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APPROACHES TO THE SYNTHESIS OF NON-ISOMERIZABLE DEWAR BENZENE DERIVATIVES

by

JOHN PATRICK BURKE

A dissertation submitted to the
Graduate Faculty in Chemistry in partial
fulfillment of the requirements for the
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1969

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TO MY WIFE RITA

AND TO OUR DAUGHTER

MAURA

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J.P.B.

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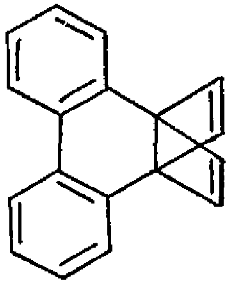
ABSTRACT

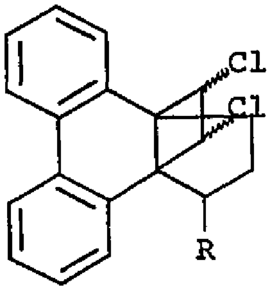
APPROACHES TO THE SYNTHESIS OF NON-ISOMERIZABLE DEWAR BENZENE DERIVATIVES

The synthesis of the non-isomerizable Dewar benzene derivative 1 is proposed and its uniqueness is discussed. The chemistry of this compound, stable to aromatization and yet highly strained, would not be expected to parallel that of known Dewar benzenes.



[1]

Several synthetic schemes are outlined and include: (1) the trapping of a phenanthrenocyclobutadiene with an acetylenic ester; (2) the photosynthesis of a tricyclo[4.2.2.0] system by the irradiation of 1'-keto-9,10-cyclobutenophenanthrene and dichloroethylene.



[2]

a) R= O

b) " OH

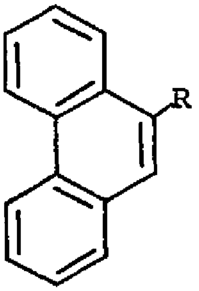
c) " 

d) " OAc

The synthesis of 12,13-dichloro-2,3-dihydro-3a,11b-ethano-1*H*-cyclopenta[*l*]phenanthren-1-one [2a] was carried out in order to demonstrate that photoaddition to an enone that is incorporated into an aromatic system, in this case

1'-keto-9,10-cyclopentenophenanthrene, is, in fact, feasible.

Compounds 3a - 3f were synthesized; a Friedel-Crafts reaction on 9-phenanthrylsuccinic anhydride [3e] provided a new route to 1'-keto-9,10-cyclopentenophenanthrene [4b]. The products 3a and 3f also served as intermediates for attempted photolytic reactions leading to phenanthrenocyclobutene derivatives. These reactions, however, took place exclusively on the side chain. The attempted trapping of 9,10-phenanthryne with substituted olefins, such as ethyl vinyl ether, was also investigated.

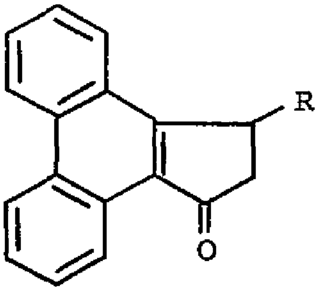


[3]

a) R= $CH{=}C(CN)CO_2Et$
b) " $CH{=}C(CN)COOH$
c) " $CH(CN)CH(CN)CO_2Et$
d) " $CH(COOH)CH_2COOH$
e) " succinic anhydride
f) " maleic anhydride

The alcohol 2b, ketal 2c, and acetate 2d were prepared in reactions directed toward the synthesis of the homologue 5 of the non-isomerizable Dewar benzene derivative 1. The problem of steric hindrance in this system is discussed.

The bromo-ketone 4c was synthesized; however, an irradiation in the presence of dichloroethylene did not yield a derivative analogous to 2a. Treatment of 1'-keto-3'-bromo-



[4]

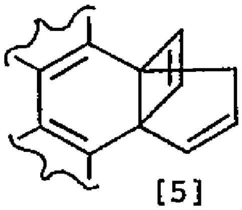
[**4**]

a) R= COOH

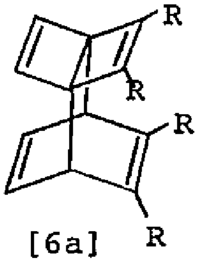
b) " H

c) " Br

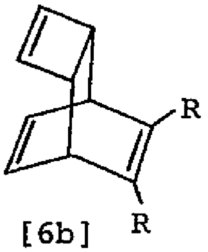
9,10-cyclopentenophenanthrene [**4c**] with triethylamine gave the dimer of 1'-keto-9,10-cyclopentadienophenanthrene, the structure of which is discussed.



[5]



[6a]

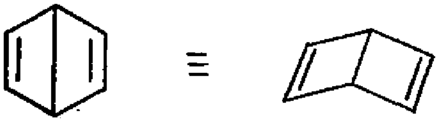


[6b]

Compound **6a**, derived from the cyclooctatetraene-dimethyl acetylenedicarboxylate adduct **6b** was considered as another example of a non-isomerizable Dewar benzene derivative. Allylic halogenation reactions on **6b** were attempted but the sole product isolated was the <u>trans</u>-dibromo addition compound. Dehydrohalogenation of the dibromo addition product did not yield a cyclobutadiene derivative.

A little over one hundred years ago, when the structural theory of organic chemistry was in its infancy, chemists were especially concerned with benzene and its derivatives.[1] In 1865, while he was Professor at Ghent, August Kekulé published two papers dealing with aromatic compounds. In the second of these, the now familiar hexagonal symbol made its first appearance, although the lines indicating double bonds were omitted. These were first incorporated in a third paper on aromatic compounds published in 1872.[2] During this period various non-Kekulé representations were presented, most of which have little significance in terms of modern theory of aromatic compounds. However, the Dewar benzene structure has lived on as a minor contribution to the resonance hybrid emerging from the valence bond description of the benzene ring.[1]

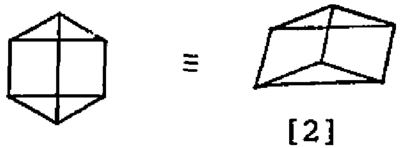
Authors who attribute to Dewar the hybrid formula of benzene, bicyclo[2.2.0]hexadiene [1], usually refer to his paper



[1]

presented to the Royal Society of Edinburgh in 1867.[3] A minor point of historical interest has been raised as to who proposed the Dewar formula. Sementsov has claimed that Dewar did not propose the bicyclic formula generally attributed to him. He states that the bridged formula was first proposed by two German chemists, R. Otto and H. Ostrum.[3]

Two years after Dewar's proposal, Ladenberg[4] suggested a trigonal prismatic structure without any double bonds **2**.

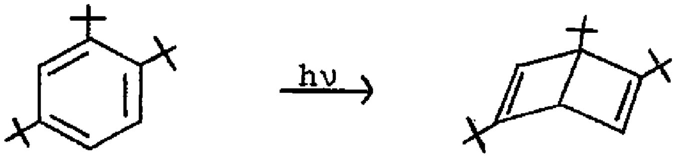


[**2**]

It has long been recognized that Dewar benzene and prismane had physical meaning as non-planar forms, and should be capable of independent existence as valence bond isomers of benzene. For many years organic chemists did not seriously consider the capture of such isomers, but by and large suspected that they would be too unstable for normal laboratory handling.[1]

During the early part of this decade, valence isomers of benzene were postulated as unstable intermediates in certain chemical reactions.[5] In an attempt to prepare a stable Dewar benzene, Van Tamelen and Pappas chose 1,2,4-tri-*t*-butylbenzene as starting material. In selecting this case for study they reasoned that the high degree of steric interference between the bulky 1,2-*t*-butyl groups would have a destabilizing effect on the benzenoid structure relative to the non-planar Dewar form in which the two large substituents are farther separated in space.[6] The photolysis reaction of 1,2,4-tri-*t*-butylbenzene did indeed give 1,2,5-tri-*t*-butylbicyclo[2.2.0]hexa-

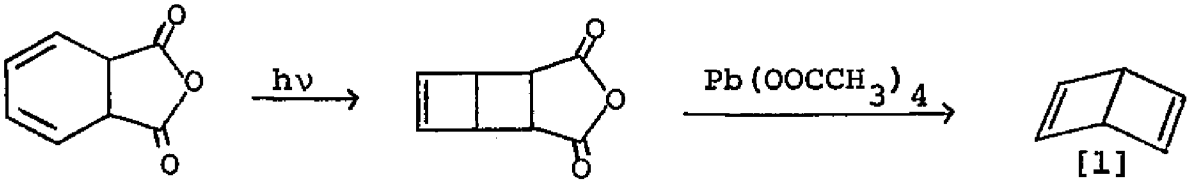
2,5-diene [3], the first Dewar benzene derivative.



[3]

The Dewar benzene 3 was found to be stable at room temperature and was aromatized in part by heating to 200° for 15 minutes.[6] However, it turned out that the steric requirements for a stable Dewar benzene were not so demanding as originally thought. The photoisomerization of hexafluorobenzene to hexafluoro Dewar benzene proceeded smoothly in 60 per cent yield.[7]

The parent compound, Dewar benzene itself [1], was synthesized in 1963 by Van Tamelen and Pappas from non-benzenoid precursors.[8]



[1]

The direct photoconversion of benzene into Dewar benzene has been reported by Ward and Wishnok.[9] They carried out a vacuum ultraviolet photolysis of liquid benzene to give three products [1, 4, 5] in a 1:5:2 ratio respectively. The

[1] [4] [5]

authors suggest the possibility that fulvene [**5**] arises from the acid-catalyzed rearrangement of benzvalene [**4**].

The photochemistry of benzene is pronouncedly different between the liquid-phase and vapor-phase photolyses. For example, when benzene is photolyzed in a hydrocarbon solvent at 2537 Å, the major product, formed in isolable quantities, is benzvalene.[10] Benzene vapor, however, is virtually inert to 2537 Å radiation.[11] When photolyzed in the vapor state at 1849 Å benzene gives fulvene and *cis*-1,3-hexadien-5-yne (as well as some polymer).[12]

The first benzvalene derivative was produced by Viehe and co-workers in 1964 by the rapid trimerization of *t*-butylfluoroacetylene in the liquid phase below 0°C.[13] Two of the three non-aromatic valence bond isomers of the substituted benzene were isolated from the trimer fraction, which accounted for two-thirds of the entire reaction product. The trimer fraction consisted of the Dewar benzene and the benzvalene in a 1:1 ratio. A third product, initially thought to be a prismane, was later shown to be a tetramer of the starting material.[4] The benzvalene product rearranged to 1,2,4-tri-*t*-butyl-trifluorobenzene during 16 hours at 220°. The Dewar benzene derivative was more sensitive and could only be separated in impure form by cautious crystallization. It readily underwent rearrangement to the planar Kekulé form. Brief heating at 100° sufficed for quantitative rearrangement.[13]

We were interested in studying the chemistry of this unusually interesting class of compounds - the Dewar benzenes. However, as Viehe pointed out in 1965, the main source of difficulty in the isolation of the non-aromatic valence isomers that he had prepared was their limited stability.[4] This was especially true of the Dewar benzene derivative. (Dewar benzene itself, prepared by Van Tamelen, has a half-life of two days at 20°.)[8] Consequently, we were prompted to devise a molecule whose geometric requirements prohibited a reduction of strain energy through aromatization. Considering the inherent strain of such a non-isomerizable Dewar benzene suggests that its chemistry might be indeed interesting. Our efforts toward the synthesis of such a system are described in Chapter II.

