been explored because of the steric strain involved in the novel ring system. It has also been found (24) that cyclopropenium cations obey Hückel's Rule in that they are aromatic. These studies have aroused interest in the possible syntheses of benzocyclopropenes and their derivatives (25). Benzocyclopropenes should be

intermediate in strain between benzocyclobutene and benzyne. If benzocyclopropene or derivatives are capable of existence, it would be of interest to study: (1) the possible partial fixation of the aromatic bonds due to the probable shortening of the bridge bond relative to the other aromatic C-C bonds. (2) the stereochemistry of the
methylene group; i.e., does it lie in or out of the plane of the aromatic system. (3) the possible synthesis of a benzocyclopropenium cation and its properties.

Attempts to prepare a benzocyclopropene and a napthocyclopropene (25A) according to the following schemes (Equations 11 and 12) failed.

\[
\begin{align*}
\text{O} & \quad \text{I)} \quad \text{NaOCH}_3 \\
\text{H} & \quad \text{CH}_3\text{OH} \\
\text{OCH}_3 & \quad \text{2)} \quad \text{CH}_3\text{Br} \\
\text{OCH}_3 & \quad \text{(II)}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{O} & \quad \text{1)} \quad \text{t-BuOK} \\
\text{O} & \quad \text{t-BuOH} \\
\text{CH}_3\text{O} & \quad \text{2)} \quad \text{CH}_3\text{Br} \\
\text{CH}_3\text{O} & \quad \text{(12)}
\end{align*}
\]

4,7-Dimethoxy-3,3-diphenylindazole (25C) has been photolyzed in an attempt to prepare 2,5-dimethoxydiphenylbenzocyclopropene, but only 1,4-dimethoxy-9-phenylfluorene was obtained (Equation 13).
While the present investigation was in progress, 3-carbomethoxycarbonyldimethylbenzocyclopropene (25B) was synthesized by photolysis of 6-carbomethoxy-3,3-dimethylindazole (Equation 14), but p-carbomethoxyisopropenylbenzene was the major product. However, the benzocyclopropene derivative is unstable in refluxing benzene and can be kept only for a few days at ordinary temperatures.

The fusion of a cyclopropene unit onto a phenanthrene nucleus at the 9,10-position might be expected to afford a stable species. The route chosen as an approach to phenanthro[9]cyclopropenes is illustrated (Equation 15).
This route is a modification of a procedure for the synthesis of cyclopropenes (26).


Two syntheses of 1,3,3-trimethylcyclopropene illustrate this procedure (Equations 16 and 17).

\[
\begin{align*}
\text{CH}_3\text{CH}_3\text{H} & \xrightarrow{\text{H}^+ / \text{Ts} \text{N} - \text{NH}_2} \text{CH}_3\text{CH}_3\text{H} \\
\text{CH}_3\text{C} = \text{C} - \text{C} = \text{O} & \xrightarrow{\Delta} \left[ \text{CH}_3\text{C} = \text{C} - \text{C} = \text{N}_2 \right] \\
\text{CH}_3\text{ONa} & \xrightarrow{\Delta} \text{H}_3\text{C} \text{C} = \text{C} - \text{C} = \text{N}_2 \\
\text{CH}_3\text{C} \equiv \text{N} & \xrightarrow{\text{hv}} \text{H}_3\text{C} \text{C} \equiv \text{C} \\
\end{align*}
\]
RESULTS AND DISCUSSION

Reactions of 9,10-phenanthrenequinone and 4-nitro-9,10-phenanthrenequinone with alkylidenetriphenylphosphoranes and with phosphonate anions


Preparation of a benzocyclopropene derivative has been reported (25B) (Equation 14), although no such compounds were known at the beginning of this study. Also the reaction of phenanthrenequinone and a Wittig reagent (8) was not reported until after initiation of the present work.

It has now been found that phenanthrenequinone reacts with alkylidenetriphenylphosphoranes to yield 10-methylene-9-phenanthrones in dimethyl sulfoxide, chloroform, methylene chloride, or methanol. Higher yields of products are realized when dimethyl sulfoxide was utilized. Solvents of high dielectric constants increase the rate of the
Wittig Reaction (4) and this point is verified in this study. Chloroform, methylene chloride, and methanol were used only when stable alkylidenetriphenylphosphoranes were employed. Unstable alkylidenetriphenylphosphoranes were prepared in situ in dimethyl sulfoxide by the sodium salt of dimethyl sulfoxide (sodium dimsyl) as base.

Reaction of phenanthrenequinone and methylenetriphenylphosphorane (1:1 stoichiometry) in dimethyl sulfoxide at room temperature or 65° did not allow isolation of 10-methylene-9-phenanthrone (XVIII); however, two yellow dimers of XVIII are obtained. The dimers are separable either by column chromatography or by crystallization technique which allow deposition of a yellow crystalline dimer of XVIII, m.p. 253°. The dimer melting at 253° has been reported previously (12) and assigned as structure XIX, 3',4'-dihydrospiro[phenanthrene-9(10H), 2'-2[H]phenanthro[9,10-b]pyran]-10-one. Dimer XIX is obtained in 12% yield at room temperature and in 16% yield at 65°. The second dimer, m.p. 151-154°, is produced in 24% yield at room temperature and in 40% yield at 65°. Numerous attempts under various conditions were made to obtain the
monomer XVIII, but to no avail. The determined molecular
weights and elemental analyses are in accord with theory
for dimeric products. A mixed melting point determination
of the two dimers gives a depression. XIX has infrared
absorption at 5.9 (carbonyl) and 9.0 μ (ether). Its
nuclear magnetic resonance spectrum was not obtained be­
cause of its insolubility in solvents suitable for spectral
purposes. The ultraviolet spectrum of XIX has bands at
251(ε 63,500), 277(ε 21,500), 297(ε 11,500), and 308μ
(ε 10,500). XIX has been assigned the indicated structure
(12) by analogy with dimers of other o-quinomethides.

The lower melting dimer absorbs at 5.89 (carbonyl)
and 9.1 μ (ether). Its ultraviolet spectrum exhibits bands at
252(ε 64,500), 279(ε 20,000), and 320μ (ε 11,500). The
nuclear magnetic resonance of this compound reveals peaks
at 5.92 (2 benzylic protons ), 6.42 (1 proton on ethereal
carbon deshielded by a carbonyl group), and 6.68 (1 proton
on an ethereal carbon not deshielded by a carbonyl group).

XIX is believed to form via Diels-Alder cyclization
of XVIII (Equation 18).
By analogy to Equation 18, the lower melting dimer may have structure XX (Equation 19).

Preparation of 10-ethyldene-9-phenanthrone (XXI) by reaction of phenanthrenequinone and ethyldenetriphenylphosphorane was only partially successful. A bright yellow crystalline solid was obtained which analyzed as
a 1:1 adduct of phenanthrenequinone and ethylidenetriphenylphosphorane. The infrared spectra of the product exhibits carbonyl absorption at 5.95 and a phenylphosphorous band at 9.0μ. The 1:1 adduct may well have the structure XXII or XXIII. A subsequent attempt to prepare XXI by warming

the mixture to 70° gave a product in very low yield which might be assigned the structure XXI.

Reaction of isopropylidenetriphenylphosphorane and phenanthrenequinone was studied at various temperatures in attempts to prepare 10-isopropylidene-9-phenanthrone (XXIV). However, only phenanthrenequinone and triphenylphosphine oxide were obtained. On workup of these reactions (and those of ethylidenetriphenylphosphorane and phenanthrenequinone), the dimethyl sulfoxide solution was
poured into ice water; a green solid was obtained which soon turned brown. It is believed that the green solid is a betaine-like intermediate which decomposes in water to phenanthrenequinone and the alkylidenetriphenylphosphorane. Triphenylphosphine oxide then arose from hydrolysis of the regenerated triphenylphosphorane.

Diphenylmethylenetriphenylphosphorane does not react with diphenylketene in refluxing benzene. Tetraphenyllallene is formed, however, when the mixture is heated at 140° (27). Diphenylketene and isopropylidenetriphenylphosphorane do not form 1,1-dimethyl-3,3-diphenyllallene under normal Wittig conditions, but rather the betaine

![XXIV](image-url)
adduct is isolated. However, when the adduct is sublimed at 150° the allene is formed (28). It is apparent that the adducts from phenanthrenequinone and ethylidenetriphenylphosphorane or isopropylidenetriphenylphosphorane are very stable and do not decompose at 70-75°. It is possible that these intermediates will yield the desired products at higher temperatures.

Since attempts to obtain a stable 10-alkylidene-9-phenanthrone by Wittig methods were unsuccessful, the possibility of preparing 10-aralkylidene-9-phenanthrones was explored. The reaction of benzylidenetriphenylphosphorane and phenanthrenequinone (1:1 stoichiometry) in dimethyl sulfoxide was investigated in an attempt to synthesize 10-benzylidene-9-phenanthrone (XXV). The reaction conditions were varied considerably, but 2,3-di-phenylphenanthro[9]dihydrofuran (XXVI) was always obtained. The dihydrofuran was also formed when excess benzylidene-triphenylphosphorane was used.

The structure of 2,3-diphenylphenanthro[ε]dihydrofuran is assigned on the following basis: (1) infrared absorption which can be assigned to a carbonyl group was absent; (2) a strong infrared absorption occurs for a vinyl ether group at 9.78μ; (3) the nuclear magnetic resonance spectrum affords doublets (1:1) at 4.19τ for a benzylic proton and at 4.33τ for a proton on an ethereal carbon; (4) the elemental analysis is approximately that of theory; (5) the molecular weight found agrees exactly with the theoretical. The stereochemistry of XXVI was not elucidated.

Parrick (6) has reported the synthesis of 10-benzylidene-9-phenanthrone from phenanthrenequinone and excess benzylidenetriphenylphosphorane. This preparation was repeated exactly as described (8) and it was found that the product obtained (47% yield) corresponded in all respects with 2,3-diphenylphenanthro[ε]dihydrofuran.
Parrick had assigned the infrared band at 1628 cm\(^{-1}\) (Fig. 3) for carbonyl in his product; this is not acceptable because of its intensity and comparison with other 10-methylene-9-phenanthrone derivatives (5.9-6.0 \(\mu\)) from the present study. It is therefore apparent that the structure of the product obtained by Parrick is XXVI. It is probable that XXVI is formed from 10-benzylidene-9-phenanthrone as illustrated (Equation 20).

Benzylidenetriphenylphosphorane thus probably undergoes Michael addition to structure XXV followed by O-alkylation
with expulsion of triphenylphosphine to yield XXVI. The triphenylphosphine is probably oxidized by dimethyl sulfoxide to triphenylphosphine oxide. The latter transformation has been observed previously (29). 2,3-Diphenyl-

(29) O. Cox, private communication, The Ohio State University.

phenanthro[9]dihydrofuran is dehydrogenated by N-bromosuccinimide to 2,3-diphenylphenanthro[9]furan (XXVII). The nuclear magnetic resonance spectrum of XXVII indicates the absence of the benzylic proton and ethereal proton found in XXVI. The molecular weight, elemental analysis, and infrared absorption are all in excellent agreement with structure XXVII.