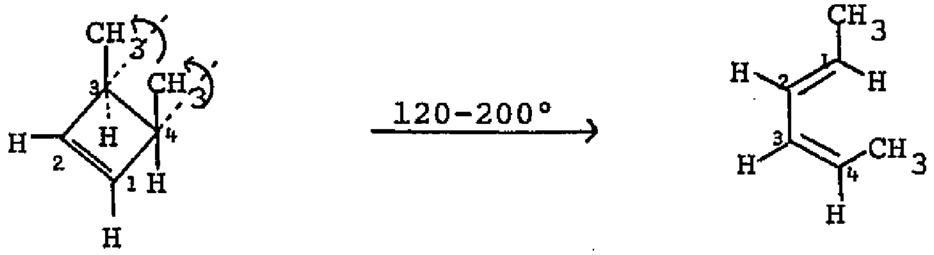
It was because of the strain in the valence isomers of benzene that the first published reports of their syntheses were met with surprise and even skepticism.[1]

The relative stability of Dewar benzene has been discussed by Van Tamelen in terms of the molecular orbital calculations of Woodward and Hoffmann.[14]

> Two thermodynamic factors, namely the strain of Dewar benzene and the resonance stability of normal benzene, reinforce each other and make for a considerable difference in ground state energies between the two structures. Morphologically, the difference between benzene and the bicyclohexadiene is so small that entropy factors should not present any great barrier to isomerization. If no other factors

> were at play, the energy path to normal benzene would be largely downhill. What property then is responsible for the stability of Dewar benzene? The answer must be given in terms of bond rehybridization, including the stereoelectronic factors in the thermally induced ring opening of a cyclobutene to a 1,3-diene.[1]

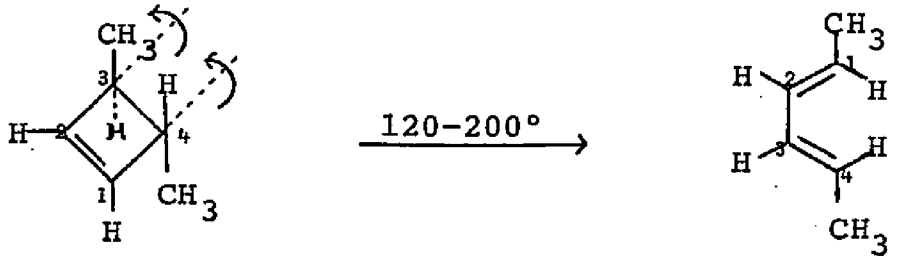
Professor R. Criegee, in his many years of work studying cyclobutenes, has observed that monocyclic cyclobutenes rearrange between 120° and 200°.[15]



I

cis-3,4-dimethylcyclobut-1-ene

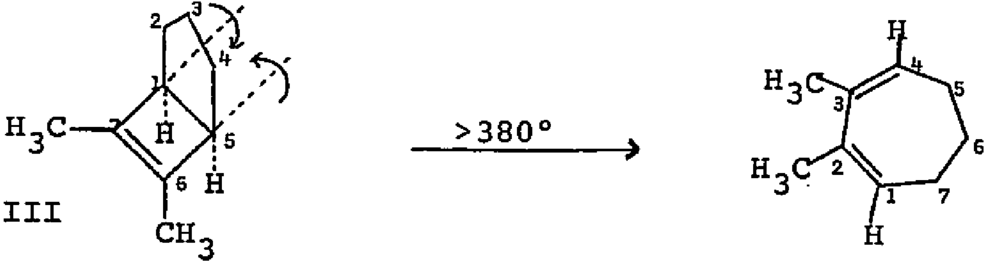
cis-trans-1,4-dimethyl-1,3-butadiene



II

trans-3,4-dimethylbut-1-ene

trans,trans-1,4-dimethyl-1,3-butadiene



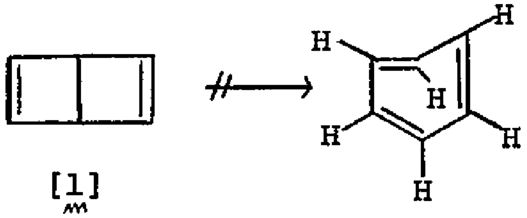
III

6,7-dimethylbicyclo[3.2.0]hept-6-ene

cis-cis-2,3-dimethyl-1,3-cyclo-heptadiene

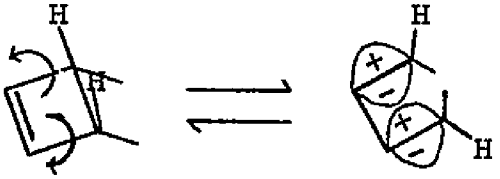
In reaction I, when the ring opens, substituent groups at C-3 and C-4 always rotate in the same direction (conrotatory transformation). A similar ring opening takes place in reaction II. However, when bicyclic cyclobutanes were rearranged, it was found that temperatures greater than 380° were necessary. In addition, a disrotatory transformation occurs in which the reaction products always have a monocyclic cis, cis-butadiene structure (the cis-trans form being too unstable in that ring system).[15] In the case of cis-bicyclo[2.2.0]hexa-2,5-diene [1] the preferred (conrotatory) mode of stereoisomerization cannot operate, since an extraordinarily strained cis,cis,trans-cyclohexa-1,3,5-triene would result.[1]

IV



[1]

V

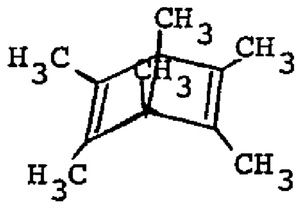


In the stereoelectronically less preferred (disrotatory) course of ring opening [V] molecular orbital symmetry favors the stability of the benzoid product, but the energy of the transition state is high enough to allow Dewar benzene comparative stability.[1]

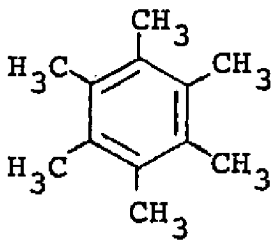
In 1966 Schäfer reported the one-step synthesis of hexamethyl Dewar benzene [6] from 2-butyne using anhydrous aluminum chloride as a catalyst.[16] Generally, the preparation of Dewar benzene derivatives requires the use of several steps in the synthesis.

This was a significant experiment because it allowed for the first time the synthesis of a stable Dewar benzene derivative to be carried out on a kilogram scale. The chemistry of hexamethyl Dewar benzene was actively investigated by Schäfer and others and has led to some interesting and controversial results which will be discussed later on in this chapter.

Hexamethyl Dewar benzene can be heated at 100° for 48 hours with less than one per cent isomerization taking place.[17] When heated above 80° rearrangement to hexamethylbenzene [7] takes place at an observable rate. The kinetic parameters have been obtained by Oth, who has estimated the strain of 6 to be 44.5 kcal/mole.[18]



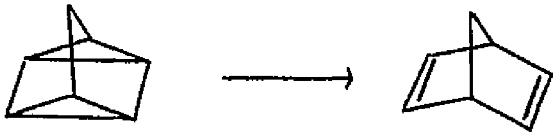
[6]



[7]

An nmr study has been made of the thermal and the transition metal catalyzed valence isomerization of 6 to 7.[19] The thermal reaction was investigated in the temperature range of 100-140°. The catalysis reaction took place in the presence of either $Rh_2(C_2H_4)_4Cl_2$, $Rh_2(CO)_4Cl_2$ or $Rh(C_4H_6)_2Cl$. The complex resulting from a displacement reaction was heated between 60°-75°. A kinetic study suggests that a penta-coordinated complex $Rh(C_{12}H_{18})_2Cl$ containing two molecules of hexamethylbicyclo[2.2.0]hexa-2,5-diene as bidentates is involved.[20] Under both thermal and catalytic conditions a quantitative formation of 7 was observed. The activation parameters were determined and it was shown that the catalyst lowers the activation energy [thermally $E_A = 31.1$ kcal·mole^{-1}, catalytically $E_A = 19.4$ kcal·mole^{-1}]. The authors speculated that the observed catalysis by transition metals was probably due to the presence in the complex of occupied molecular orbitals of the correct symmetries, so as to make the disrotatory ring opening an allowed process.[19]

An analogous reaction, also thermally "forbidden" by the concept of conservation of molecular orbital symmetry,[14] is the valence isomerization of quadricyclene [8] to norbornadiene [9]. It is strongly accelerated by the presence of small amounts of transition metal - olefin or allyl complexes.[21]

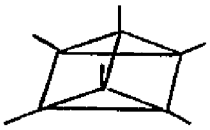


[8] [9]

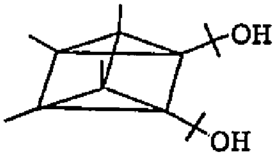
Mango and Schachtschneider have proposed that the above reaction and other transformations of this kind can be rendered allowed by an appropriate transition metal system. In this catalysis, the authors suggest that the metal and the fusing olefin ligands exchange electron pairs as the reaction proceeds.[22] In the transition metal catalyzed bis(acetylene)-cyclobutadiene interconversion the above authors have drawn correlation diagrams constructed from extended Hückel molecular orbital calculations.[23]

Hexamethyl Dewar benzene can be quantitatively converted to hexamethylbenzene by aluminum chloride. This isomerization can also be brought about by other Lewis acids, such as ferric chloride, antimony pentachloride, titanium tetrachloride, or, on gentle heating, by antimony trichloride, stannic chloride and zinc chloride.[17]

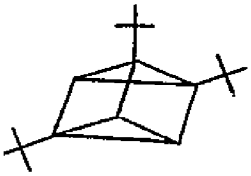
From the viewpoint of preparation, the Dewar benzene derivatives occupy a unique place among the derivatives of the valence isomers of benzene, since all the preparations of prismanes yet accomplished are based on the photochemical excitation of Dewar benzene derivatives.[17] A case in point is the irradiation of hexamethyl Dewar benzene with a low-pressure uv lamp (254 mμ) which leads mainly to hexamethylbenzene; in addition, a 20-25 per cent yield of hexamethylprismane [**10a**] is obtained.[17] Two other prismane derivatives are now known, **10b** and **10c**.[24a,b]



[10a]



[10b]



[10c]

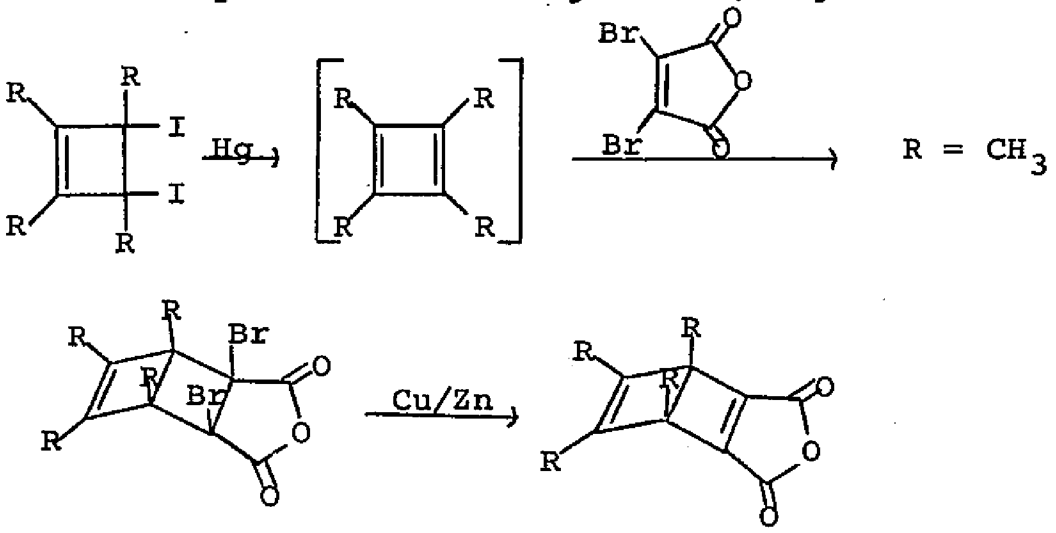
They were also obtained by irradiation of the corresponding Dewar benzenes with uv light (254 mμ).

Schäfer and Hellmann in their review article on Dewar benzene have outlined the five current methods of synthesis.[17] (Some of these methods are pertinent to our work and are discussed in greater detail in the next chapter.)

(1) Photoisomerization of benzene derivatives.

(2) Degradation of bicyclo[2.2.0]hexa-5-ene-2,3-carboxylic anhydride with lead tetraacetate.

(3) Addition of cyclobutadiene in situ to dihalogenomaleic anhydride and dehalogenation, e.g.



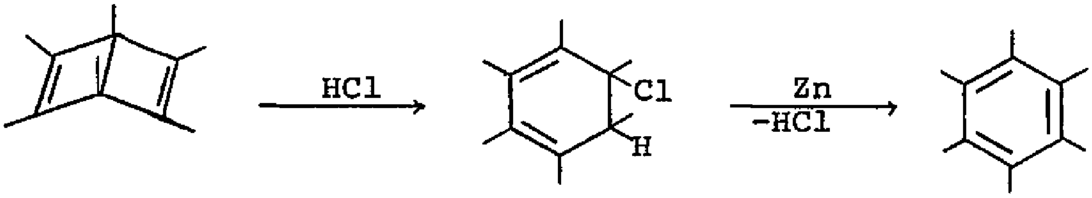
(4) Addition of cyclobutadiene in situ to acetylenes.

(5) Bicyclotrimerization of acetylenes.

The commercial availability of hexamethyl Dewar benzene may[17] or may not[25] have eliminated the valence isomers of benzene as an esoteric class of compounds, but at any rate this formerly elusive derivative is now under active investigation and has led to some interesting chemistry.

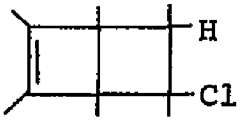
Earlier in this chapter we had proposed, and will discuss in detail in Chapter II, the synthesis and the chemistry of a stable but uniquely different Dewar benzene. It is because of our ancillary interest in the chemistry of the stable hexamethyl Dewar benzene that we would like to discuss at this point some recent publications that are significantly at variance with each other concerning some aspects of that chemistry.

Schäfer and Hellmann have reported that exposure of hexamethyl Dewar benzene to hydrochloric acid in methylene chloride at -30°, 0° or +40° leads to a new, vacuum distillable compound in 80-85 per cent yield.[17] Elemental analysis showed that this new substance was formed by the up-take of one equivalent of hydrogen chloride. The addition of acids (besides hydrochloric acid, acetic, chlorinated acetic acids and even methanol were used) was always accompanied by a deep violet coloration of the reaction mixture, indicative, in the authors' view, of an ionic mechanism. The structure of the new compound **11** was deduced by the authors from spectral data (not given) as well as from dehydrochlorination experiments using Lewis acids, such as zinc chloride or aluminum chloride. Hexamethylbenzene is obtained in each case in quantitative yield even under very mild conditions. Gentle heating with zinc dust or iron powder leads to the same results.



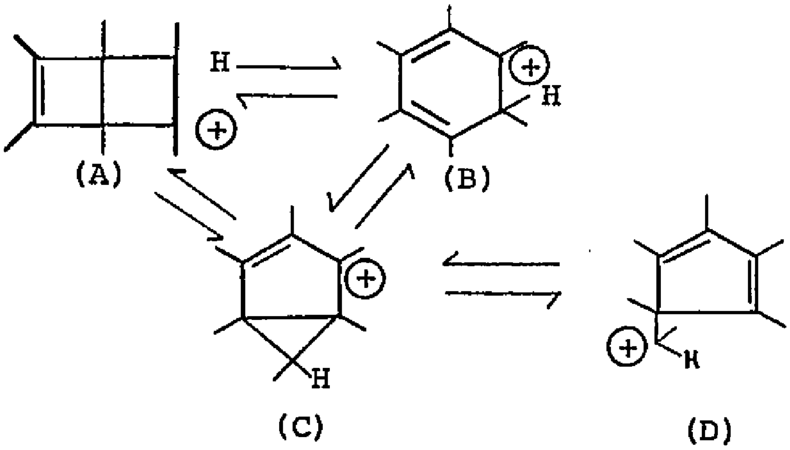
[11]

A second product formed in yields up to 15 per cent has been assigned the structure 12.



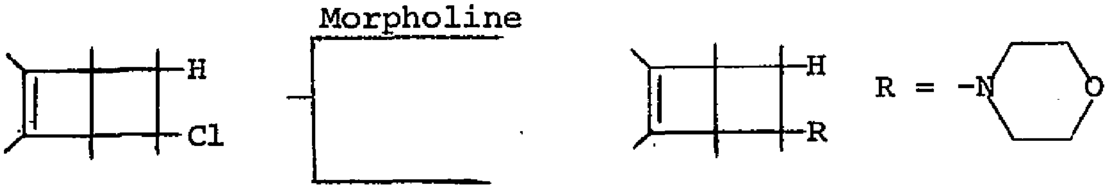
[12]

In an attempt to find chemical proof of the structure of the major product 11 the authors obtained a series of unexpected compounds. They postulated the following equilibrium as an explanation of these products:



The question whether stabilization takes place by substitution or by deprotonation and whether the product is a derivative of A, B, C, or D depends on the reaction conditions and on the nature of the attacking reagent.[17]

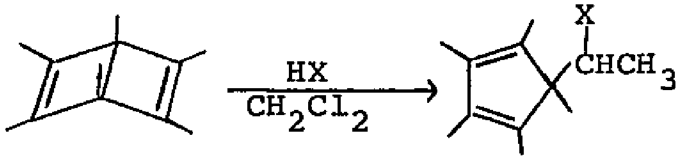
When hexamethyl-5-chloro-6H-bicyclo[2.2.0]hex-2-ene [**12**] was refluxed for several hours with morpholine, the substitution product hexamethyl-5-morpholino-6H-bicyclo[2.2.0]hex-2-ene [**13**] and a mixture of elimination products, including hexamethylbenzene are obtained in a yield of about 50 per cent each. The chlorinated Dewar benzene behaves in a similar manner on treatment with methanolic sodium methoxide solution.[17]



[**12**] CH_3ONa [**13**] $= OCH_3$

Hexamethyl-5-chloro-6H-cyclohexa-1,3-diene [**11**] adds a further mole of hydrochloric acid to form a colorless, salt-like compound which is moderately stable at low temperatures only, and which readily decomposes into hydrogen chloride and **11**.[17]

A parallel study with contradictory conclusions was made by Paquette and Krow.[25] They treated hexamethyl Dewar benzene in methylene chloride with a stream of dry hydrogen chloride or hydrogen bromide. The previously cited generation of a deep purple color was again reported.



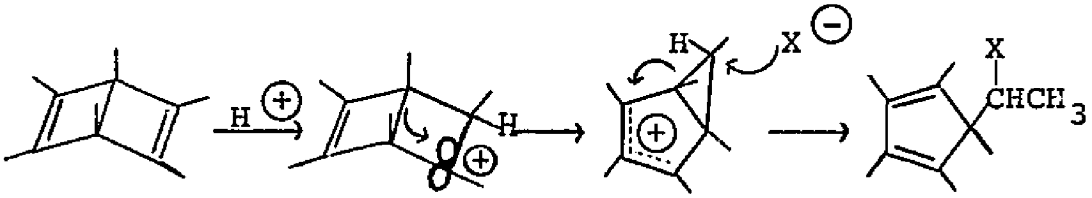
(a) X = Cl, (b) Br, (c) OCH_3

[6] [14]

After work-up, 14 was obtained in good yield (60-80 per cent). A solution of 6 in methanol containing 1-2 drops of 60 per cent perchloric acid likewise became highly colored after standing for 48 hours at 30°. The methoxy derivative 14c was obtained in 45 per cent yield.

Evidence for the assigned structure was provided by ultraviolet and nuclear magnetic resonance spectra. Further evidence was provided by Paquette and Krow from the catalytic reduction of the methoxy derivative to a tetrahydro derivative whose nmr, the authors claim, clearly establishes the fact that the starting methoxy compound 14c contained four allylic methyl groups and a 1-(methoxy)ethyl side-chain.[25]

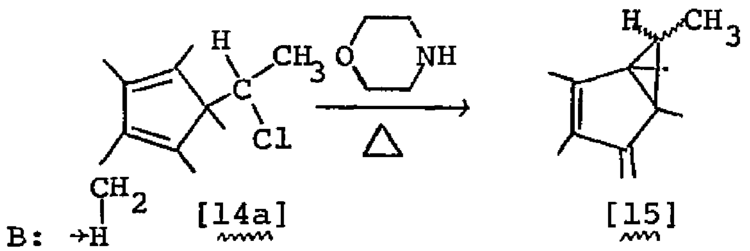
Paquette and Krow[25] account for the striking, and perhaps unique, fact that these ionic transformations result in HX being bonded to a single carbon atom in 14 by proposing the following mechanism:



[6] [6a]

Protonation of **6** from its endo surface and subsequent or concerted migration of the central bond in **6a** is proposed. Paquette raises the point of a fundamental energy requirement (bonding to the lower lobe has been recognized by other authors as unfavorable[26]); the central bond must become attached to the upper lobe of the vacant p-orbital. The geometric consequence is to provide access to the cis-fused bicyclo[3.1.0]cyclohexyl carbonium ion in which the cyclopropyl proton possesses the endo configuration.[25]

Paquette and Krow also report that the heating of **14a** in excess morpholine afforded the diene **15** (again at variance with the report of Schäfer and Hellmann).

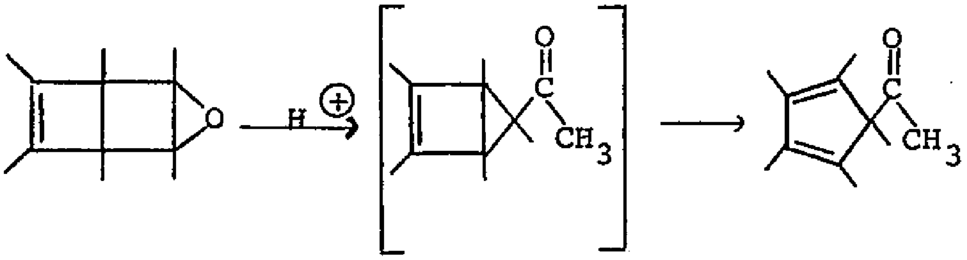


[**14a**] [**15**]

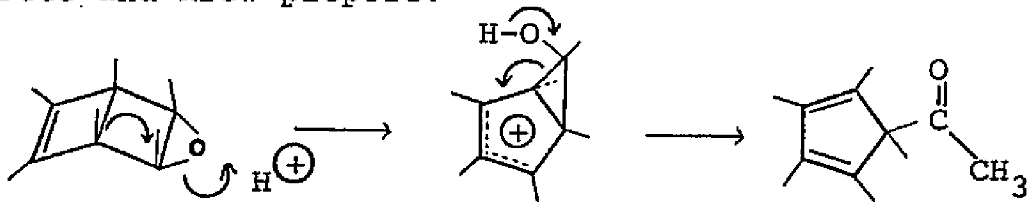
Although a single isomer appears to have been isolated, the authors have not yet established its stereochemistry unequivocally.[25]

While both research groups agree that the epoxide resulting from hexamethyl Dewar benzene gives pentamethyl-5-acetylcyclopentadiene upon acid rearrangement they again disagree on the mechanism.

Schäfer and Hellmann suggest a proton catalyzed ring contraction followed by valence isomerization.[17]

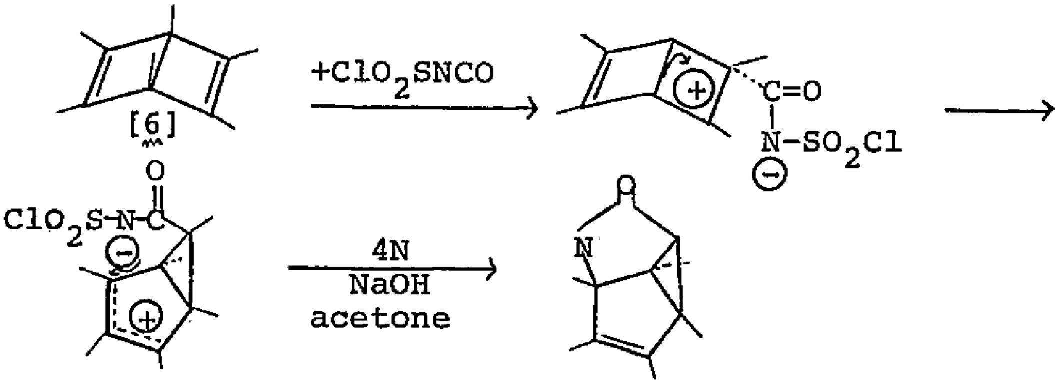


Paquette and Krow propose:



[16]

Paquette and Krow have provided additional evidence that cyclopropylcarbinyl cations such as 16 are intermediates in these rearrangements.[25] They treated 6 with chlorosulfonyl isocyanate (previously shown to be an effective trap for the homotropylium cation[27]) in methylene chloride solution. Direct hydrolysis of the resulting N-(chlorosulfonyl) lactam afforded 17 in 87 per cent yield.[25] The authors suggest

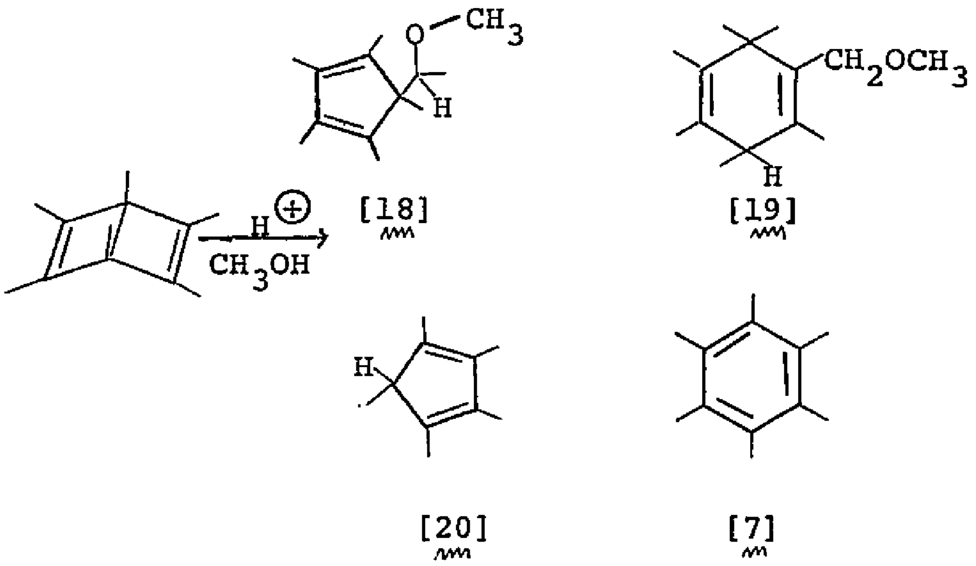


[17]

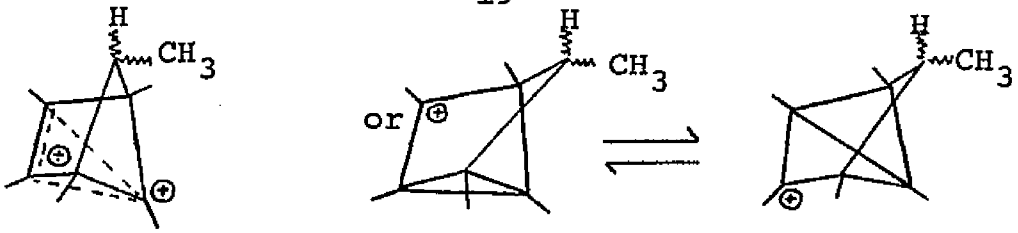
that the driving force behind these interesting skeletal rearrangements is no doubt attributable to the strain of the system and the stability associated with the resulting cycloalkenyl cation **16**.