![XXVII]

A study was then initiated of possible synthesis of 10-benzylidene-9-phenanthrone. Excess phenanthrenequinone
reacts with benzyldenetriphenylphosphorane in dimethyl sulfoxide at room temperature to yield the desired colorless 10-benzyldene-9-phenanthrone (XXV). The infrared spectrum exhibits carbonyl absorption at 5.98μ. The nuclear magnetic resonance spectrum has, in addition to an unresolved multiplet for aromatic protons, a peak at 3.17τ for the vinyl proton (intensities-13:1). However, when this compound is warmed or the original reaction mixture is warmed, two dimers of XXV are obtained. The major dimer is colorless and shows infrared absorption at 5.95μ for a carbonyl group. This dimer has a complex nuclear magnetic resonance spectrum with three sets of triplets at 3.3, 3.4, and 3.7τ. The molecular weight and elemental analysis agree for the dimer. The second dimer, a light yellow material, is isolated in trace amounts. Its infrared spectrum reveals carbonyl absorption at 5.95μ; the experimental molecular weight and elemental analysis are in accord with theory. A nuclear magnetic resonance spectrum of the yellow dimer has not been obtained because of the lack of sufficient material for spectral determination. The two dimers are tentatively
assigned as XXVIII A or B and no attempt was made to dis­tin­guish between them.

In order to test the generality of formation of phen­anthro[\ell]dihydrofurans from ylides and dicarbonyl compounds, phenanthrenequinone and p-bromobenzylidenetriphenylphosphor­ane (1:1 stoichiometry) were reacted and 2,3-di-(p-bromo­phenyl)phenanthro[\ell]dihydrofuran (XXIX) was obtained in­stead of 10-(p-bromobenzylidene)-9-phenanthrone (XXX).
The presence of an ether band at 9.32\textmu and the absence of carbonyl infrared absorption supports structure XXIX as does the elemental analysis. The nuclear magnetic reson­ance spectrum of XXIX exhibits doublets (1:1) at 4.42\tau for a benzylic proton and at 5.25\tau for a proton on ethereal carbon. The molecular weight is in good agreement with the structure assigned. The stereochemistry of XXIX was not determined. Dihydrofuran XXIX is probably formed as illustrated previously (Equation 20).
When p-bromobenzylidenetriphenylphosphorane reacts with excess phenanthrenequinone, 10-bromobenzylidene-9-phenanthrone (XXX) is obtained in two geometrical forms along with a third unidentified product. The major isomer of XXX is colorless and is isolated in 21% yield. The minor isomer is yellow and is obtained in only 1% yield. The infrared spectra of the isomers are quite similar and both compounds analyze properly. The nuclear magnetic resonance spectrum of the minor isomer could not be obtained because insufficient sample was available to attain the proper concentration for the spectral determination. The molecular weights of the two isomers agree well with that of structure XXX. The nuclear magnetic resonance spectrum of the major isomer reveals a vinyl proton at 3.17 ppm (intensity=12 aromatic protons:1 vinyl proton).

10-Benzylidene-4-nitro-9-phenanthrone (XXXI) is prepared in 24% yield from reaction of benzylidenetriphenylphosphorane and 4-nitrophenanthrenequinone. A second product is isolated in trace amount which appears to be 2,3-diphenyl-4-nitrophenanthro[2]dihydrofuran because of the absence of carbonyl absorption and the similarity of
its infrared spectra to that of 2,3-diphenylphenanthro[\(\mathcal{E}\)]-dihydrofuran (XXVI) and 2,3-di-(p-bromophenyl)phenanthro-[
\(\mathcal{E}\)]dihydrofuran (XXIX), respectively. 10-Benzylidene-4-nitro-9-phenanthrone (XXXI) exhibits infrared absorption at 5.98\(\mu\) for carbonyl and at 6.57, 7.4, and 7.48\(\mu\) for nitro. The nuclear magnetic resonance spectrum exhibits aromatic protons at 2.53\(\tau\) and a vinyl proton at 2.86\(\tau\) (intensities--12:1). The molecular weight and elemental analysis are consistent with the structure assigned.

The carbonyl group meta to the nitro group is postulated as having been attacked by the ylide. It has been noted (4) that meta - chlorobenzaldehyde reacts faster than does para-chlorobenzaldehyde with ylides. Similarly, arylketones or araldehydes with electron-withdrawing substituents in the m- or p- positions react faster with ylides than does benzaldehyde.
Diphenylmethylenetriphenylphosphorane and phenanthrenequinone did not react under various conditions in attempts to prepare 10-diphenylmethylene-9-phenanthrone (XXXII). The reagents were stirred at 75° in dimethyl sulfoxide for several days, but no reaction occurred. Benzene, chloroform, methanol, and methylene chloride were also used as reaction solvents, but to no avail. However, when 4-nitrophenanthrenequinone was substituted for phenanthrenequinone, condensation occurred to afford 4-nitro-10-diphenylmethylene-9-phenanthrone (XXXIII) in 63% yield. The elemental analysis, molecular weight, and infrared spectrum of the product are in accord with that expected.

Considerable interest in cyclopropenium ions has been expressed (24) because of their stability. 1,2,3-Triphenylcyclopropenium fluoborate has been synthesized as illustrated (Equation 21).
It was, therefore, desirable to obtain 10-(α-cyanobenzylidene)-9-phenanthrone (XXXIV) for subsequent possible transformation to XXXV and thence to the phenanthrocyclopropenium cation (XXXVI). Attempts to obtain XXXIV from phenanthrenequinone and α-cyanobenzylidenetriphenylphosphorane failed. However, when the ylide reacts with 4-nitrophenanthrenequinone in dimethyl sulfoxide, 10-(α-cyanobenzylidene)-4-nitro-9-phenanthrone (XXXVII) is obtained in 60% yield. The infrared spectrum of the product exhibits bands at 4.54\(\mu\) for nitrile, 5.98\(\mu\) for ketone, 6.6 and 7.4\(\mu\) for the nitro group. The elemental
analysis and molecular weight are consistent with XXXVII.

\[ \text{XXXVII} \]

10-(α-Cyanobenzylidene)-4-nitro-9-phenanthrone and tosylhydrazide react in the presence of a small amount of dilute hydrochloric acid to afford 3-methoxy-4'-nitro-3-phenylphenanthro[9]valerolactone (XXXVIII). The infrared spectrum of XXXVIII has a band at 5.6μ (lactone). The nuclear magnetic resonance spectrum of XXXVIII exhibits a band at 6.7τ (3H, methoxy) in addition to the aromatic protons (13H). The elemental analysis and molecular weight are in good agreement with the structure proposed. XXXVIII is also obtained when tosylhydrazide is omitted.
Fluorenylidenetriphenylphosphorane is reported (1) to be one of the most stable ylides and is thus generally useless for synthesis. 10-Fluorenylidene-9-phenanthrone (XXXIX) may possibly be an excellent intermediate for conversion to 9-fluorenylidene[2]phenanthro[7]cyclopropene (XL). Phenanthrenequinone and fluorenylidenetriphenylphosphorane react equally well in refluxing chloroform or dimethyl sulfoxide at 75° to give XXXIX. 10-Fluorenylidene-9-phenanthrone has a brilliant red color and exhibits a strong carbonyl band at 6.01 μ. The elemental analysis and molecular weight are in excellent agreement with that of theory.

\[
\text{XXXIX} \quad \text{XL}
\]

Since a phenanthrocyclopropenium cation might be generated from 9-carboethoxy[2]phenanthro[7]cyclopropene (XLI),
the possible synthesis of 10-(a-carboethoxymethylene)-9-phenanthrone (XLII) was undertaken from phenanthrenequinone and carboethoxymethylenetriphenylphosphorane. XLII was obtained in 47% yield. The infrared absorption of XLII reveals a broad carbonyl peak at 5.8μ, but a 3% chloroform solution of XLII exhibits a doublet at 5.79 (ester carbonyl) and 5.87μ (ketone carbonyl). The nuclear magnetic resonance spectrum exhibits a quartet at 8.67 for the methyl group, a triplet at 5.55 for methylene protons, a singlet at 3.5 for the vinyl proton, and multiplets at 1.75 and 2.5 (intensities—3:2:1:8). The elemental analysis of XLII is in good agreement with theory. The molecular weight, 281, agrees well with the calculated value of 278.

Another source of a phenanthrocyclopropenium cation might be from 9,9-dibromophenanthrocyclopropene which can
possibly be obtained from 10-dibromomethylene-9-phenanthrone (XLIII). Reaction of dibromomethylenetriphenylphosphorane (one equivalent) and phenanthrenequinone in methylene chloride yields yellow plates of XLIII and 1,1,2,2-tetra-bromophenan thro[\ell]cyclobutene (XLIV). XLIII is the major product and exhibits a strong carbonyl peak at 6.0u. The molecular weight and elemental analysis are consistent with the assigned structure. The colorless phenanthro[\ell]cyclobutene (XLIV) is identified by its molecular weight, elemental analysis, and infrared spectrum. 10-Dibromomethylene-9-phenanthrone (XLIII) is converted to 1,1,2,2-tetrabromophenan thro[\ell]cyclobutene (XLIV) in 8% yield by dibromomethylenetriphenylphosphorane. XLIV probably results from intramolecular cyclization of the quinodi-methane (XLV) because of steric factors (Equation 22). Molecular models of XLV indicate that a bromine atom of each methylene group collides with a bromine atom of the other methylene group and there is serious interaction of the hydrogens in positions 1 and 8 with one of the bromine atoms of each methylene. However, these steric conditions are relieved in XLV.
Phenanthrenequinone and diethyl phenacylphosphonate anion (1:1 stoichiometry) affords 10-(a-benzoylmethylene)-9-phenanthrone (XLVI) in 44% yield and 1,2-dibenzoylphenanthro[2]cyclobutene (XLVII) in 46% yield. XLVI exhibits a doublet for carbonyl groups at 5.99–6.0 μ in the infrared. Its nuclear magnetic resonance spectrum could not be obtained because of the difficulty in obtaining the proper concentration for spectral purposes. The molecular weight and elemental analysis of XLVI correspond well with that
of theory. XLVII exhibits a single infrared carbonyl peak at 6.0 μ, and its nuclear magnetic resonance spectrum has a peak at 5.04 δ for two tertiary protons in addition to aromatic protons. The nuclear magnetic resonance intensities of the aromatic to aliphatic protons are 18:2.

\[ \text{XLVI} \]
\[ \text{XLVII} \]

α-Benzoylmethylenetriphenylphosphorane reacts with phenanthrenequinone (1:1 stoichiometry) to afford XLVI in 32% and XLVII in 65% yields. These two compounds agree, in all respects, with those from the previous phosphonate anion reaction. There were no existing reports of phenanthro[\( \ell \)]cyclobutenes in the literature before the synthesis of XLVII. After successful syntheses of phenanthro[\( \ell \)]cyclobutenes were realized in the present study, the preparation of \textit{trans}-1,2-diphenylphenanthro[\( \ell \)]cyclobutene (XVI) (23) was reported. Studies of the nuclear magnetic resonance
spectra of cis- and trans- 1,2-diphenylbenzocyclobutene (30)


reveal that the benzylic protons of the cis-isomer absorb at 4.80\textdegree while those of the trans-isomer are at 5.56\textdegree. Likewise, the benzylic protons of cis- 1,2-diphenylnaphtho-[b]cyclobutene (31) are found at 4.66 and those of trans- 1,2-diphenylnaphtho-[b]cyclobutene occur at 5.33\textdegree. The assignment of trans to 1,2-diphenylphenanthro[9]cyclobutene (XVI) (23) was made on the basis of the high value of 6.22\textdegree for the benzylic protons. These studies indicate that in a trans-isomer there is considerable shielding of the benzylic protons and thus they appear at a higher tau value than in the cis-isomer. Since the benzylic protons of XLVI resonate at 5.04\textdegree, this compound by analogy may have the cis configuration. It is not known yet, however, whether the benzoyl groups deshield the benzylic protons in the trans configuration causing a shift to a lower tau value.
It was desirable to test the generality of the synthesis of phenanthro[\(\ell\)]cyclobutenes from Wittig Reactions or the phosphonate anion-olefin synthesis. One equivalent of phenanthrenequinone reacts with one equivalent of \(\alpha\)-\(\beta\)-bromobenzoylmethylenetriphenylphosphorane in chloroform to afford 1,2-di(\(\beta\)-bromobenzoyl)phenanthro[\(\ell\)]cyclobutene (XLVIII) and 9,10-phenanthroquinodi-(\(\alpha\)-\(\beta\)-bromobenzoyl)-methane (XLIX). XLIX is the only quinodimethane isolated in this study. The two compounds are separated by column chromatography. XLVIII, when warmed in glyme, is partially converted to XLIX as determined by infrared analysis.