Hogeveen and Volger in an nmr study of hexamethyl Dewar benzene in HF or HF-BF_3 at -80° have been unable to confirm the equilibrium of carbonium ions cited by Schäfer and Hellmann (see p.13). Their results suggest that these equilibria do not exist.[28]

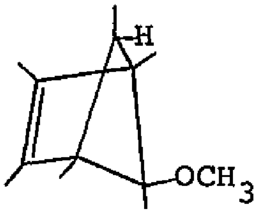
Criegee and Grüner have recently reported that when hexamethyl Dewar benzene was boiled for 40 hours with 0.03 per cent sulfuric acid in methanol, compounds **7**, **18**, **19**, **20** were formed in 13, 55, 24 and 4 per cent yields, respectively.



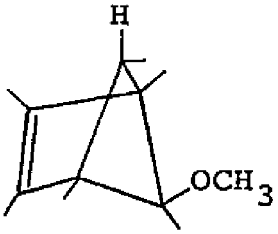
Olah and Paquette have recently reported on the protonation of hexamethyl Dewar benzene in fluorosulfuric acid - antimony pentafluoride at -78°.[30] Two cations (in a 3:1 ratio) were observed in the temperature dependent spectra to which the following structures have been assigned:



Corroborative evidence for these structures was obtained when the solution was quenched at -78° with excess sodium methoxide in methanol. Two ethers [**21** and **22**] were obtained in a 3:1 ratio.[30]



[**21**]



[**22**]

The major product was assigned structure **21** and the minor product structure **22** (in a tentative assignment).

The substances proposed for study in the next chapter are Dewar benzenes whose unique construction does not allow, in all probability, reaction pathways analogous to that cited for hexamethyl Dewar benzene. If obtained, they would provide another series in which the relationship of structure and chemical reaction can be examined.

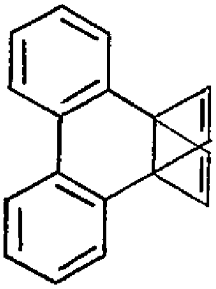
Chapter II

PART A

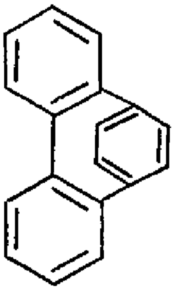
Preparation of the Tricyclo[4.3.2.0] System

The general reaction of a Dewar benzene on heating involves a rearrangement to the thermodynamically more stable aromatic system. If one could remove this pathway by making it energetically unfavorable, one would have a molecule stable to aromatization and yet highly strained.

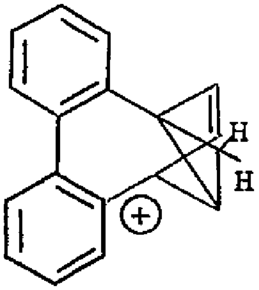
Our efforts were directed toward a molecule whose geometric requirements would make aromatization prohibitive and we chose to attempt the synthesis of 23. Isomerization would place a six-membered ring within the normal bonding distance of a 9,10-phenanthrene double bond in structure 24.



[23]



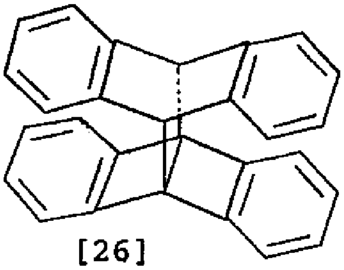
[24]



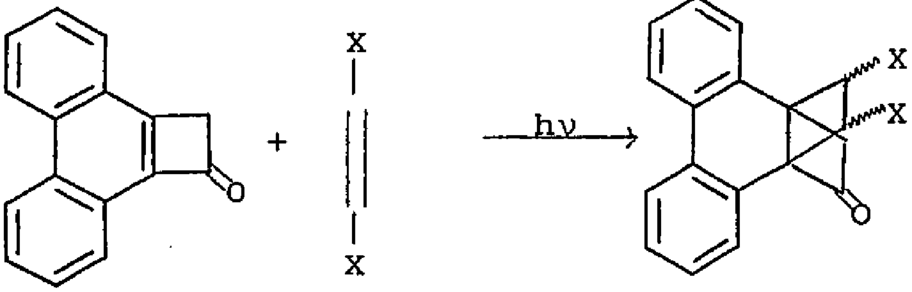
[25]

Compound 23 would be unique in another way. Paquette has attributed the driving force of the interesting skeletal rearrangements of protonated hexamethyl Dewar benzene to the strain of the system and the stability associated with the resulting cycloalkenyl cation 16.[25] The analogous cation 25 derived from compound 23 would contain a bridgehead carbonium ion and consequently be energetically unfavorable. Accordingly, the chemistry of 23 should not be expected to parallel that of hexamethyl Dewar benzene.

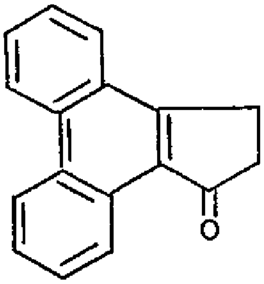
Prior to the beginning of our work there was one published report of a non-isomerizable Dewar benzene, that being the Dewar anthracene [26] synthesized by Applequist and Searle.[31] However, as Van Tamelen pointed out, this Dewar structure has its unsaturation incorporated into benzene rings.[1] This would preclude a study of the chemistry of the basic system.


[26]

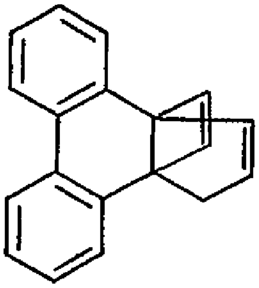
It will be seen later that a lack of success with several synthetic schemes that would have led to 23 prompted us to consider the following photochemical reaction as an entry into the desired ring system.



The availability[32a] of the related cyclopentenone 27 postponed a direct investigation of the above reaction. It offered a convenient way

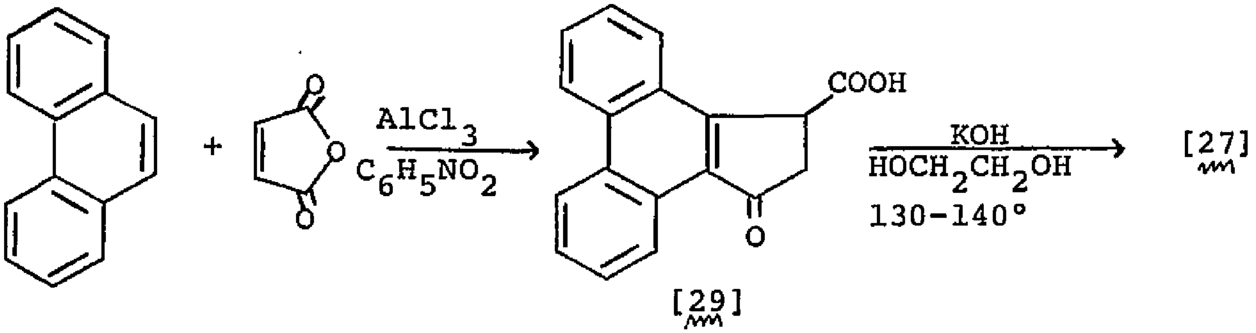

[27]

of demonstrating whether or not photoaddition to an enone that is incorporated into an aromatic system is, in fact, feasible (it had not been demonstrated previously). In addition, the chemistry of the tricyclo[4.3.2.0] undecatetraene system 28 that would emerge from this route would be of interest, especially when compared to that of 23. The above route was based on recent work in the synthesis of four-membered rings from the photolysis of α,β-unsaturated ketones with olefins. These cycloaddition reactions are, in general, one step, efficient processes involving a photoactive double bond with an unactivated double bond. Corey has investigated the scope, orientation and stereochemistry of the photolysis of 2-cyclohexenone and other conjugated enones with a variety of unsaturated substances.[33] De Mayo has recently reported on a mechanistic study of the photolytic reaction of cyclopentenone with a variety of olefins. His results indicate a rapid reaction involving a triplet state intermediate.[34] Other relevant work includes the photolysis of cyclohexenones and cyclopentenones with 1,2-dichloroethylene.[35a-e]



[28]

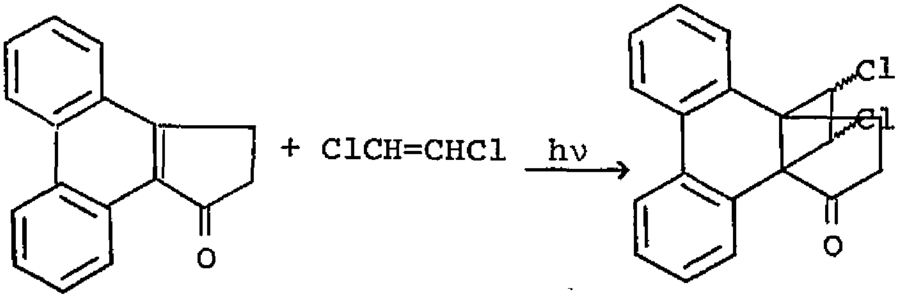
Using Schowalter's method 1'-keto-3'-carboxy-9,10-cyclopentenophenanthrene [29] was synthesized from phenanthrene and maleic anhydride under Friedel-Crafts conditions using nitrobenzene and aluminum chloride;[32a] in our experience the yield was much poorer than the literature report. However, a personal communication from the Director of the Laboratory from where the Literature Report emanated has confirmed our work.[32b]



The keto-acid 29 was decarboxylated smoothly in base by warming to 130-140° for 10-15 minutes.[32a] After work-up, light tan crystals, mp 162-165°, were obtained in 45 per cent yield. The ultraviolet spectrum agreed well with a literature report of compound 27 prepared by a different route.[36]

1'-Keto-9,10-cyclopentenophenanthrene [27] was dissolved in *cis*- and *trans*- dichloroethylene and the resulting solution was photolyzed with a 200-watt high-pressure mercury lamp for 50 minutes through a corex filter (corex transmits light above 2800 Å). The reaction was followed by ultraviolet analysis by examining the loss of absorption at 357, 313 and 285 mμ and the appearance of new bands at 278 and 271 mμ.

The infrared spectrum showed a loss of the 1686 cm^{-1} peak with a new peak appearing at 1745 cm^{-1}. The mass spectrum showed a very small parent ion with the base peak at m/e 232 corresponding to the thermal loss of dichloroethylene. The only other abundant ion showed the loss of C, H and O (CO +H·). The nmr was consistent with the structure assigned **30**; the problem of stereochemistry is discussed on page 45.



[27] **[30]**

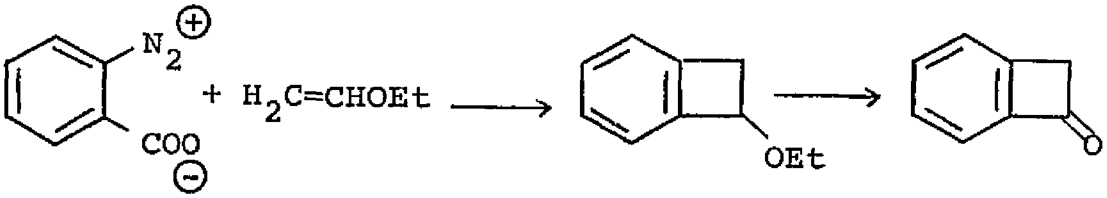
The reaction went in 58-76 per cent yield and the white needle crystals, mp 166-167°, gave a satisfactory elemental analysis.

PART B

Attempted Preparation of Cyclobutenophenanthrene Derivatives from 9,10-Dichlorophenanthrene

Having synthesized a derivative of our model compound we approached the problem of the tricyclo[4.2.2.0] synthesis. Two attractive possibilities presented themselves. The first was to extend the photolysis of cyclopentenones with dichloroethylene to the cyclobutenone series (which had not been demonstrated previously). The second route, discussed on page 26, was to trap a cyclobutadiene intermediate.

An efficient route to benzocyclobutene derivatives has been developed by Wasserman.[37] Cycloaddition reactions of benzynes with olefins are relatively rare, generally yielding with simple olefins mixtures of products resulting from hydrogen abstraction. However, Wasserman found that the reaction of benzyne with electron-rich systems such as ethyl vinyl ether and ethyl vinyl acetate led to synthetically useful yields of benzocyclobutenol derivatives.[37]



Wittig was able to form and trap 9,10-dehydrophenanthrene (9,10-phenanthryne) by refluxing a THF solution containing 9,10-dichlorophenanthrene with magnesium in the presence of anthracene to furnish, after work-up, a 10 per cent yield of the dibenzotriptycene (along with a 63 per cent yield of phenanthrene).[38]

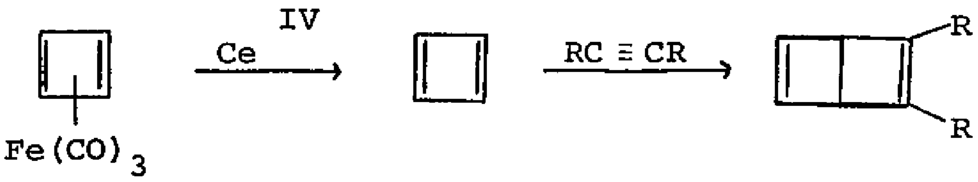
Millar had found previously that 9,10-dichlorophenanthrene reacts with magnesium in boiling THF to form a trimer of phenanthrene (presumably through phenanthryne).[39]

A solution of 9,10-dichlorophenanthrene, prepared according to a modification of the literature preparation,[40] was refluxed with ethyl vinyl ether as co-solvent for 24 hours over magnesium. Work-up yielded as the major product a compound which decomposed (charred) at 390° (literature for the trimer of phenanthrene: mp 380°[39]). A second fraction showed three components on tlc but nmr ruled out the desired phenanthrenocyclobutenyl ether as a product. There was no evidence of an ethoxy group and the region from 2.3-8.6τ was blank.

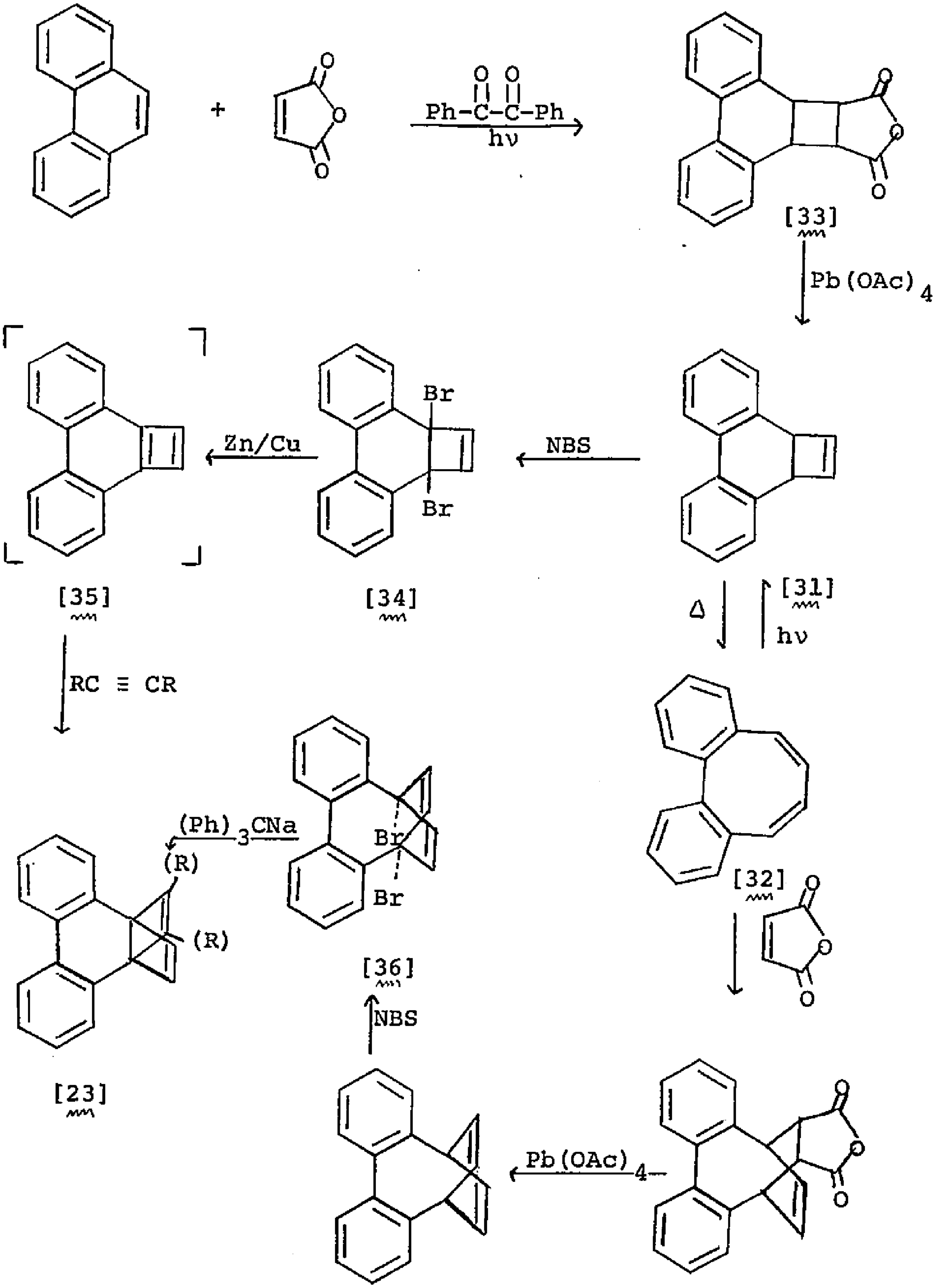
PART C

Attempted Preparation of Phenanthrenocyclobutadiene as a Route to the Tricyclo[4.2.2.0] System

While work was pursued on other pathways to the cyclobutenone system, described in a later section, we investigated our second route to a Dewar system incorporating phenanthrene. This route is outlined on Scheme I. The central reaction in Scheme I is derived from the work of Petit.[41] He has shown in an elegant experiment that cyclobutadiene has a finite lifetime and can be isolated and combined with acetylenic esters to yield Dewar benzene derivatives.



SCHEME I


+
Ph–C–C–Ph
hν
[33]
Pb(OAc)4
NBS
Br
Br
Zn/Cu
[35]
[34]
Δ
[31]
hν
RC ≡ CR
[32]
(Ph)3CNa
Br
Br
(R)
(R)
[36]
NBS
[23]
Pb(OAc)4
O

The synthesis of 9,10-dihydro-9,10-cyclobutenophenanthrene [31], a key intermediate in Scheme I, was accomplished by Vogel in two ways.[42] One route involved the photochemically induced electrocyclic closure of 1,2,3,4-dibenzocyclooctatetraene [32] (itself the product of a several step synthesis) and the other pathway utilized the photoadduct 33. The latter compound had been initially prepared in low yield by Bryce-Smith from the sensitized irradiation of phenanthrene and maleic anhydride in hexane.[43]

Compound 31 offers two routes to a Dewar benzene derivative. An allylic (benzylic) bromination[44] to 34 followed by a debromination (analogous to Criegee's[45] synthesis of a Dewar benzene, see pg. 11) would generate a cyclobutadiene 35 which could be trapped, using Petit's method, as the Dewar benzene derivative 23.

An alternative path involves a known thermal rearrangement of 31 to 32.[42] A Diels-Alder reaction with maleic anhydride followed by an oxidative decarboxylation and a benzylic bromination would be expected to give 36. A debromination using triphenylmethylsodium in the same fashion that Applequist[31] used in the preparation of 26 would yield the non-isomerizable Dewar benzene 23.

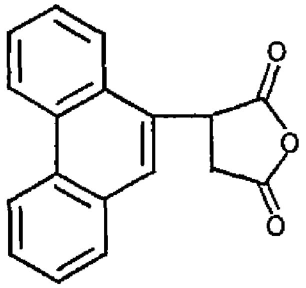
Bryce-Smith's procedure for the preparation of the key intermediate 33 was repeated. The reaction was run in hexane and a thin layer of solids, sufficient to cut out most of the light entering the photolysis chamber, was deposited on the well containing the mercury lamp. The amount of solid was negligible, synthetically speaking, and did not appear to contain aromatic peaks in the infrared spectrum. An ultraviolet analysis of the residual solution showed no change. Similar difficulties in a different photolysis reaction involving maleic anhydride are discussed on pg. 52. An added complication in these photolyses is the probable competitive photodimerization of maleic anhydride reported by Griffin.[46]

In order to keep the well free of solids, the reaction was run under homogeneous conditions using acetone, hexane-acetone or tetrahydrofuran as solvents under a variety of conditions. However, under these conditions a largely intractable product resulted which we were unable to purify.

PART D

Synthesis of Some New Phenanthrene Derivatives for Use in Photocyclization Reactions

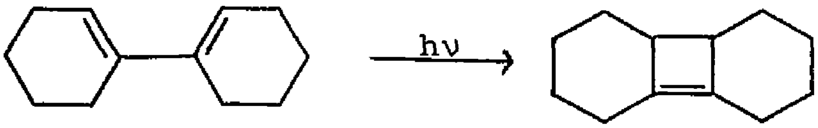
As an alternative path to 35 we considered the synthesis of 9-phenanthrylmaleic anhydride [37]. The photolysis of 37 would offer a new route, albeit a longer one to the desired intermediate



[37]

35. It would have compensating advantages. A precursor, 9-phenanthrylsuccinic anhydride [38] (see Scheme II) would be expected to cyclize under Friedel-Crafts conditions. This would constitute a new route to 1'-keto-3'-carboxy-9,10-cyclopentenophenanthrene [29] and to our model compound, the tricyclic[4.3.2.0]derivative 28 whose chemistry was of interest to us. Furthermore, 28 belongs to a series of compounds, the propellanes, which are currently under active investigation.[47] In addition, if our more direct routes to the phenanthrenocyclobutenone 39 were unsuccessful, the cyclopentenone 27 could be contracted to 40 via the photolysis of the corresponding diazo ketone 41.[48] Cyclobutanecarboxylic acid derivatives have been converted in good yield to cyclobutanones.[49]

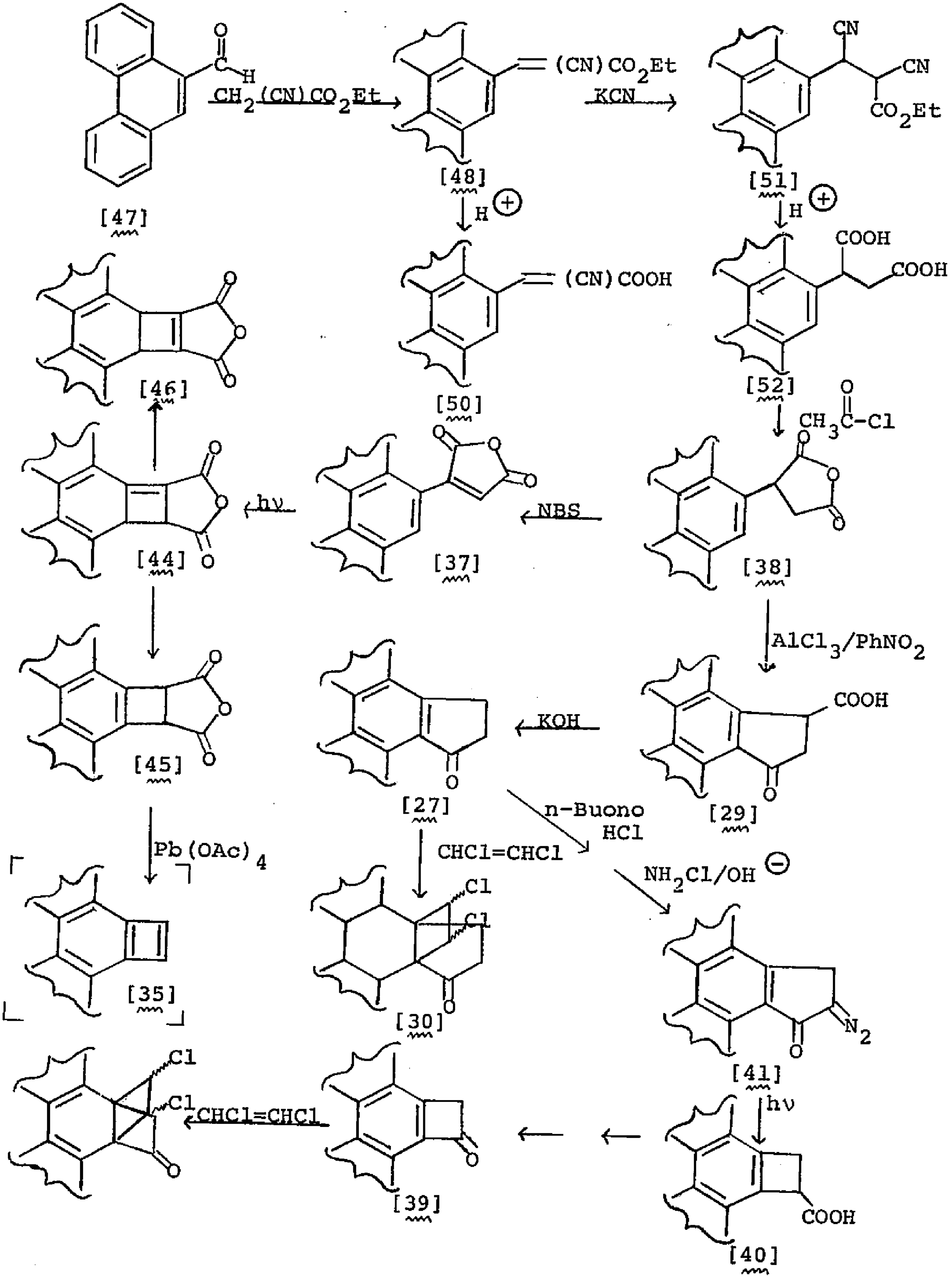
The feasibility of employing 37 for the indicated reactions is suggested by Crowley's photolytic conversion of 42 to 43.[50] Compound 44, if it did not aromatize under irradiative conditions, would be expected to be capable of rearrangement to a more conjugated system, either 45 or 46