XLVIII is assigned the phenanthro[\(\ell\)]cyclobutene structure because of the similarity of its infrared and ultraviolet spectra to that of 1,2-dibenzoylphenanthro[\(\ell\)]cyclobutene (XLVII) and its color (white). The infrared spectrum of XLVIII exhibits a carbonyl band (singlet) at 5.95\(\mu\). XLVIII has bands in the ultraviolet at 257(\(\epsilon\) 58,400), 266(\(\epsilon\) 75,000) and 328\(\mu\)(\(\epsilon\) 27,750). XLIX is assigned as a quinodimethane because of its yellow color and its infrared spectrum contained a carbonyl band at 6.0\(\mu\) (singlet) and a strong vinyl band at 11.58\(\mu\). The ultraviolet spectrum of XLIX exhibits bands at 253(\(\epsilon\) 69,000), 261(\(\epsilon\) 72,500),
284(ε 41,000), 308(ε 31,000), and 360mυ(ε 10,000). Both compounds have approximately the same experimental molecular weight and elemental analysis; however, it was not possible to obtain nuclear magnetic resonance spectra because of the insolubility of these compounds in solvents suitable for spectral purposes.

XLVII and XLVIII probably result from orientations (cis, cis; cis, trans; trans, trans) of the benzoyl groups in a quinodimethane system, such as XLIX, which results in crowding of the groups and thus intramolecular cyclization occurs. The hydrogen atoms in positions 1 and 8 also present serious interactions with the benzoylmethylene groups. However, formation of XLVIII relieves these conditions by allowing the benzoyl groups to be either above or below the plane of the molecule.
Reactions of Benzil and 1,2-Naphthoquinone with Wittig Reagents

Benzil and benzylidenetriphenylphosphorane are reported to yield geometrical isomers of 1,2,3-triphenylprop-2-en-1-one (8). Since phenanthrenequinone and benzylidenetriphenylphosphorane have been found to yield 2,3-diphenylphenanthro[10]dihydrofuran, it was desirable to repeat the reaction of the ylide with benzil. When two equivalents of benzylidenetriphenylphosphorane react with one equivalent of benzil, both geometrical isomers of 1,2,3-triphenylprop-2-en-1-one (A and B) are obtained in 75.3% (higher melting isomer) and 21.1% yields respectively. The reaction of one equivalent of ylide and one equivalent of benzil affords only 1,2,3-triphenylprop-2-en-1-one (A) in 82% yield.

The nuclear magnetic resonance spectrum of 1,2,3-triphenylprop-2-en-1-one (A) reveals a multiplet from 2.17-2.57 for fifteen aromatic protons and a singlet for one vinyl proton at 2.97. Its ultraviolet spectrum exhibits bands at 240 (ε 12,931), 255 (ε 13,423), and 303 μ (ε 12,684). The compound absorbs at 6.1 μ (carbonyl) in the infrared.

1,2,3-Triphenylprop-2-en-1-one (B) exhibits a peak at 6.0 μ (carbonyl) in the infrared. Its nuclear magnetic
resonance spectrum has only a multiplet centered at 2.67t. It appears that the vinyl proton is deshielded by the carbonyl group and is buried beneath the aromatic peaks. The ultraviolet spectrum has bands at 240(ε 34,403), 261(ε 47,700), and 285με (ε 48,623). On the basis of the spectral data, 1,2,3-triphenylprop-2-en-1-one (A) may have structure L and LI may be the structure of 1,2,3-triphenylprop-2-en-1-one (B).

![Chemical structures](image)

The absence of a dihydrofuran product suggests that the α,β-unsaturated ketone chromophores of L and LI are in a transoid configuration and the Michael addition of benzyldenetriphenylphosphorane to L and LI does not occur. However, 10-benzylidene-9-phenanthrone (Equation 20) has a cisoid configuration and 2,3-diphenylphenanthro[ε]dihydrofuran (XXVI) does form for cyclization is favored.

α-Benzoyl-β-carbomethoxystyrene LII is obtained in 45% yield when benzil reacts with carbomethoxymethyleneetriphenylphosphorane. The infrared spectrum of LII has
bands at 5.8μ (ester carbonyl) and 6.0μ (ketone carbonyl).
The nuclear magnetic resonance spectrum exhibits a
multiplet at 2.6τ for ten aromatic protons, a singlet at
3.4τ for one vinyl proton and a singlet at 7.35τ for three
methoxy protons. The molecular weight and elemental
analysis agree with the structure.

\[
\begin{align*}
\Phi - \text{C} - \text{C} = \text{C} - \text{CO}_2\text{CH}_3
\end{align*}
\]

1,2-Naphthoquinone was subjected to the Wittig Reac-
tion in order to observe whether the reaction would afford
a methylenenaphthalenone derivative or whether a Michael
type addition might occur at the localized double bond.
Benzylidenetriphenylphosphorane does not react with 1,2-
naphthoquinone at room temperature in dimethyl sulfoxide.
When the reaction mixture was warmed at 65° for a short
time, an intractable tar is obtained. Reaction of 1,2-
naphthoquinone and fluorenylidetriphenylphosphorane also
occurs; however, upon workup of the reaction mixture only
fluorenone was obtained. Reaction of 1,2-naphthoquinone
with α-phenacylmethylenetriphenylphosphorane gives in low
yield an unidentified white solid. The infrared spectrum exhibits a single carbonyl peak at 5.99 µ and ether bands at 9.3 and 10.1 µ. The product may be either structure LIII or structure LIV, but this has not been verified.

Reactions of Some 10-Methylene-9-Phenanthrones

Attention of the study was then turned to its second objective: namely possible syntheses of phenanthro[6]cyclopropenes. It was advisable to work with those 10-methylene-9-phenanthrones which could be synthesized readily and in good yields by Wittig methods. Therefore, 10-fluorenylidene-9-phenanthrone, 10-(α-cyanobenzylidene)-4-nitro-9-phenanthrone and 10-(α-carboethoxymethylene)-9-phenanthrone were chosen for further study.

Synthesis of 9,9-dibromophenanthro[6]cyclopropene was undertaken because it is a possible source of a
phenanthrocyclopropenium cation. However, 10-dibromomethylene-9-phenanthrone does not react with tosylhydrazide in refluxing benzene or methanol. Reaction did not take place upon addition of acid. Hydrazine reacts with 10-dibromomethylene-9-phenanthrone to give a salt of a hydrazone, but the bromine atoms are also displaced during the reaction. This product was not examined further because it can not be used for possible conversion to 9,9-dibromophenanthro[4]cyclopropene.

Tosylhydrazide does not react with 10-fluorenylidene-9-phenanthrone in refluxing methanol or benzene. Acid catalysis of the reaction in methanol affords an unidentified brown solid, but not the tosylhydrazone.

Reactions of tosylhydrazide and 10-(α-carboethoxy-methylene)-9-phenanthrone to afford the tosylhydrazone failed.

Reaction of methanesulfonylhydrazide and 10-fluorenylidene-9-phenanthrone gives the corresponding mesylhydrazone in 41% yield (LV). This compound has infrared absorption at 3.0μ(−NH₂), 6.1μ(C=N), and 7.5 and 8.5μ (SO₂). When excess mesylhydrazide is used, the crude mixture contains the mesylhydrazone as well as
10-fluorenylidene-9-diazophenanthrene (LVI) as observed in the infrared spectrum. The excess mesylhydrazide acts as a base in this reaction. This reaction was not pursued further, because the reaction of the ketone with hydrazine appeared more promising.

The reaction of hydrazine and 10-fluorenylidene-9-phenanthrone affords the yellow hydrazone of 10-fluorenylidene-9-phenanthrone (LVII) in 97% yield. The infrared spectrum, molecular weight, and elemental analysis support the structure assigned. The infrared spectrum exhibits a moderate band at \(3.0\mu\text{(-NH}_2\text{)}\) and a strong band at \(6.1\mu\text{(-C=N)}\). LVII is unstable to light and air and is used as soon as possible.
The cyclic structure (LVIII) is eliminated from consideration due to the strong band at 6.2μ in the infrared for a C=N group.

9-Diazo-10-fluorenylidene-9,10-dihydrophenanthrene (LVI) is obtained from the mercuric oxide oxidation of the hydrazone (LVII) in excellent yield at 10-20°. The infrared spectrum exhibits a strong band at 4.9μ for the diazo group. Attempts to purify LVI by chromatography on basic-washed or neutral alumina have been only partially successful because decomposition occurs.
Attempts to prepare 10-alkylidene-9-diazophenanthrenes from reactions of 10-diazo-9-phenanthrone with ylides or diethyl alkylphosphonate anions did not give the desired products because the reaction occurs at the diazo group rather than at the carbonyl. The products of these reactions were not examined further.

Photolysis of an ethereal solution of LVI did not give the expected 9-fluorenylidenephenanthro[9]cyclopropene (XL) or nitrogen evolution. It appears that the ether participated in the reaction to give unidentified products. The diazo band of LVI was not present in the infrared spectrum of the photolysis products.
EXPERIMENTAL

General Information

Melting points.—Melting points were determined with a stirred bath of Dow Corning 550 silicone oil and on a melting point block manufactured by the Fisher Scientific Company. All melting points are uncorrected.

Elemental analyses.—Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee, Microanalyses Inc., Wilmington, Delaware, and Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Infrared spectra.—Infrared spectra were obtained with a Perkin-Elmer Infracord Spectrophotometer. The spectra of solid samples were obtained from potassium bromide wafers.

Ultraviolet spectra.—Ultraviolet spectra were obtained with a Perkin-Elmer No. 202 recording spectrophotometer. The solvent used was methylene chloride.

Nuclear magnetic resonance spectra.—Nuclear magnetic
resonance spectra were determined with an A-60 instrument manufactured by Varian Associates. All samples were calibrated with tetramethyl silane. The solvent used, unless specified, was deuterated chloroform.

**Molecular weights.**—Molecular weights were obtained by using a vapor pressure osmometer, model 301A, manufactured by Mechrolab, Incorporated. The solvent used was chloroform.

**Solvents.**—Dimethyl sulfoxide and 1,2-dimethoxyethane were dried over calcium hydride pellets and used without further purification. Chloroform and dichloromethane were dried by elution on a column of basic alumina. Ether was dried over sodium wire.

**Chemicals.**—Triethylphosphite and trimethylphosphite were kindly provided by the Virginia-Carolina Chemical Co., and were dried over sodium wire and distilled. Sodium hydride was used as a 53.4% mineral oil dispersion. α-Carbomethoxymethylenetriphenylphosphorane was provided by Mr. John Asunskis. All alumina used was Woelm Alumina—activity grade 1.
Preparation of Intermediates

Phenanthrenequinone.—Phenanthrene was oxidized by chromic acid to yield phenanthrenequinone (31).


2-Nitro- and 4-nitrophenanthrenequinones.—Nitration of phenanthrenequinone yielded 2-nitro- and 4-nitrophenanthrenequinones (32).


9-Bromofluorene.—Reaction of fluorene and n-bromo-succinimide afforded 9-bromofluorene (33).

(33) G. Wittig and G. Felletschiv, Ann., 555, 133 (1944).

Bromodiphenylmethane.—This compound was prepared by the bromination of diphenylmethane (34).

The adduct of phenanthrenequinone and trimethylphosphite.--Reaction of trimethylphosphite and phenanthrenequinone at 20° under nitrogen gave an adduct (35).


10,10-Dibromo-9-phenanthrone.--Reaction of bromine and the adduct of trimethylphosphite and phenanthrenequinone gave 10,10-dibromo-9-phenanthrone (36).


10-Diazo-9-phenanthrone.--Phenanthrenequinone and p-toluenesulfonylhydrazide react (37) to yield 10-diazo-9-phenanthrone.


α-Bromopropionamide.--Ammonolysis of methyl-α-bromo-propionitrile afforded α-bromopropionamide (38).

\( \alpha \)-Chloropropionitrile.—Treatment of lactonitrile with thionyl chloride afforded \( \alpha \)-chloropropionitrile \((39)\).


Methanesulfonylhydrazide \((40)\).—A stirred mixture of

\((40)\) H. Kloes, Ger. 1,069, 637, Nov. 26, 1959.

Hydrazine \((64 \text{ g.}, 2 \text{ moles})\), sodium hydroxide \((3.5 \text{ g.})\),
and dioxane \((125 \text{ ml.})\) was cooled to 15-20\(^\circ\). Methanesulfonyl chloride \((114 \text{ g.}, 1 \text{ mole})\) in dioxane \((60 \text{ ml.})\) was added slowly and a solid was obtained. The mixture was stirred for 4 hours, filtered, and the solvent removed to yield methanesulfonylhydrazide \((76 \text{ g.}, 69\%)\) as a thick syrup, \(n_D^{25} = 1.4950\). The syrup slowly crystallized after about a week of infrequent scratching, m.p. 48\(^\circ\).

Alkyl- and Aralkyltriphenylphosphonium Salts

General procedure for the preparation of triphenylphosphonium salts.—The alkyl or aralkyl halide was dissolved in benzene along with an equivalent amount of
triphenylphosphine. The solution was refluxed for 2 to 10 hours; the crystalline precipitate obtained was filtered, washed with benzene and dried. With certain secondary halides, it was necessary to either fuse the compound at 100° with triphenylphosphine or to place the halide, triphenylphosphine, and acetonitrile in a bomb and heat at 150° for several hours.

The triphenylphosphonium salts were used, after thorough drying, without further purification although they could, for the most part, be recrystallized from alcohol and water or alcohol and ether.

9-Fluorenyltriphenylphosphonium bromide. — m.p. 297° (dec.), lit. (11) 301°.


Carboethoxymethyltriphenylphosphonium bromide. — m.p. 161°, lit. (12) 158°.

Methyltriphenylphosphonium iodide.—m.p. 187°, lit. (43) 184-186°.


Ethyltriphenylphosphonium bromide.—m.p. 201°, lit. (44) 203-205°.


Isopropyltriphenylphosphonium bromide.—m.p. 235°, lit. (45) 238-239°.


Phenacyltriphosphonium bromide.—m.p. 267°


Cyanomethyltriphosphonium chloride.—m.p. 273–274°, lit. (49) 278°.


p-Bromobenzyltriphosphonium bromide.—m.p. 271°, lit. (50) 278°.

α-Cyanobenzyltriphenylphosphonium bromide.—Bromine (176 g., 1.1 moles) was added to benzyl cyanide (117 g., 1 mole) at 105-110° in one hour. The temperature was maintained for an additional 15 minutes and dry nitrogen was then bubbled through the mixture until all of the hydrogen bromide was expelled. The liquid was mixed with triphenylphosphine (131 g., 0.5 mole) and benzene (200 ml.) and then refluxed for 8 hours. The solid (114.3 g., 50%), α-cyanobenzyltriphenylphosphonium bromide, obtained was collected, dried, and recrystallized from methanol as colorless plates, m.p. 256°.

Anal. Calcd. for C_{26}H_{21}BrNP: C, 68.27; H, 4.59;
Br, 17.72; N, 3.06.

Found: C, 68.38; H, 4.57;
Br, 17.66; N, 3.06.

α-Carboethoxyethyltriphenylphosphonium bromide.—A solution of triphenylphosphine (26.1 g., 0.1 mole), benzene (300 ml.), and ethyl α-bromopropionate (18.1 g., 0.1 mole) was warmed at 55-60° for 12 hours. The solvent was removed and the oil was triturated with ether to give a solid. The collected solid was washed with ether and
dried. The solid was recrystallized from ethyl acetate and petroleum ether to yield \( \alpha \)-carboethoxyethyltriphenylphosphonium bromide (25.8 g., 58.4\%), m.p. 195\(^\circ\), lit. (42) 199-200\(^\circ\).

\( \alpha \)-Carbomethoxyethyltriphenylphosphonium bromide.—A stirred solution of triphenylphosphine (26.1 g., 0.1 mole), benzene (300 ml.), and methyl \( \alpha \)-bromopropionate (16.7 g., 0.1 mole) was heated at 60\(^\circ\) for 12 hours. A small amount of solid precipitated. The solution was decanted from the solid and then evaporated. The resulting oil upon trituration with ether yielded a solid. The two solids were combined, washed thoroughly with ether, and then dried. The solid was recrystallized from ethyl acetate and petroleum ether to yield \( \alpha \)-carbomethoxyethyltriphenylphosphonium bromide (22 g., 51.4\%), m.p. 175\(^\circ\), lit. (42) 178-180\(^\circ\).

**Stable Alkylidene- and Aralkylidene-triphenylphosphoranes**

**General handling procedure.**—These compounds are generally stable to air and moisture. It is desirable to dry them thoroughly and store under nitrogen. These compounds,
however, should not be warmed with aqueous bases and even in their preparation, aqueous bases should be added with caution.

**9-Fluorenylidenediarylphosphorane.** — 9-Fluorenylidenediarylphosphorane (10.12 g., 0.02 mole), in methanol (100 ml.), on treatment with sodium methoxide (1.08 g., 0.02 mole) gave 9-fluorenylidenediarylphosphorane (8.5 g., 100%) as a yellow crystalline material, m.p. 276°, lit. (41) 276°.

**Diphenylmethylenetriarylphosphorane.** — Reaction of a suspension of diphenylmethylenetriarylphosphorane (10.16 g., 0.02 mole), in benzene (100 ml.), with potassium t-butoxide (3 g., 0.027 mole) gave a bright red solution after stirring for 2 hours. The mixture was concentrated and cooled to give red crystalline diphenylmethylenetriarylphosphorane (7.69 g., 90%), m.p. 172°, lit. (41) 172°.

**α-Carboethoxymethylenetriarylphosphorane.** — α-Carboethoxymethylenetriarylphosphorane was converted quantitatively to α-carboethoxymethylenetriarylphosphorane by 3N sodium hydroxide according to known procedures (42), m.p. 116°.
α-Carbomethoxyethylidenetriphenylphosphorane (42).—

Reaction of α-carbomethoxyethyltriphenylphosphonium bromide with 3N sodium hydroxide gave α-carbomethoxyethylidenetriphenylphosphorane in 80% yield, m.p. 150°.

α-Carboethoxyethylidenetriphenylphosphorane (42).—

α-Carboethoxyethyltriphenylphosphonium bromide was converted to α-carboethoxyethylidenetriphenylphosphorane in 86% yield, m.p. 156°.

α-Benzoylmethylenetriphenylphosphorane. Addition of 3N sodium hydroxide (5.4 g., 0.135 mole) to a suspension of α-benzoylmethyltriphenylphosphonium bromide gave a white precipitate. The mixture was stirred for 1 hour and then filtered. The solid was dried thoroughly and found to be α-benzoylmethylenetriphenylphosphorane (48 g., 96%), m.p. 178°, lit. (47) 178-180°.

α-(p-Bromobenzoyl)methylenetriphenylphosphorane. α-(p-Bromobenzoyl)methyltriphenylphosphonium bromide (10.78 g., 0.02 mole) was suspended in water (60 ml.) and then treated with 3N sodium hydroxide (0.8 g., 0.02 mole). The white solid was dried and identified as α-(p-bromobenzoyl)methylenetriphenylphosphorane (8.26 g., 90%), m.p. 200°, lit. (48) 201-201.5°.
Preparation of Alkyl- and Aralkylphosphonates

Triethyl phosphonoacetate.--Ethyl bromoacetate (66.8 g., 0.4 mole) was added dropwise to triethyl phosphite (66.48 g., 0.4 mole) at 80°. The pot temperature was raised to 130° until ethyl bromide ceased to be collected. The mixture on distillation at 112-115°/1 mm. gave triethyl phosphonoacetate (51) (73.4 g., 82.3%), \( n_D^{25} 1.4280 \).


Diethyl cyanomethylphosphonate.--Triethyl phosphite (66.48 g., 0.4 mole) was heated to 80° and chloroacetonitrile (30 g., 0.4 mole) was added dropwise. The temperature was raised to 125-130° until ethyl chloride stopped distilling. Distillation of the mixture at 120-122°/1 mm. gave diethyl cyanomethylphosphonate (45 g., 64%), \( n_D^{25} 1.4319 \), lit. (52) 127-131°/1 mm.

**Diethyl diphenylmethylphosphonate.**—Bromodiphenylmethane (131 g., 0.53 mole) and triethyl phosphite (88 g., 0.53 mole) were heated at 165° until ethyl bromide ceased to distill. The viscous oil, on distillation at 180-182°/1 mm., gave diethyl diphenylmethylphosphonate (51) (87.8 g., 55%).

**Diethyl benzylphosphonate.**—Benzyl chloride (101 g., 0.8 mole) was added dropwise to triethyl phosphite (95.2 g., 0.8 mole). The temperature was raised to 150° until all of the ethyl chloride was removed. Distillation, 132-134°/1 mm., of the viscous oil gave diethyl benzylphosphonate (51) (113 g., 62%).

**Diethyl phenacylphosphonate.**—Triethyl phosphite (44 g., 0.26 mole) and phenacyl bromide (51 g., 0.26 mole) on mixing gave a mild exothermic reaction. The mixture was heated to 150° until the ethyl bromide ceased to distill. The oil, on distillation at 155-165°/0.1 mm., gave diethyl phenacylphosphonate (51) (56 g., 86%).
Reactions of Phenanthrenequinone with Alkylidenetriphenylphosphoranes and Alkylphosphonate Anions

General procedure.—All reactions with triphenylphosphoranes and phosphonate anions were conducted under nitrogen. Unstable triphenylphosphoranes were prepared in a 250 ml., 4 neck round bottom flask equipped with a stopcock leading to a 24/40 ground glass male joint. The flask was then used as a dropping funnel in order to add the triphenylphosphorane to phenanthrenequinone or 1-nitrophenanthrenequinone, thus avoiding contact with either air or moisture. All reactions of sodium hydride with dimethyl sulfoxide or phosphonate esters were conducted under nitrogen.