[42] [43]

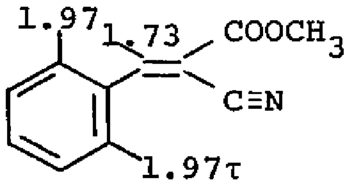
(which could be treated in a fashion similar to 31).

SCHEME II



O
H
CH2(CN)CO2Et
[47]
(CN)CO2Et
KCN
[48]
H ⊕
CN
CN
CO2Et
[51]
H ⊕
(CN)COOH
[50]
COOH
COOH
[52]
O
CH3C-Cl
[46]
[44]
hν
[37]
NBS
[38]
AlCl3/PhNO2
[45]
[27]
KOH
COOH
[29]
O
Pb(OAc)4
CHCl=CHCl
n-Buono
HCl
NH2Cl/OH ⊖
Cl
Cl
[35]
[30]
N2
[41]
hν
Cl
Cl
CHCl=CHCl
[39]
COOH
[40]

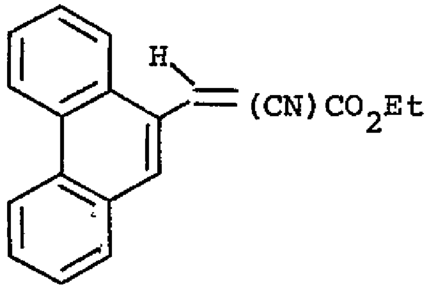
A successful route to 37 began with a Knoevenagel reaction analogous to that in the tetrahydronaphthalene series.[51a] When phenanthrene-9-carboxaldehyde [47] was heated with ethyl cyanoacetate, pyridine and piperidine in absolute ethanol and held at reflux for three minutes, compound 48, as yellow crystals, was obtained in 89 per cent yield. An infrared spectrum exhibited peaks at 2200 cm^{-1} (nitrile), 1724 cm^{-1} (α,β-unsaturated ester) and 1608 cm^{-1} (conjugated double bond). The longest wavelength absorption in the ultraviolet occurred at 362 mμ. The nmr spectrum showed the characteristic quartet (5.57τ, J = 6.9 Hz) and triplet (8.56τ, J = 6.9 Hz) of the ethyl ester and the vinyl proton appeared well downfield from TMS at 1.00τ (s); the aromatic protons absorbed at 1.41(m) and 2.23(m)τ. This assignment is consistent with 49 in which the vinyl proton is also assigned to a lower field resonance than the aromatic protons.[51b]



[49]

An analytical sample melted at 143.5-144.0° and gave a satisfactory analysis.

The hydrolysis of ethyl α-cyano-β-(9-phenanthryl)acrylate [48] to the corresponding cyanoacrylic acid 50 was accomplished by refluxing overnight with concentrated hydrochloric acid-glacial ace-

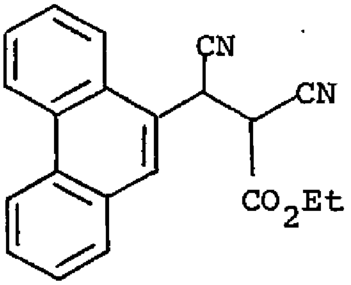


[48]

tic acid. After work-up there was obtained beautiful bright yellow needles that decomposed at 255°. An infrared spectrum showed that the nitrile was still intact, absorbing at 2217 cm^{-1}, and the peaks at 1686 and 2700-2500 cm^{-1} were assigned to the unsaturated acid. The conjugated double bond appeared at 1600 cm^{-1}. The ultraviolet spectrum was shifted to a somewhat shorter wavelength (λ_m 337 mμ) than the parent ester and a vinyl proton was again shifted downfield to 1.19τ (s).

There was no reaction between **50** and $K_4Ni(CN)_6$ (a reagent recently reported[52] to reduce α,β-unsaturated acids rapidly in high yield to the saturated acids); the starting material was unchanged (ultraviolet analysis) after four hours. Reduction of **50** followed by hydrolysis would be expected to lead to β-(9-phenanthryl)propionic acid which has been cyclized to **27** upon treatment with phosphorous pentoxide.[53] Cyclization has also been reported to have taken place when the corresponding acyl halide was reacted with aluminum chloride in nitrobenzene[54] or stannic chloride in benzene.[36] A common intermediate in these reactions is β-(9-phenanthryl)acrylic acid prepared by Bachmann from 9-phenanthrenecarboxaldehyde and malonic acid.[54] A repetition of the Bachmann synthesis gave, as a major product, a substance that was not soluble in hot ammonium hydroxide, in contrast to the Literature Report. Repetition of this experiment did not significantly improve the yield of the desired soluble product and we then proceeded with the Knoevenagel reaction.

Potassium cyanide reacted smoothly with ethyl α-cyano-β-(9-phenanthryl)acrylate [48] to give 51 in 80 per cent yield after one recrystallization from 95 per cent ethanol. (White needles, mp 128.5-131.0°.) An analytical sample, mp 132.0-133.0°, gave a satisfactory elemental analysis. The saturation of the acrylic acid side-chain was shown conclusively by the loss of the longer wavelength absorption at 337 mμ and the appearance of the well defined, characteristic phenanthrene-like absorption with λ_m at 297 mμ in the ultraviolet spectrum.

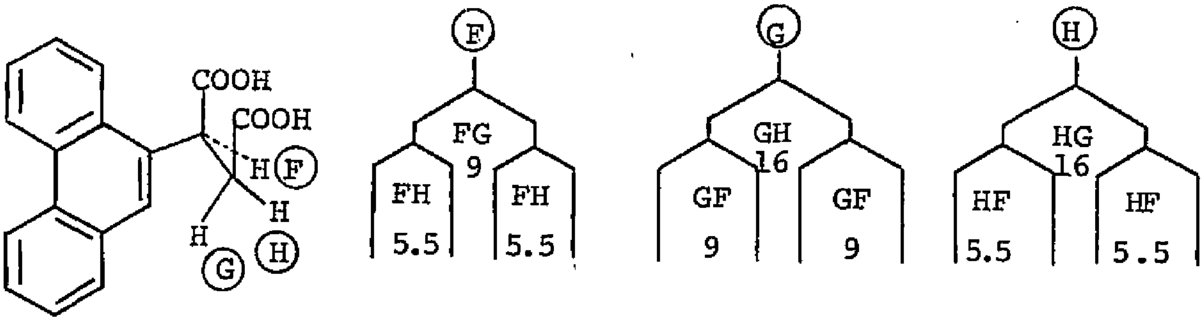


[51]

Confirmatory evidence was provided from an infrared spectrum by the shift of the ester carbonyl absorption to higher frequency at 1742 cm^{-1} and the carbon-carbon double bond to 1618 cm^{-1}. The cyano peaks appeared at 2242 cm^{-1}. The nmr spectrum reflected the disappearance of the unsaturation in the side chain by the appearance of a pair of doublets at 4.69 and 5.93τ

Hydrolysis of ethyl α,β-dicyano-β-(9-phenanthryl)propionate [51] to 9-phenanthrylsuccinic acid [52] was accomplished by refluxing overnight with a 2:1 solution of concentrated hydrochloric acid and glacial acetic acid. An 81 per cent yield of the diacid, as fine white needles, was obtained. The compound gave a neutralization equivalent of 148 (theory 147) and the ultraviolet spectrum displayed the typical phenanthrene peaks with λ_m at 297 mμ.

The nmr was particularly interesting in that a nearly first-order ABX*pattern occurred resulting from the asymmetric center on the side-chain carbon alpha to the ring.



[52]

Reaction of 9-phenanthrylsuccinic acid with refluxing acetyl chloride produced the anhydride **38**. Beautiful white needles obtained in an 87 per cent yield, mp 144.3-145.0°, gave a satisfactory elemental analysis. Reaction of the diacid with phosphorous pentoxide-polyphosphoric acid or phosphorous pentachloride-stannic chloride led exclusively to anhydride without any ring closure onto the phenanthrene moiety being observed (via ultraviolet analysis). The infrared spectrum exhibited the characteristic anhydride peaks at 1859 and 1779 $cm^{-1}$and an ultraviolet spectrum resembled that of the diacid with λ_m at 299 mμ. Nmr showed a triplet (or

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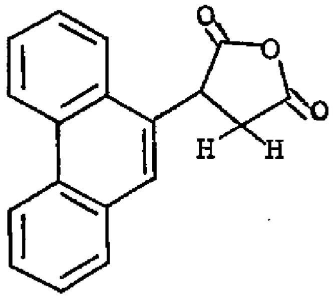
*) Treated as an approximate AMX pattern.

overlapping quartet) at 4.46τ and an 8 peak multiplet at 6.29τ intergrating for one and two protons respectively.

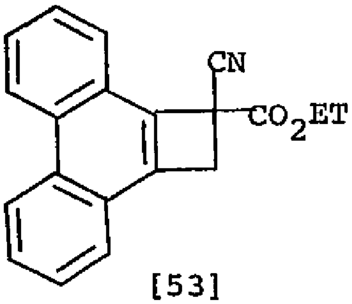


[38]

After 9-phenanthrylsuccinic anhydride was heated in refluxing carbon tetrachloride with N-bromosuccinimide and benzoyl peroxide for twelve hours, deep yellow rectangular plates were isolated in 51 per cent yield. They gave a negative halogen test in a sodium fusion analysis. The infrared spectrum showed that the anhydride had shifted to lower frequencies, 1842 and 1773 cm^{-1}, and a carbon-carbon double bond appeared at 1610 cm^{-1}; the ultraviolet absorptions occurred at longer wavelengths with tailing out to 355 mμ. The nmr spectrum showed a vinyl proton at 2.99τ (s). On the basis of the spectral evidence, elemental analysis and analogy to a similar reaction on phenylmaleic anhydride,[55] the structure was assigned as 9-phenanthrylmaleic anhydride [37].

We were now in a position to attempt the synthesis of 44 by irradiating 9-phenanthrylmaleic anhydride and a photosensitizer (benzil) in diethyl ether. The irradiation was carried out in a nitrogen atmosphere using a 450-watt high-pressure mercury lamp through a pyrex filter; after 4-1/2 hours reaction had taken place. An ultraviolet shift to shorter wavelengths gave rise to a typical phenanthrene-like spectrum with λ_m at 301 mμ. This is not inconsistent with structure 45. However, work-up gave as the major product a grey solid melting between 240.5-243.0° whose infrared spectrum showed no anhydride! A strong absorption was found at 1710 cm^{-1} along with a saturated carbon-hydrogen stretch at 2915 cm^{-1}. (When the reaction was run without a photosensitizer through a corex filter no change was observed in the ultraviolet spectrum after five hours of irradiation.)