Reaction of phenanthrenequinone and methylenetriphenylphosphorane.—A suspension of dimethyl sulfoxide (60 ml.) and sodium hydride (0.9 g., 0.02 mole, 53.4%) was warmed at 65-75° until the evolution of hydrogen was complete. Methyltriphenylphosphonium iodide (8.06 g., 0.02 mole) in dimethyl sulfoxide (35 ml.) was slowly added to the light yellow solution at 20-25°. A bright yellow solution was obtained. Stirring was continued for
0.5 hour and the solution then slowly added to a stirred mixture of phenanthrenequinone (4.16 g., 0.02 mole) and dimethyl sulfoxide (100 ml.). The mixture turned green and increased in temperature 5°; it was stirred at room temperature for 6 hours and poured on ice. The precipitate was collected, dissolved in chloroform, washed well with water, and dried. The solvent was removed at 25°; the solid upon chromatography on acid-washed alumina with benzene gave two dimers. (These dimers may also be separated by dissolving the mixture in a small amount of chloroform. After standing for 2 hours, a crude dimer (melting at 245°) is obtained. The solution is evaporated to give a lower melting dimer.) The first dimer was 3',4'-dihydrospiro[phenanthrene-9(10H),2'-2[H]phenanthro[9,10-b]pyran]-10-one, a dimer of 10-methylene-9-phenanthrone (0.977 g., 12.1%) which was recrystallized from benzene, m.p. 253°, lit. (12) 251-252°. The compound showed strong infrared absorption (Fig. 1) at 6.0 (carbonyl) and 9.0 μ (ether band). It was not possible to obtain a nuclear magnetic resonance spectrum of the dimer because of its insolubility in spectral solvents; ultraviolet absorption (Fig. 46):
251( ε 63,500), 277( ε 21,500), 297( ε 11,500), and 308μ ( ε 10,500).

**Anal. Calcd. for C₃₀H₂₀O₂:** C, 87.38; H, 4.85;
mol. wt. 412.

**Found:** C, 87.20; H, 4.63;
mol. wt. 425.

The second dimer was a light yellow solid which was rechromatographed twice and recrystallized from ligroin as yellow plates, m.p. 151-154°. The solid (2.01 g., 24.3%) was identified as a second dimer of 10-methylene-9-phenanthrone. The infrared spectrum (Fig. 2) exhibits strong bands at 5.89μ(carbonyl); nuclear magnetic resonance spectrum (Fig. 32) has in addition to aromatic protons (16H), three singlets at 5.92 (2 benzylic H), 6.42 (1H on ethereal carbon deshield by a carbonyl group), and 6.68μ(1H on ethereal carbon); ultraviolet absorption (Fig. 47); 252( ε 64,500), 279( ε 20,000), and 320μ( ε 11,500).

**Anal. Calcd. for C₃₀H₂₀O₂:** C, 87.38; H, 4.85;
mol. wt. 412.

**Found:** C, 86.96; H, 4.73;
mol. wt. 414.
Reaction of phenanthrenequinone and benzylidenetriphenylphosphorane.—The anion of dimethyl sulfoxide was prepared by heating dimethyl sulfoxide (60 ml.) and sodium hydride (1.8 g., 0.04 mole, 53.4%) at 75° until evolution of hydrogen was complete. Benzyltriphenylphosphonium bromide (17.27 g., 0.04 mole) in dimethyl sulfoxide (100 ml.) was added to the stirred solution at 20-25°; the orange solution was stirred for 15 minutes at 25°. Phenanthrenequinone (4.16 g., 0.02 mole) in dimethyl sulfoxide (100 ml.) was added dropwise to the triphenylphosphorane solution. The temperature increased 7° and the solution changed color. The mixture was stirred and heated at 70° for 2 hours, cooled, and poured onto cracked ice. The solid obtained was collected, dried, dissolved in ligroin (200 ml.), and the solution cooled. The triphenylphosphine oxide was filtered, the filtrate evaporated, and the residue dissolved in benzene and chromatographed on acid-washed alumina. The major band was collected and the solvent removed. The oily residue was dissolved in ligroin (65-100°) and upon cooling deposited colorless plates of 2,3-diphenylphenanthro[9]dihydrofuran
(6.13 g., 86%), m.p. 145-147°. Infrared absorption (Fig. 3): 6.1 (C=C), 6.23 (aromatic C=C), and 9.78 μ(C=O-); nuclear magnetic resonance (Fig. 33): 2.67 (18 aromatic H, m.), 4.19 (benzylic 1H, d.), and 4.33 (1H on ethereal C,d); ultraviolet absorption (Fig. 48): 253(ε 65,000), 259 (ε 66,000), 280(ε 21,500), and 315μμ(ε 15,500).

Anal. Calcd. for C_{28}H_{20}O: C, 90.32; H, 5.38;
mol. wt. 372.

Found: C, 89.88; H, 5.29;
mol. wt. 372.

Reaction of phenanthrenequinone and benzylidenetriphenylphosphorane.--Phenanthrenequinone (2.08 g., 0.01 mole) was reacted with benzylidenetriphenylphosphorane (7.02 g., 0.02 mole) according to the procedure of Parrick (8); 2,3-diphenylphenanthro[2]dihydrofuran (1.702 g., 46%), m.p. 146-147°, was obtained. Its mixed melting point with an authentic sample was not depressed and the infrared spectra of the two samples were superimposable. It is therefore concluded that the product is not 10-benzylidene-9-phenanthrone as formulated by Parrick. The nuclear magnetic resonance spectrum was
the same as that of an authentic sample of 2,3-diphenyl-

Reaction of benzyldenetriphenylphosphorane and excess
phenanthrenequinone.—Dimethyl sulfoxide (60 ml.) and
sodium hydride (0.9 g., 0.02 mole, 53.4%) were heated at
75° until evolution of hydrogen was complete. The light
yellow solution upon dropwise treatment at 20-25° with
benzyltriphenylphosphonium bromide (8.64 g., 0.02 mole)
in dimethyl sulfoxide (60 ml.) turned bright orange. The
benzyldenetriphenylphosphorane was slowly added to a
mixture of phenanthrenequinone (6.24 g., 0.03 mole) and
dimethyl sulfoxide (100 ml.). The mixture increased in
temperature 6° and darkened in color. After having been
stirred overnight at room temperature, the mixture was
poured on ice to obtain a solid. The mixture was extracted
with chloroform, the extract dried, the solvent removed,
and the oil chromatographed on acid-washed alumina with
benzene. Colorless needles of 10-benzyldene-9-phenanthrone
(0.851 g., 15.1%) were obtained. Infrared absorption
(Fig. 4): 5.98μ(carbonyl); nuclear magnetic resonance
spectrum:(Fig. 34): 2.92 (13H, m) and 3.17τ(1H, s).
When this compound was recrystallized from ligroin or the original reaction mixture was warmed at 65°, two dimers of 10-benzylidene-9-phenanthrone were obtained and separated on acid-washed alumina with benzene. The colorless dimer (A) melted at 250° (dec.). Infrared absorption (Fig. 5): 5.95\mu (carbonyl); nuclear magnetic resonance (Fig. 35): 2.85T(m, aromatic) and 3.3, 3.4 and 3.7T(3 triplets); ultraviolet absorption (Fig. 49): 255(\epsilon 65,212), 279(\epsilon 27,752), and 311\mu (\epsilon 11,563).

**Anal. Calcd. for C_{21}H_{14}O:** C, 89.36; H, 4.96;

mol. wt. 564.

**Found:** C, 89.31; H, 5.18;

mol. wt. 535.

The second fraction consisted of a trace of yellow solid (B) which was recrystallized from ligroin, m.p. 248-250°. This product may be a geometrical isomer of the first dimer. Infrared absorption (Fig. 6): 5.97\mu (carbonyl).

**Anal. Calcd. for C_{21}H_{14}O:** C, 89.36; H, 4.96;

mol. wt. 564.

**Found:** C, 88.63; H, 4.87;

mol. wt. 515.
Attempted reaction of phenanthrenequinone and diethyl benzylphosphonate anion.— Dimethyl sulfoxide (40 ml.), glyme (80 ml.), and sodium hydride (2.24 g., 0.05 mole, 53.4%) were heated at 65-75° until evolution of hydrogen ceased. Diethyl benzylphosphonate (11.35 g., 0.05 mole) was added to the stirred solution at 20°. The deep red solution was slowly added to a stirred mixture of phenanthrenequinone (5.2 g., 0.025 mole) and glyme (75 ml.). The mixture was stirred overnight and then refluxed for 3 hours. The solution was cooled, diluted with water and ice, and extracted with chloroform. The extract was washed thoroughly with water and dried. The solution was concentrated and chromatographed on acid-washed alumina to give a brown fraction. Upon removal of the solvent and trituration of the oil with ligroin, phenanthrenequinone (5 g., 96.2% recovery), m.p. 206°, was obtained. No other products were found.

2,3-Diphenylphenanthro[9]furan

2,3-Diphenylphenanthro[9]dihydrofuran (3.72 g., 0.01 mole) in carbon tetrachloride (60 ml.) was refluxed with α-bromosuccinimide (3.56 g., 0.02 mole) and benzoyl
peroxide (20 mg.). After 3 hours, the cooled solution was filtered and the solvent was removed. The solid was recrystallized from ligroin as white plates of 2,3-diphenylphenanthro[ε]furan (3.0 g., 81.1%), m.p. 194°. Infrared absorption (Fig. 7): 9.1 μ(vinyl ether); nuclear magnetic resonance (Fig. 36): 2.5 (1H, m); ultraviolet absorption (Fig. 50): 245(ε 41,000), 282(ε 56,500, 330 (ε 26,660), and 365μ(ε 7,333).

Anal. Calcd. for C_{28}H_{18}O: C, 90.81; H, 4.86;
mol. wt. 370.

Found: C, 90.67; H, 4.86;
mol. wt 358.

2,3-Di-(p-bromophenyl)phenanthro[ε]dihydrofuran.—Dimethyl sulfoxide (60 ml.) and sodium hydride (0.9 g., 0.02 mole, 53.4%) were warmed at 75° until all of the hydrogen had evolved. p-Bromobenzyltriphenylphosphonium bromide (5.11 g., 0.02 mole) in dimethyl sulfoxide (60 ml.) was carefully added at 20-25° to the stirred mixture. A deep orange solution of p-bromobenzylidenetriphenylphosphorane resulted. phenanthrenequinone (2.08 g., 0.01 mole) in dimethyl sulfoxide (75 ml.) was added slowly to the
triphenylphosphorane solution. Stirring was continued for 0.75 hour and the mixture was heated at 65° for 4 hours. The cooled solution was poured on cracked ice and the mixture was extracted with chloroform. The extract was dried, the solvent evaporated, and the oil was extracted with hot ligroin to give triphenylphosphine oxide on cooling. The filtrate was evaporated. The oil upon dissolution in benzene and chromatography on acid-washed alumina gave only one band. On removal of the solvent, a white solid was obtained which on recrystallization from ligroin yielded colorless plates of 2,3-di-(p-bromophenyl) phenanthro[9]dihydrofuran (3.5 g, 66.8%), m.p. 149-152°. Infrared absorption (Fig. 8): 9.85 μ(C=O-); ultraviolet absorption (Fig. 51): 237(ε 19,565), 258(ε 24,565), 280(ε 9,130), 315(ε 5,434), and 370μ(ε 1,521); nuclear magnetic resonance (Fig. 37): 2.59τ(16H, m), 4.42τ(1H on benzylic carbon, d.) and 5.25τ(1H on ethereal carbon, d.).