The above result was not very promising and it was decided to have a look at an analogous reaction, i.e. the photolysis of ethyl α-cyano-β-(9-phenanthryl)acrylate [48]. This compound was photolyzed in a similar fashion except through quartz and without a photosensitizer. Ultraviolet analysis showed that reaction was complete after 36 hours of irradiation. A yellow oil was isolated that showed a shift in the infrared from 1724 cm^{-1} to 1736 cm^{-1}, a reduction in the intensity of the 1608 cm^{-1} peak and again a dramatic shift in the ultraviolet with the 360 mμ absorption disappearing and a typical, well-defined phenanthrene-like spectrum appearing. This is, again, not inconsistent with 53, a compound which would be expected to lead to a key intermediate, the phenanthrocyclobutenone 39. However, it is also consistent with a dimer, or polymer, of



[53]

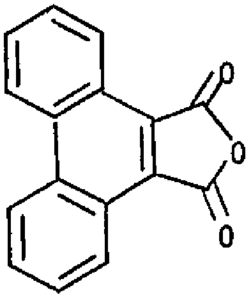
the unsaturated side-chain.

Chromatography of the photolyzed cyano-ester product gave a yellow glass that revealed more saturated than aromatic hydrogens in the nmr. The glass remained inert after twelve hours of reflux in a 1:1 concentrated hydrochloric acid : glacial acetic acid mixture due to a lack of solubility; basic hydrolysis gave a resinous product. The evidence seemed to indicate that these photolytic products were polymeric and not the desired compounds 53 and 45.

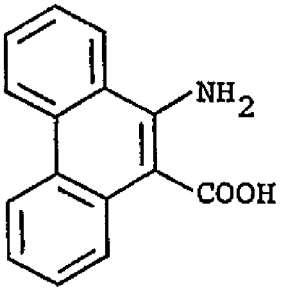
PART E

Further Explorations Toward 9,10-Phenanthryne and Phenanthrocyclobutene Derivatives

As previously discussed in Part B, the reaction of 9,10-phenanthryne (generated from 9,10-dichlorophenanthrene) and ethyl vinyl ether did not give the desired four-membered ring. One of the more efficient routes to a benzyne that successfully undergoes addition reactions is through anthranilic acid.[37] It was expected that 9,10-dicarboxyphenanthrene anhydride would lead to the corresponding phenanthryne precursor, 9-amino-10-carboxyphenthrene [55], upon reaction with



[54]

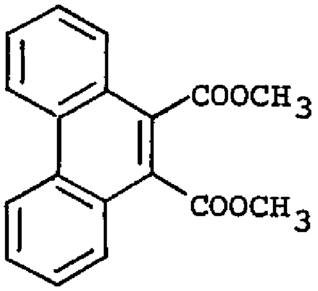


[55]

hydrazoic acid. (Another possible precursor, 9-bromo-10-nitro-phenanthrene had been reported to be inaccessible.[56] However, 54 proved inert under Schmidt conditions.

An attempt to prepare a half-ester of 54 in order to facilitate a Schmidt or Curtius reaction was unsuccessful as the sodium salt of the half-ester always closed to the anhydride when acidified in the work-up (the extraordinary propensity for ring closure, which blocked our efforts,had been previously noted by Adams[57]).

Recent advances in preparing four-membered ring acyloins from diesters using chlorotrimethylsilane[58] prompted us to attempt to make the diester 56. Adams and Jeans reported that it was impossible to convert 9,10-dicarboxyphenanthrene anhydride to the dimethyl ester by means of methanol and sulfuric acid; however, they did report diester formation (no yield given) in a reaction of the anhydride with potassium hydroxide and dimethyl sulfate.[57] A repetition of this reaction did not give a useful yield.

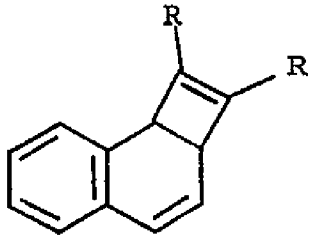


[56]

PART F

Attempted Thermal and Photolytic Reactions of Substituted Olefins and Acetylenes with Phenanthrene

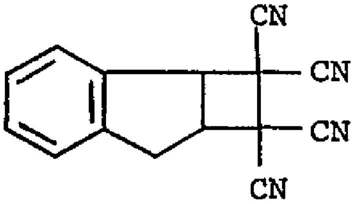
Naphthalene has been shown to form a photoadduct with diphenylacetylene via 57 as an intermediate.[59] Benzene has also undergone photolytic reactions with acetylenes.[60]



[57]

Diphenylacetylene and phenanthrene were irradiated with a 450-watt high-pressure mercury lamp through pyrex and also through quartz, but the only product formed turned out to be an artifact, the dimer of anthracene, originating from a small amount of anthracene in the phenanthrene; irradiation later served as a useful method of removing anthracene from phenanthrene.

Huebner has reported on the thermal reaction of indene and tetracyanoethylene (TCNE) in refluxing glyme to yield 58.[61] Phenanthrene and TCNE were treated in a similar fashion. An infrared spectrum of the resulting mixture showed only starting material. When a capillary sample was taken to 180° a violent reaction took



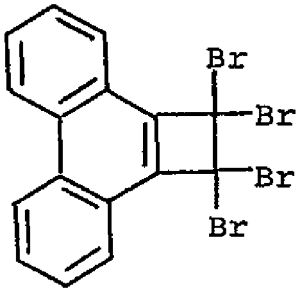
[58]

place within the tube; the nature of this reaction was not pursued although, conceivably, it could be of some interest.

Cargill and Willcott have studied the photochemical cycloaddition of dimethyl maleate and dimethyl fumarate to norbornene.[62] Under similar conditions using phenanthrene, only a polymer-like material resulted which lacked the necessary ultraviolet absorption [λ_m 277 mμ] for a phenanthrene derivative saturated at the 9,10 position.

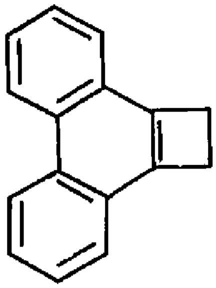
Phenanthrene and TCNE were also photolyzed but remained inert toward each other under the reaction conditions employed.

Schechter very recently reported on the synthesis of substituted phenanthrocyclobutenes.[63] The reaction of 9,10-phenanthrenequinone with dibromomethylenetriphenylphosphorane affords 59 (no yield was given but related reactions involving other ylides went in good yield).



[59]

A related compound 60 had been synthesized by a base reaction on trimethyl-10-methyl-9-phenanthrylmethyl ammonium chloride followed by an irradiation to give 9,10-cyclobutenophenanthrene in 3.7 per cent yield.[64] The photolysis of the hydrazone of 1,2-diphenylcyclopropene-3-carboxaldehyde in the presence of sodium methoxide has



[60]

also been reported to give 60.[65]

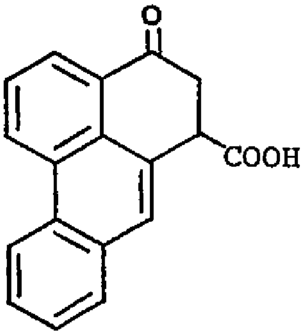
PART G

A New Route to 1'-Keto-9,10-cyclopentenophenanthrene

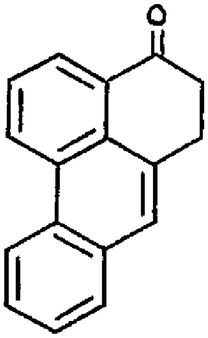
Our attention was focused next on the Friedel-Crafts reaction of 9-phenanthrylsuccinic anhydride [38] (see Scheme II) as a new route to 1'-keto-3'-carboxy-9,10-cyclopentenophenthrene [29] in order to explore further the chemistry of the tricyclo system 30.

Cyclization was effected by adding a cold solution of the anhydride in nitrobenzene to a solution of aluminum chloride, also in nitrobenzene, at 0-5°. This temperature was maintained for 4-5 hours. After work-up, a light tan solid, mp 180-190°, was carefully extracted with chloroform which yielded beautiful straw colored rectangular plates, mp 200° (dec) (lit: 200-201°[32a]) in a four per cent yield. The reaction was repeated and varied a number of times but the yield of the keto acid 29 was not improved significantly (8-10 per cent).

Work-up of the unextracted product included a decarboxylation step whereby any unextracted 29 reacted. This allowed the six-membered ring keto-acid 61 to be separated in a basic extraction. The major product 61 melted at 192-194°. An infrared spectrum showed the ketone at 1689 cm^{-1} and the acid at $1724_{(sh)}$ cm^{-1} and at 2740-2551 cm^{-1}. The ultraviolet spectrum (λ_m 367 mμ) resembled the reported spectrum of 62.[36] The nmr exhibited a triplet at 5.53τ (J = 4 Hz) and a doublet at 6.89τ (J = 4 Hz) attributable to the hydrogens on the saturated carbons.



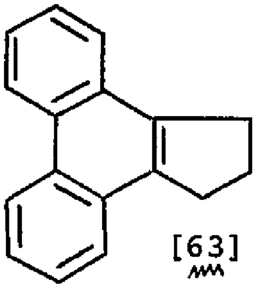
[61]



[62]

The Friedel-Crafts cyclization of 9-phenanthrylsuccinic anhydride followed by a decarboxylation gave a total of one gram of 1'-keto-9,10-cyclopentenophenanthrene [27] in an overall yield of two to five per cent from the anhydride 38. This enabled us to investigate some of the chemistry of the propellane derivative, the tricyclo[4.3.2.0] photoadduct 30 prepared earlier by another route (see pg.23).

A compound, 9,10-cyclopentenophenanthrene [63], related to 27, has been reported in a recent communication to have been synthesized by a new route.[66] A Friedel-Crafts reaction of 1,2,3,4-tetrahydrophenanthrene with β-chloropropionyl chloride yielded 1'-keto-1,2,3,4-tetrahydro-9,10-cyclopentenophenanthrene



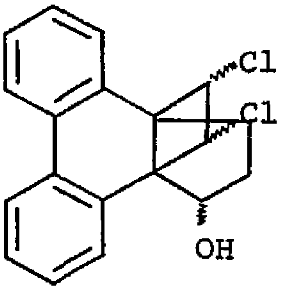
[63]

which was reduced in a Clemmensen (or Huang-Minlon) reaction; aromatization was accomplished by using palladium black to give pure 63 in an apparently low overall yield.

PART H

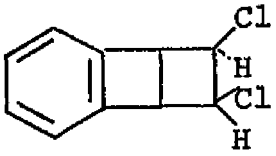
Synthesis of Some Derivatives of the Photoadduct 30 Based on the Model Compound 28

The ketone 27 was photolyzed with dichloroethylene and the photoadduct was reduced smoothly with sodium borohydride to give 12,13-dichloro-2,3-dihydro-3a,11b-ethano-1H-cyclopenta[l]phenanthren-1-ol [64] in 89 per cent yield. An infrared spectrum showed the presence of an alcohol at $3584_{(s)}$ and $3400_{(b)}$ cm^{-1} and a loss of the carbonyl peak at 1739 cm^{-1}.



[64]

An elemental analysis was satisfactory and a mass spectrum m/e 330 revealed the major loss of $C_2H_2Cl_2$ to the base peak, m/e 234. The next most abundant ion corresponded to the loss of oxygen and hydrogen. In the nmr spectrum the hydrogens on the cyclobutane ring appeared as a pair of doublets at 4.87 and 5.10τ with a coupling constant of 7.6 Hz.



[65]

McDonald and Frickey have reported a coupling constant of 0.9 Hz for the cis-hydrogens on the chlorinated carbons of 65.[67]

Wendisch and Metzner have reported on an nmr study of cyclobutanoindanes with vicinal chlorines on the four-membered ring.[68] When the cis hydrogens on the chlorinated carbons were anti (to the indane system) they found a coupling constant of 7.46 Hz and when syn a coupling constant of 7.26 Hz; the trans hydrogens gave J values of 6.34 and 6.01 Hz.

Considering the small differences between the cis and trans coupling constants in the cyclobutanoindanes, one would not be able to use the above compounds as models for the assignment of the chlorine cis-trans geometry based on the coupling constants of their respective hydrogens. Consequently, the stereochemistry of 30 and 61 remains unassigned.

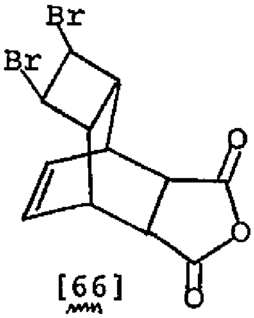
De Mayo has conducted a mechanistic study of the photochemical cycloaddition reaction of cyclopentenone and cis- and trans-dichloroethylene (among other olefins) and has concluded, in the cases studied, that a rapid reaction occurs involving a triplet state in nonstereospecific process.[34]

It would be expected that the favored path for a hydride ion attack on the ketone 30 would be from the endo side of the cyclopentanone ring (the chlorinated cyclobutane ring should offer considerable steric resistance to an exo attack).