**Anal. Calcd. for C28H18Br2O:**
C, 63.39; H, 3.40; Br, 30.19; mol. wt. 530.

**Found:**
C, 63.44; H, 3.55; Br, 30.22; mol. wt. 520.
10-(p-Bromobenzylidene)-9-phenanthrone.—Dimethyl sulfoxide (60 ml.) and sodium hydride (0.9 g., 0.02 mole, 53.4%) were warmed at 75° until all of the hydrogen had evolved. p-Bromobenzyltriphenylphosphonium bromide (10.22 g., 0.02 mole) in dimethyl sulfoxide (70 ml.), upon being slowly added to the stirred yellow solution at 20-25°, gave a deep orange-colored solution. The p-bromobenzylidenetriphenylphosphorane was added dropwise to a mixture of phenanthrenequinone (6.24 g., 0.03 mole) and dimethyl sulfoxide (100 ml.). The mixture warmed 5° and changed in color. Stirring was continued for 2 hours and the mixture was heated at 65° for 1 hour. The solution was cooled and poured on ice. The mixture was extracted with chloroform, the extract dried, and the solvent removed. The residue, upon extraction with hot ligroin and cooling, gave triphenylphosphine oxide and phenanthrenequinone (2.9 g.). The filtrate was evaporated and the oil obtained was dissolved in benzene and chromatographed on acid-washed alumina. Fraction 1, after boiling with hot ligroin, yielded a white solid which was recrystallized from ligroin as colorless plates of
10-(p-bromobenzylidene)-9-phenanthrone (1.2942 g., 21.7%), m.p. 290°. Infrared absorption (Fig. 9): 5.99 µ(C=0); ultraviolet absorption (Fig. 52): 255(ε 39,516), 278(ε 13,709), and 312µε(ε 4,838); nuclear magnetic resonance (Fig. 38): 2.7τ(12H, m) and 3.17τ(1H, s).

*Anal.* Calcd. for C_{21}H_{13}BrO: C, 69.81; H, 3.60; Br, 22.16; mol. wt. 361.

Found: C, 70.01; H, 3.76; Br, 21.55; mol. wt. 370.

The second fraction on evaporation gave a yellow solid (0.1241 g.) which was decolorized and recrystallized from ligroin as colorless needles, m.p. 285-286°. Infrared absorption: 6.0 (C=0)µ. It was not possible to obtain meaningful analytical data for this product and it was not investigated further.

*Anal.* Found: C, 62.37; H, 3.30; Br, 18.90.

The third fraction, on concentration, yielded a yellow solid. Crystallization from ligroin gave orange clusters (44.6 mg., 1%), m.p. 150-151°. Infrared absorption (Fig. 10): 6.0µ(C=0); ultraviolet absorption (Fig. 53): 254(ε 26,000), 300(ε 9,250), and 355µε(ε 5,600).
Anal. Calcd. for $C_{21}H_{13}BrO$:  
$C$, 69.81;  
$H$, 3.60;  
$Br$, 22.16;  
mol. wt. 361.

$C$, 68.67;  
$H$, 3.67;  
$Br$, 21.22;  
mol. wt. 335.

This compound appears to be a geometrical isomer of
10-($\alpha$-p-bromobenzylidene)-9-phenanthrone. However, no
attempt was made to assign the stereochemistry of the
two products.

10-Benzylidene-$h$-nitro-9-phenanthrone.--Dimethyl sulfoxide (50 ml.) and sodium hydride (0.45 g., 0.01 mole) were
warmed at 75° until evolution of hydrogen was complete.
Benzyltriphenylphosphonium bromide (4.32 g., 0.01 mole) in
dimethyl sulfoxide (50 ml.) was added slowly at 20-25°.
The light red solution of benzylidenetriphenylphosphorane
was added to a stirred mixture of $h$-nitrophenanthrene-
quinone (2.53 g., 0.01 mole) and dimethyl sulfoxide
(150 ml.). After the mixture had increased in temperature
6°, it was stirred for 2 hours at 26°, then stirred and
warmed at 65° for 2 hours. After the solution had been
poured on ice, the mixture was extracted with chloroform;
the extract was washed thoroughly with water and dried.
Removal of solvent yielded an oil which was chromatographed
on acid-washed alumina with benzene to give 2 bands. The first band gave a yellow solid (~30 mg.) which is believed to be 2,3-diphenyl-4-nitrophenanthro[9]dihydrofuran because of the lack of a carbonyl peak in its infrared spectrum and a similarity to 2,3-diphenylphenanthro[9]dihydrofuran.

The second band gave a yellow solid which, on recrystallization from ligroin, gave yellow needles of 10-benzylidene-4-nitro-9-phenanthrone (0.785 g., 24%), m.p. 205-207°. Infrared absorption (Fig. 11): 5.98 (C=O), 6.57, and 7.48 (–NO2); ultraviolet absorption (Fig. 54): 246(ε 26,425) and 345(ε 10,514); nuclear magnetic resonance (Fig. 39): 2.55 (12H, m) and 2.86 (1H, s).

Anal. Calcd. for C21H13NO3: C, 77.06; H, 3.98; N, 4.13; mol. wt. 327.

Found: C, 76.69; H, 4.14; N, 4.05; mol. wt. 328.

Attempted preparation of 10-diphenylmethylene-9-phenanthrone—Diphenylmethylenetriphenylphosphorane (4.27 g., 0.01 mole) in dimethyl sulfoxide (50 ml.) was added to a suspension of phenanthrenequinone (2.08 g., 0.01 mole) and dimethyl sulfoxide (75 ml.). The mixture was stirred and warmed at 75° for 15 hours. The solution
was poured onto ice and the solid was collected. The solid
was chromatographed on acid-washed alumina with methylene
chloride. Only phenanthrenequinone (2.0 g., 96.2% recovery), m.p. 208° was found.

This reaction was also attempted using benzene and
chloroform as solvents. In both cases, phenanthrenequinone was recovered in almost quantitative yield.

10-Diphenylmethylenne-4-nitro-9-phenanthrone.—Diphenyl-
methylenetriphenylphosphorane (4.25 g., 0.01 mole) in
dimethyl sulfoxide (60 ml.) was added to a stirred mixture
of 4-nitrophenanthrenequinone (2.53 g., 0.01 mole) and
dimethyl sulfoxide (100 ml.). Stirring was continued
overnight, and the mixture was warmed at 50° for 0.5 hour.
The mixture was poured on ice to yield a solid which was
collected, dissolved in chloroform, and dried. The sol-
vent was removed, the residue upon extraction with hot
ligroin and cooling deposited triphenylphosphine oxide.
Evaporation of the filtrate and chromatography of
the residue on acid-washed alumina with benzene gave
a solid and 4-nitrophenanthrenequinone (1.0 g.). The
solid, on recrystallization from ligroin, yielded orange
needles of 10-diphenylmethylene-4-nitro-9-phenanthrone (1.508 g., 62.6%), m.p. 235-237°. Infrared absorption (Fig. 12): 6.0 (C=O), 6.6 and 7.4μ(-NO₂); ultraviolet absorption (Fig. 55): 250(ε 34,000) and 340μ(ε 12,500).

Anal. Calcd. for C₂₇H₁₇NO₃: C, 80.37; H, 4.22;
        N, 3.47; mol. wt. 403.
        Found: C, 80.53; H, 4.41;
        N, 3.81; mol. wt. 393.

10-(α-Cyanobenzylidene)-4-nitro-9-phenanthrone.—

Dimethyl sulfoxide (60 ml.) and sodium hydride (0.45 g., 0.01 mole, 53.4%) were warmed at 75° until all of the hydrogen had evolved. α-Cyanobenzyltriphenylphosphonium bromide (4.57 g., 0.01 mole) in dimethyl sulfoxide (40 ml.) was added to the stirred solution at 20-25°. The yellow solution of α-cyanobenzylidenetriphenylphosphorane was added slowly to a stirred mixture of 4-nitrophenanthrenequinone (2.53 g., 0.01 mole) in dimethyl sulfoxide (200 ml.). The mixture was stirred for 2 hours at room temperature and then was heated at 75° for 2 hours. The solution was poured on cracked ice and extracted with chloroform. The extract was washed well with water and dried. The solvent was removed and the residue extracted with hot ligroin and
cooled to yield triphenylphosphine oxide. The filtrate was evaporated; chromatography of the oil on acid-washed alumina with benzene yielded a yellow band. Removal of the solvent gave a solid which after recrystallization from ligroin yielded yellow plates of 10-(a-cyanobenzylidene)-4-nitro-9-phenanthrone (2.1 g., 60%), m.p. 238°. Infrared absorption (Fig. 13): 4.54 (-C=\textit{H}), 5.98 (C=O), 6.6 and 7.4\mu (\textit{NO}_2); ultraviolet absorption (Fig. 55): 260 (\epsilon 29,600) and 340\mu (\epsilon 13,200).

**Anal. Calcd. for C_{22}H_{12}N_{2}O_{3}:** C, 75.00; H, 3.41;
\[\text{N}, 7.95; \text{mol. wt. 352.}\]

**Found:** C, 75.23; H, 3.58;
\[\text{N}, 7.52; \text{mol. wt. 337.}\]

**3-Methoxy-4'-nitro-3-phenylphenanthro[9]valerolactone**

10-(a-Cyanobenzylidene)-4-nitro-9-phenanthrone (0.176 g., 0.0005 mole), methanol (200 ml.), p-toluene-sulfonylhydrazide (0.1 g., 0.0005 mole), and hydrochloric acid (6 drops, 1N) were refluxed for 14 hours. The solvent was removed, methanol (6 ml.) was added to the residue, and the solid was collected. The solid was recrystallized from methanol as yellow needles of
3-methoxy-4'-nitro-3-phenylphenanthro[9]valerolactone (0.165 g., 86%), m.p. 208–209°. Infrared absorption (Fig. 14): 5.6 (lactone carbonyl), 6.5 (NO₂), and 9.25 μ (OCH₃); nuclear magnetic resonance (Fig. 40): 6.7 (3H singlet, OCH₃) and 2.67 μ (12H multiplet, aromatic); ultraviolet absorption (Fig. 57): 245 (ε 26,666) and 320 μ (ε 14,814).

**Anal.** Calcd. for C₂₃H₁₅NO₅: C, 71.61; H, 3.89; N, 3.63.

Found: C, 71.75; H, 4.10; N, 3.67.

When the reaction was repeated without p-toluene-sulfonylhydrazide, 3-methoxy-3-phenylphenanthro[9]valerolactone was obtained in 90% yield.

**10-Fluorenylidene-9-phenanthrone.**—Fluorenylidene-triphenylphosphorane (21.25 g., 0.05 mole) in chloroform (60 ml.) was added to a mixture of phenanthrenequinone (10.4 g., 0.05 mole) and chloroform (100 ml.). The mixture was stirred for 3 hours at room temperature and then refluxed for 2 hours. The solvent was removed and the solid was chromatographed on acid-washed alumina with
benzene. The solvent was removed and the red oil was triturated with ethanol (15 ml.). The red solid, 10-fluorenlylidene-9-phenanthrone, was recrystallized from ligroin as red plates (10.1 g., 57%), m.p. 204-205°. The compound had a strong carbonyl absorption at 6.01μ in its infrared spectrum (Fig. 15); ultraviolet absorption (Fig. 58):

\[
\begin{align*}
245(\epsilon 47,200), 272(\epsilon 55,200), & \text{ and } 380\mu(\epsilon 16,000).
\end{align*}
\]

Anal. Calcd. for C_{27}H_{16}O: C, 91.01; H, 4.49; mol. wt. 356.

Found: C, 91.47; H, 4.99; mol. wt. 348.

The product was obtained in approximately the same yield when fluorenylidenetriphenylphosphorane was prepared in situ using dimethyl sulfoxide anion as base in dimethyl sulfoxide.

10-(α-Carboethoxymethylene)-9-phenanthrone.—α-Carboethoxymethylenetriphenylphosphorane (10.49 g., 0.03 mole) in methylene chloride (30 ml.) was added slowly to a stirred mixture of phenanthrenequinone (6.24 g., 0.03 mole) and glyme (70 ml.). The reaction mixture warmed 3° and was stirred for 3 hours at room temperature and refluxed.
for 3 hours. The green solution was evaporated to dryness, the solid was extracted with hot ligroin (150 ml.), and the extract was cooled and deposited triphenylphosphine oxide. The solid was collected, the filtrate was evaporated, and the solid was chromatographed on acid-washed alumina. The product was placed on the column with methylene chloride and eluted with benzene to obtain a yellow fraction. The solvent was removed; upon trituration of the solid with absolute ethanol 10-((α-carboethoxy-methylene)-9-phenanthrone (4.1 g., 48%) was obtained. The product was recrystallized from ligroin as yellow plates, m.p. 157-158°. The infrared absorption (Fig. 16) of a potassium bromide wafer of the compound showed bands at: 5.8 (broad, ester C=O and ketone C=O) and 8.0μ(C=O). A 5% chloroform solution of the product exhibited strong infrared absorption at 5.79 (ester, C=O) and 5.87μ(ketone C=O); nuclear magnetic resonance (Fig. 41): 1.84τ and 2.59 (8H, m), 3.59 (1H, S), 5.5 (2H, q), and 8.67τ(3H, t); ultraviolet absorption (Fig. 59): 255 (ε 46,721), 293 (ε 11,885), and 370μ(τ 8,196).
Reaction of phenanthrenequinone and dibromomethylene-triphenylphosphorane.—Triphenylphosphine (26.1 g., 0.1 mole) in dry methylene chloride (30 ml.) was slowly added to a stirred solution of dry methylene chloride (80 ml.) and carbon tetrabromide (16.66 g., 0.05 mole). The deep red solution was added to a stirred mixture of phenanthrenequinone (5.2 g., 0.025 mole) and methylene chloride (100 ml.). The mixture darkened and its temperature increased 5°. The mixture was stirred overnight, washed with water, and the organic layer was dried. The solvent was removed; the solid was placed on an acid-washed alumina column with methylene chloride and eluted with benzene to obtain two bands. The colorless fraction was recrystallized from ligroin and was identified as 1,1,2,2-tetramethoxymethane (61 mg., 1%), m.p. 165-167°. The infrared spectrum (Fig. 17) showed strong absorption at 13.3 (1:2 aromatic substitution) and at
13.76 (C-Br₂); ultraviolet absorption (Fig. 60): 253 (ɛ 34,700), 270 (ɛ 24,253), and 320μɛ (ɛ 7,246).

**Anal. Calcd. for C₁₄H₈Br₄:** C, 36.92; H, 1.52; Br, 61.53; mol. wt. 520.

**Found:** C, 36.62; H, 1.55; Br, 61.44; mol. wt. 500.

The yellow fraction was 10-dibromomethylene-9-phenanthrone (3.3 g., 36.3%). The solid was recrystallized from ligroin as yellow plates, m.p. 135°; infrared absorption (Fig. 18): 5.96 (C=O), 7.8 (C-0) and 13.8μ(ε-C-Br₂); ultraviolet absorption (Fig. 61): 260(ɛ 36,075), 288(ɛ 12,658), and 320μɛ (ɛ 7,246).

**Anal. Calcd. for C₁₅H₉Br₂:** C, 49.45; H, 2.20; Br, 43.96; mol. wt. 364.

**Found:** C, 49.59; H, 2.17; Br, 43.66; mol. wt. 353.

**Reaction of 10-dibromomethylene-9-phenanthrone and dibromomethylenetriphenylphosphorane.**—Triphenylphosphine (1.44 g., 5.5 mmoles) in methylene chloride (20 ml.) was added to a stirred solution of methylene chloride (20 ml.) and carbon tetrabromide (0.913 g., 3 mmoles). 10-Dibromomethylene-9-phenanthrone (2.0 g., 5.5 mmoles) in methylene
chloride (50 ml.) was added to the stirred red solution. Stirring was continued for 2 hours and the mixture was then refluxed overnight. The solution was concentrated and placed on an acid-washed alumina column. Two fractions were obtained: 1,1,2,2-tetrabromophenanthro[2]cyclobutene (0.16 g., 8.6%), m.p. 165-167° and 10-dibromomethylene-9-phenanthrone (0.7 g.).

Phenanthrenequinone and diethyl phenacylphosphonate anion.---Diethyl phenacylphosphonate (18.2 g., 0.075 mole) was slowly added to a stirred suspension of sodium hydride (3.36 g., 0.075 mole, 53.4%) and glyme (30 ml.) at 10°. After evolution of hydrogen was completed, the red solution was slowly added to a stirred mixture of phenanthrenequinone (15.6 g., 0.075 mole) at 8°. The mixture was stirred for 41 hours at room temperature, poured into ice water, and filtered. The solid was chromatographed on acid-washed alumina with methylene chloride to give three fractions. The first fraction was recrystallized from glyme as colorless needles and found to be 1,2-dibenzoylphenanthro[2]cyclobutene (5.0 g., 45.6%), m.p. 232°. \( \lambda^{KBr} \) (Fig. 19) 5.98\( \mu \) (s, carbonyl); nuclear magnetic
resonance (DMSO) (Fig. 42): 5.04\(\tau\)(2H, protons on tertiary carbon atom) and 2.04\(\tau\)(18H, aromatic protons); ultraviolet absorption (Fig. 62): 256(\(\varepsilon\) 64,545), 275(\(\varepsilon\) 49,090), and 324\(\mu\)u(\(\varepsilon\) 29,545).

**Anal. Calcd. for** C\(_{30}\)H\(_{20}\)O\(_2\):  C, 87.35; H, 4.81;  
mol. wt. 412.  
**Found:**  C, 87.52; H, 4.96;  
mol. wt. 415.

The second fraction was 10-(a-benzoylmethylene)-9-phenanthrone (3.5 g., 44%) and was recrystallized from glyme as yellow needles, m.p. 222-222.5\(^\circ\). The infrared spectrum (Fig. 20) exhibited a doublet for the carbonyl groups at 5.99 and 6.0\(\mu\); ultraviolet spectrum (Fig. 63): 252(\(\varepsilon\) 57,024), 322(\(\varepsilon\) 25,206), and 368\(\mu\)u(\(\varepsilon\) 5,371).

**Anal. Calcd. for** C\(_{22}\)H\(_{14}\)O\(_2\):  C, 85.16; H, 4.52;  
mol. wt. 310.  
**Found:**  C, 84.99; H, 4.41;  
mol. wt. 317.

The third fraction was phenanthrenequinone (5 g.).
Phenanthrenequinone and \( \alpha \)-benzoylmethylenetriphenylphosphorane

-Benzoylmethylenetriphenylphosphorane (7.58 g., 0.02 mole) in chloroform (65 ml.) was slowly added to a well stirred solution of phenanthrenequinone (4.16 g., 0.02 mole) and chloroform (60 ml.). The reaction mixture was stirred overnight and the dark red solution then refluxed for 1 hour. Upon removal of solvent and the trituration of the residue with benzene, a red solution and a white solid were obtained. The benzene extract was evaporated and the residue was chromatographed on acid-washed alumina with methylene chloride as eluent to give a white solid and a yellow solid. The fractions of white solids were combined and identified as 1,2-di-benzoylphenanthro[\( \mathcal{L} \)]cyclobutene (2.7 g., 64.7%), m.p. 232°. The yellow solid was 10-\( \alpha \)-benzoylmethylene-9-phenanthrone (1 g., 31.5%), m.p. 222°.

Reaction of phenanthrenequinone and \( \text{p-bromobenzoylmethylenetriphenylphosphorane} \)

-\( \text{p-Bromobenzoylmethylenetriphenylphosphorane} \) (7.18 g., 0.02 mole) in chloroform (60 ml.) was added to a stirred solution of phenanthrenequinone (4.16 g., 0.02 mole) in chloroform (60 ml.) After stirring for 1 hour, the red solution was refluxed
for 2 hours. The solution was concentrated and chromatographed on acid-washed alumina; a colorless band and a yellow band were obtained. The colorless band was removed, and the white solid recrystallized from ligroin to give colorless needles of 1,2-di-(p-bromobenzoyl)phenanthro[9]-cyclobutene (6.8 g., 60%), m.p. 274-275°. Infrared absorption (Fig. 21): 5.94 μ (carbonyl); ultraviolet absorption (Fig. 64): 257(ε 58,400), 266(ε 75,000), and 328μμ (ε 27,750).

Anal. Calcd. for C30H18Br2O2: C, 63.15; H, 3.16; Br, 28.07; mol. wt. 570.

Found: C, 62.78; H, 2.97; Br, 27.53; mol. wt. 532.

The yellow band was removed and the yellow solid recrystallized from ligroin as yellow needles of 9,10-phenanthroquinodi-(α-p-bromobenzoyl)dimethane (2.3 g., 20%), m.p. 254-255°. Infrared absorption (Fig. 22): 6.0μ (C=O); ultraviolet absorption (Fig. 65): 253(ε 69,000), 261(ε 72,500), 284(ε 41,000), 308(ε 31,000) and 360μμ (ε 10,000). It was not possible to obtain a nuclear
magnetic resonance spectrum of this compound because of the insolubility of the product in spectral solvents.

**Anal.** Calcd. for C\(_{30}\)H\(_{18}\)Br\(_2\)O\(_2\): C, 63.15; H, 3.16; Br, 28.07; mol. wt. 570.

Found: C, 62.78; H, 3.06; Br, 27.48; mol. wt. 549.

**Reactions of Alkylidenetriphenylphosphoranes with Fluorenone, Benzil, and 1,2-Naphthoquinone**

9-Dichloromethylenefluorene.--Chloroform (11.95 g., 0.1 mole) was added dropwise to a stirred slurry of triphenylphosphine (26 g., 0.1 mole), sublimed potassium t-butoxide (11.2 g., 0.1 mole), and heptane (200 ml.) at 0-10°. Fluorenone (17.0 g., 0.1 mole) in benzene (100 ml.) was then added to the yellow slurry. The mixture was refluxed for 3 hours, cooled, and filtered. The filtrate was concentrated to 0.5 the original volume and cooled to deposit triphenylphosphine oxide. The filtrate was evaporated; chromatography of the yellow solid on acid-washed alumina with benzene yielded a yellow band. The solvent was evaporated and the solid recrystallized from methanol as yellow needles of 9-dichloromethylenefluorene.
95

(11 g., 44%), m.p. 129-130°, lit. (53) 129-130° Infrared absorption (Fig. 23): 6.3 (C=C) and 13.9μ(CCl₂).

9-Dibromomethylenefluorene.--Triphenylphosphine (26.1 g., 0.1 mole) in methylene chloride (70 ml.) was carefully added to a stirred solution of carbon tetrabromide (16.66 g., 0.05 mole) in methylene chloride (200 ml.) at 20°. Fluorenone (9.0 g., 0.05 mole) in methylene chloride (100 ml.) was then added to the stirred orange solution and the mixture was stirred for 3 hours at room temperature. The mixture was refluxed for 1.5 hours, washed with water, and dried. The solution was concentrated to 40 ml. and on chromatography on acid-washed alumina gave one band. The solvent was removed and the solid was recrystallized from methanol as yellow needles of 9-dibromomethylenefluorene (8.5 g., 50.5%), m.p. 127-129°. Infrared absorption (Fig. 24): 6.3 (C=C) and 14.0μ(CBr₂).
Anal. Calcd. for C_{14}H_{8}Br_{2}: C, 50.0; H, 2.38; Br, 47.9.

Found: C, 50.37; H, 2.45; Br, 47.44.

1,2,3-Triphenylprop-2-en-1-one (A).—Sodium hydride (0.9 g., 0.02 mole, 53.4%) and dimethyl sulfoxide (60 ml.) were warmed at 75° until evolution of hydrogen was complete. Benzyltriphenylphosphonium bromide (8.64 g., 0.02 mole) in dimethyl sulfoxide (50 ml.) was slowly added to the stirred solution at 20-25°. The orange solution of benzylidene-triphenylphosphorane was slowly added to a stirred solution of benzil (4.2 g., 0.02 mole) in dimethyl sulfoxide (100 ml.) and the solution was stirred at room temperature for 3 hours. The reaction mixture was warmed at 65° for 1 hour. The cooled solution was poured on ice and extracted with chloroform. The extract was washed with water and dried. Upon removal of solvent, the resulting oil was extracted with hot ligroin and deposited triphenylphosphine oxide on cooling. The filtrate upon concentration and chromatography on acid-washed alumina gave benzil (1.4 g.) and a solid. Upon recrystallization from ethanol, the solid yielded 1,2,3-triphenylprop-2-en-1-one (3.1 g., 82%), m.p. 98°, 19t. (6) 98-99°. Infrared absorption
(Fig. 25): 6.1μ(carbonyl); nuclear magnetic resonance
(Fig. 43): 2.17-2.5τ(15H, aromatic) and 2.9τ(1H singlet);
ultraviolet absorption (Fig. 66): 240(ε 12,931), 255
(ε 13,423), and 303μ(ε 12,684).

Mol. wt. Calcd. for C21H16O: 284
Found: 285

This product was designated as 1,2,3-triphenylprop-2-en-
1-one (A).

1,2,3-Triphenylprop-2-en-1-one(B).—Sodium hydride
(0.9 g., 0.02 mole, 53.4%) and dimethyl sulfoxide (60 ml.)
were heated at 75°. A yellow solution was obtained upon
completion of hydrogen evolution. Benzyltriphenyolphos-
phonium bromide (8.64 g., 0.02 mole) in dimethyl sulfoxide
(60 ml.) was slowly added to the stirred solution at 20°
to yield an orange solution of benzylidenetriphenylphos-
phorane. Benzil (2.1 g., 0.01 mole) in dimethyl sulfoxide
(80 ml.) was added, dropwise, to the orange solution and
the mixture was stirred at room temperature for 1 hour and
then heated overnight at 65°. The cooled solution was
poured on ice and extracted with chloroform. After the
organic layer was washed with water and dried, the solvent
was removed. The resulting oil was extracted with hot
ligroin and the extract deposited triphenylphosphine oxide on cooling. The filtrate was concentrated and chromato-
graphed on acid-washed alumina. A single band was ob-
tained. The solvent was removed and the oil was fraction-
ally crystallized from ethanol. The lesser soluble isomer of 1,2,3-triphenylprop-2-en-1-one (A) (2.08 g., 72.5%),
m.p. 98°, lit. (6) 98-99° was obtained first. The more soluble isomer of 1,2,3-triphenylprop-2-en-1-one (0.6 g.,
21.1%), m.p. 81-82°, lit. (6) 89° subsequently separated.
Infrared absorption (Fig. 26): 6.0 μ (carbonyl); nuclear magnetic resonance (Fig. 44): 2.67 (16H, m.); ultraviolet absorption (Fig. 68): 240 (ε 34,403), 261 (ε 47,700), and 285 μ (ε 48,623).

Found: 296.

Reaction of benzil with α-carbomethoxymethylenetri-
phenylphosphorane. --α-Carbomethoxymethylenetriphenylphos-
phorane (3.33 g., 0.01 mole) in dimethyl sulfoxide (40 ml.) was added slowly to a stirred solution of benzil (2.1 g.,
0.01 mole) in dimethyl sulfoxide (100 ml.). The mixture was stirred at 25° for 1 hour and was then stirred at 65° for 3 hours. The solution was poured on ice, the mixture
was extracted with chloroform; the extract was washed with water, and dried. The solvent was removed and the oil was treated with methanol. The resulting solid was recrystallized from chloroform as white plates of α-benzoyl-β-carbomethoxystyrene (1.2 g., 45.1%), m.p. 215°. Infrared absorption (Fig. 27): 5.85 (ester carbonyl), 6.0 (keto carbonyl), and 11.5μ (C=CH-); ultraviolet absorption (Fig. 68): 250(e 19,238) and 275μv (e 17,142); nuclear magnetic resonance (Fig. 45): 2.0 (2H, multiplet, ortho to carbonyl), 2.39 (8H, multiplet, aromatic), 3.47 (1H singlet, vinyl proton) and 6.44 τ (3H singlet, OCH₃).

**Anal. Calcd. for C₁₇H₁₄O₃:**
C, 76.65; H, 5.26;
mol. wt. 266.

**Found:**
C, 76.78; H, 5.06;
mol. wt. 276.

**Reaction of 1,2-naphthoquinone and fluorenylidetriphenylphosphorane.**—Fluorenylidetriphenylphosphorane (4.25 g., 0.01 mole), 1,2-naphthoquinone (1.58 g., 0.01 mole), and chloroform (110 ml.) were stirred overnight. The solution was evaporated to dryness and the residue
was chromatographed on acid-washed alumina. Only fluor­
enone (0.14 g., 7.8%), m.p. 82-83°, was obtained. No
other products were found.

**Reaction of 1,2-naphthoquinone and benzylidenetri-
phenylphosphorane.**—Dimethyl sulfoxide (60 ml.) was
warmed at 75° with sodium hydride (0.9 g., 0.02 mole,
53.4%) until evolution of hydrogen was complete. Benzyl-
triphenyolphosphonium bromide (8.64 g., 0.02 mole) in
dimethyl sulfoxide (50 ml.) was added to the stirred
mixture. The yellow solution was added to 1,2-naphtho-
quinone (2.16 g., 0.02 mole) in dimethyl sulfoxide (100 ml.).
The mixture was stirred at room temperature for 10 minutes
and was then warmed at 65° for 1.5 hours. The cooled
solution was poured on ice, the mixture was extracted with
chloroform and the extract was washed with water and dried.
Upon removal of solvent, an oil was obtained which when
treated with benzene gave an insoluble carbon-like material.
The benzene solution yielded only triphenylphosphine oxide
upon chromatography. No products were found.

**Reaction of 1,2-naphthoquinone and α-phenacylidene-
triphenylphosphorane.**—α-Phenacylidenetriphenylphosphorane
(3.79 g., 0.01 mole) in chloroform (50 ml.) was carefully added to a stirred solution of 1,2-naphthoquinone (1.58 g., 0.01 mole) in chloroform (60 ml.) and the mixture was stirred overnight. The solution was evaporated to dryness and the residue was extracted with hot ligroin. Triphenylphosphine oxide was deposited on cooling. The filtrate was evaporated and the residue was dissolved in benzene. Chromatography on acid-washed alumina yielded one band. The solvent was removed and the white solid was recrystallized from ligroin as white plates of unidentified product (0.085 g.), m.p. 145°. Infrared absorption (Fig. 28): 5.94 (carbonyl), 9.3 and 10.1 μ(ether).

Anal. Calcd. for C₁₈H₁₂O₂: C, 83.1; H, 4.61.
Found: C, 83.94; H, 4.63.

**Attempted reaction of p-toluene-sulfonylhydrazide and 10-dibromomethylene-9-phenanthrone**

10-Dibromomethylene-9-phenanthrone (2 g., 0.0055 mole), p-toluenesulfonylhydrazide (1.02 g., 0.0055 mole), and benzene (150 ml.) were refluxed for 2 hours. The cooled solution was filtered free of p-toluenesulfonylhydrazide,
and was then concentrated to a small volume. 10-Fluorenylidene-9-phenanthrone (3.53 g., 99.1% recovery) was recovered.

The mesyldrazone of 10-fluorenylidene-9-phenanthrone

10-Fluorenylidene-9-phenanthrone (2.0 g., 0.0056 mole), methanesulfonylhydrazide (0.62 g., 0.0056 mole), benzene (30 ml.), and methanol (100 ml.) were refluxed overnight. The solvent was removed. The dark residue was dissolved in hot methanol, clarified, and allowed to cool to deposit colorless crystals of the mesyldrazone of 10-fluorenylidene-9-phenanthrone (1.2 g., 41%). It decomposed from 90-110°, but did not melt. Infrared spectrum (Fig. 29): 3.0 (NH₂), 6.1 (C=N), and 7.5 and 8.5 (SO₂).

When excess methanesulfonylhydrazide was used, the crude reaction was found to contain 10-fluorenylidene-9-diazophenanthrene in addition to the mesyldrazone.

  Found: N, 5.98.

10-Fluorenylidene-9-phenanthrone hydrazone

10-Fluorenylidene-9-phenanthrone (3.56 g., 0.01 mole) in benzene (80 ml.) was treated dropwise with hydrazine
(3 ml., 97.5%) at 10°. The solution was stirred for 0.75 hour at 10°, then washed with water and dried. The solvent was removed in vacuo and the tan solid was recrystallized from a small portion of ether as light yellow plates of 10-fluorenylidene-9-phenanthrone hydrazone (3.59 g., 97%), m.p. 137° (dec.). The hydrazone is not stable to light and air. Infrared absorption (Fig. 30): 2.91 and 3.05 (NH₂) and 6.2μ(C=N).

**Anal. Calcd. for C_{27}H_{18}N₂:**  
N, 7.56%;  
mol. wt. 362.

**Found:**  
N, 7.04%;  
mol. wt. 361.

**9-Diazo-10-fluorenylidene-9,10-dihydrophenanthrene**

10-Fluorenylidene-9-phenanthrone hydrazone (3.7 g., 0.01 mole), ether (80 ml.), mercuric oxide (3.25 g., 0.015 mole), and anhydrous sodium sulfate (4.32 g.) were mixed thoroughly. Potassium hydroxide (0.0168 g., 0.0003 mole) in methanol (2 ml.) was added to the stirred solution at 20° and the yellow color was instantly discharged to a deep red color. The temperature of the mixture was immediately lowered to 10° and stirring was continued for 1 hour. The solution was filtered and the
filtrate was washed with water and dried. The solvent was removed. The red oil was dissolved in benzene and chromatographed rapidly on a short column of basic alumina to obtain a light red solution along with some decomposition on the column. The solvent on evaporation yielded light red needles of 9-diazo-10-fluorenylidene-9,10-dihydrophenanthrene (2 g., 54.3%), m.p. 77-78°. Infrared absorption (31): \( \nu_{\text{diazo nitrogen}} \) and 6.2\( \mu \) (C=N).
Figures 7, 8, and 9 show spectra of different chemical compounds. The y-axis represents the transmittance and absorbance, while the x-axis represents the wavelength in microns. The spectra are plotted in the range of 4000 to 3000 cm\(^{-1}\).
Figure 31
Figura 34
Figure 37
Figure 38
Figure 43

$\text{CH}_2\text{CH}$

$\text{TM}_3$
Figure 44

\[ \sigma - \text{C-C-C} = \text{CH}\sigma (B) \]

TMS

0 PPMB
Figure 45

\[ \gamma-C-C=CHCOCH_3 \]
Figure 48
Figure 49

Absorbance

Wavelength (mč)
Figure 50
Figure 52

![Absorbance vs Wavelength graph with molecular structure (A)]
Figure 53
Figure 54
Figure 55
Figure 56

Absorbance

Wavelength (mÅ)

200 250 300 350 390

O2N

C

C

CN
Figure 57
Figure 58
Figure 59
Figure 6.1

[Graph showing absorption spectrum with wavelength in nm on the x-axis and absorbance on the y-axis, with a compound structure at the bottom right corner.]
Figure 63
Figure 65
Figure 66

Absorbance

Wavelength (m\(\mu\))

\(\phi-C-C=CH\phi\) (A)
Figure 67

\[ \phi - C - C = CH\phi (B) \]
Figure 68

\[ \phi - C - C = H - C O_2 C H_3 \]