An attempt to dehalogenate the dichloro-alcohol 64 proved unsuccessful after 14 hours of refluxing with a zinc-copper couple in diethyl ether. Similar results were obtained with activated zinc and acetic acid in refluxing diethyl ether or in refluxing tetrahydrofuran. Starting material was recovered in each case. The lack of reactivity is most probably steric in nature and reactions discussed later will lend some supporting evidence for this conclusion.

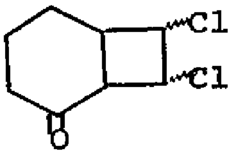
The reaction of sodium in liquid ammonia with 64 gave a crude oil that contained little or no starting material. The infrared spectrum showed no absorption in the 1550 cm^{-1} region where one would expect the carbon-carbon double bond of a cyclobutene to appear.[69] Chromatography failed to give a manageable product.

Bromine has been reported to have been eliminated from 66 by a reaction with lithium aluminum hydride in refluxing tetrahydrofuran for 12 hours.[70] We attempted an analogous reaction on the dichloroketone 30 and the dichloroalcohol 64, but were unsuccessful; details are discussed in the experimental section.



[66]

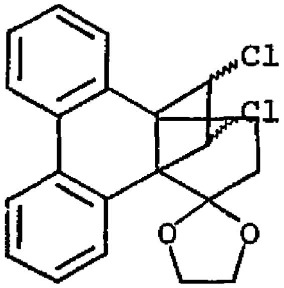
When House and Cronin photolyzed cyclohexenone with dichloroethylene they were unable to isolate 67.[35a] This intermediate decomposed and



[67]

consequently was isolated as the ketal which was dehalogenated with sodium and liquid ammonia.

The ketal of 30 could not be formed under the usual conditions but did form when the ketone 30 and p-toluenesulfonic acid were heated to 168° in ethylene glycol (when the reaction was carried out in refluxing benzene for 18-1/2 hours only starting material was recovered). The ketal was obtained as white plates, mp 184.7-185.1°, and gave a satisfactory elemental analysis. An infrared spectrum showed a loss of the carbonyl absorption at 1739 cm^{-1} and the appearance of peaks at 1152 and 1041 cm^{-1}. Intergration of the nmr spectrum showed the four additional dioxolane hydrogens in the 5.72-8.50τ (m) region.



[68]

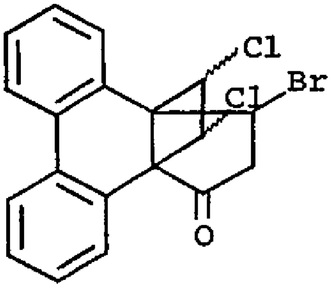
The unusual conditions necessary for ketal formation were most probably due to steric factors caused by excessive crowding. The ketal 68 was depleted in a reaction with excess sodium in liquid ammonia giving a crude oil with no absorption in the 1550 cm^{-1} region.[69] The product was apparently polymeric and the reaction was not investigated further.

A very recent communication suggests that polymers result when dichloroacetals, specifically that of 67, are treated with sodium metal.[71] Dehalogenation of vicinal dihalides leading to cyclobutenes was accomplished by use of sodium dihydronaphthylide, sodium dihydrobiphenylylide[71] and disodium dihydrophenanthrylide.[67]

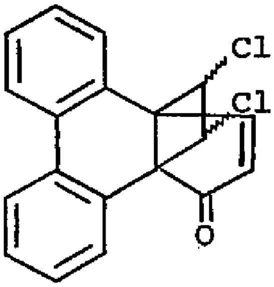
An attempt to form the tosylate of 64 failed. Reaction with tosyl chloride in pyridine yielded only starting material after 23 hours of reflux. (Reaction with 2,6-lutidine was also unsuccessful.) Apparently we are dealing with a highly hindered molecule. An attempted dehydration reaction on the alcohol 64, using potassium bisulfate in refluxing acetic anhydride, led only to the corresponding acetate; an infrared spectrum revealed a new peak at 1724 cm^{-1} and the loss of the alcohol absorption at 3584 and 3400 cm^{-1}.

It was of interest to see what effect introduction of a double bond into the five-membered ring would have upon dehalogenation reactions, i.e. would a reduction of the crowding between the four and the five-membered ring facilitate the removal of a dihalide from the cyclobutane portion of the molecule.

As our initial dehydration reaction was unsuccessful we planned to make 69 which would lead to 70.

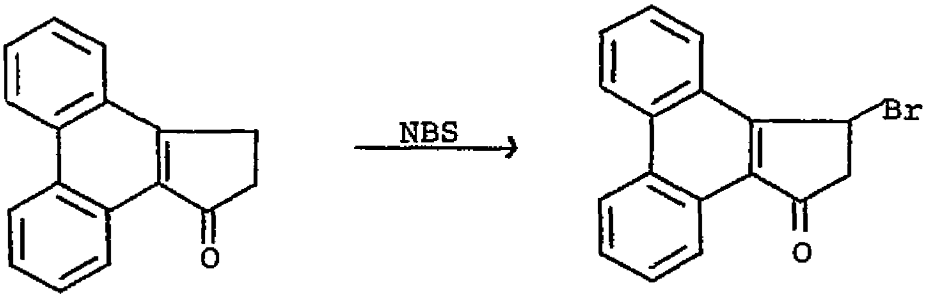


[69]



[70]

The route to **69** began with the ketone **27** which was treated with N-bromosuccinimide and benzoyl peroxide in refluxing carbon tetrachloride and gave deep yellow rectangular plates in good yield.

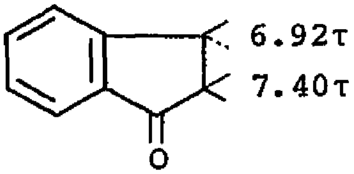


[**27**] [**71**]

An elemental analysis was satisfactory for a monobrominated product. The infrared spectrum showed a shift in the carbonyl frequency from 1686 cm^{-1} to 1709 cm^{-1} and the longest band in the ultraviolet was shifted to shorter wavelengths from 356 to 324 mμ in **71**.

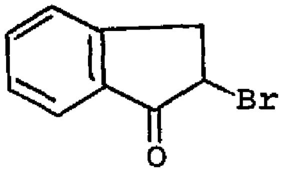
The assignment of structure to **71** derives from the spectral data discussed below. (The chemistry of **71** will be resumed on pg. 50.)

The protons on the α-carbon in the ketone **27** were assigned at 7.32 τ (m) and those of the β-carbon were assigned at 6.80τ (m) using **72** as a model compound.[72]



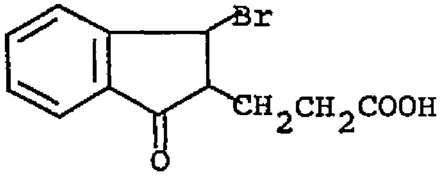
[**72**]

The proton splitting in the monobrominated ketone **71** could not enable one to differentiate a 2' from a 3'-cyclopenteno derivative (see experimental for details). Assignment on the basis of chemical shift without the appropriate model compounds would be unrealiable.



[73]

House prepared 73 via an ionic bromination. No nmr evidence was reported but the carbonyl absorption in the infrared spectrum was listed at 1725 cm^{-1}. This α-bromoketone could not be dehydrohalogenated with a variety of bases.[73]

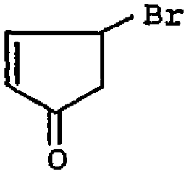


[74]

Compound 74 prepared by House under free radical conditions was not characterized but did dehydrobrominate with ease.[73]

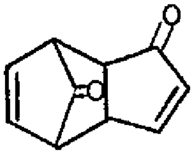
Marvel and Hinman prepared 3-bromoindanone from indanone and N-bromosuccinimide.[74] The product was not characterized spectrally but did give indone upon treatment with collidine.

De Puy treated cyclopentenone with NBS and prepared 4-bromocyclopentenone [75] in high yield. Structural assignment was made on the basis of nmr (not reported) and ample analogy for substitution in the 4-position in this system.[75]

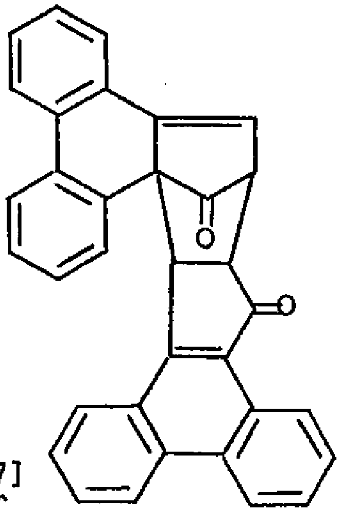


[75]

The 1'-keto-3'-bromo-9,10-cyclopentenophenanthrene [71] was stirred for one hour at room temperature with triethylamine. Work-up gave a single compound, as indicated by tlc, that absorbed strongly in the infrared at 1773 and 1686 cm^{-1}. Assignment of structure 77 was based on the infrared characteristics of the dimer of cyclopentadienone 76



[76]



[77]

that absorbed at 1786 and 1709 cm^{-1}. It is assumed that De Puy's dimer 76 and the dimer from 71 are formed by Diels-Alder reactions. This consideration suggests 77 as a possible structure.

Based on the analogous examples of the preparation and elimination of the monobrominated cyclopentenone derivatives cited previously, the structure of 71 is assigned as the 3'-bromo derivative.

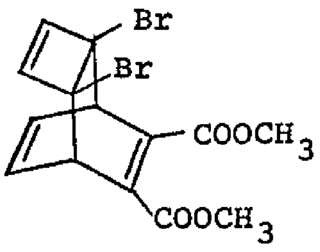
Irradiation of 1'-keto-3'-bromo-9,10-cyclopentenophenanthrene [71] with *cis*- and *trans*-dichloroethylene was carried out under conditions described previously for the photolysis of the unbrominated parent compound 27. The solution turned red during irradiation and there was an ultraviolet shift to shorter wavelengths. However, the expected shift to 277 mμ, as found in the photolysis of 27, did not materialize, indicating that the desired saturation of the 9,10-double bond did not take place. The resulting red product was not investigated further since it was not of immediate interest.

In another irradiation, 9,10-(1'-keto)cyclopentenophenanthrene [27] was photolyzed with maleic anhydride in hexane for 16 hours without any change occurring in the ultraviolet spectrum. Interestingly enough, the photolysis well was coated with a tan solid that lacked aromatic absorption in the infrared spectrum (a situation similar to that which had occurred in the photolysis reaction of phenanthrene and maleic anhydride and which presumably had been quenched by a reduction of light into the reaction chamber). The irradiation, if successful, would have allowed an oxidative decarboxylation experiment leading to a cyclobuteno-photoadduct of 27.

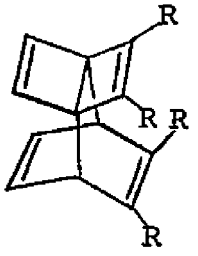
PART I

An Approach to Another Non-Isomerizable Dewar Benzene

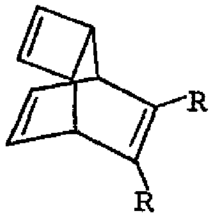
The synthesis of 2,5-dibromo-7,8-dicarbomethoxytricyclo-[4.2.2.0$^{2.5}$]deca-3,7,9-triene [78] would be expected to lead to another non-isomerizable Dewar benzene derivative. A sequence involving debromination in the presence of an acetylenic ester, as discussed on pg. 28, would give the desired compound 79.



[78]

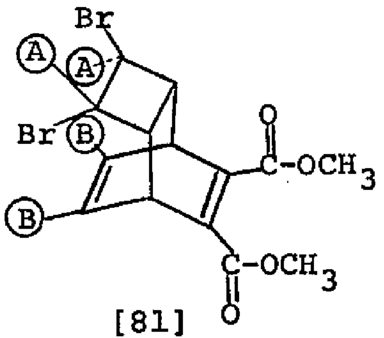


[79]

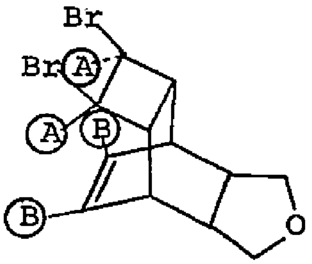


[80]

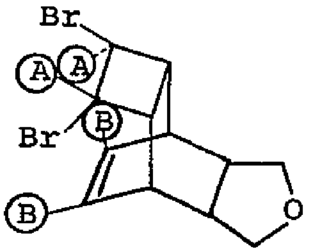
The starting material for this synthesis was the known cyclooctatetraene-acetylenedicarboxylic ester adduct 80 prepared by a modification of the literature report.[76] An allylic bromination with N-bromosuccinimide and benzoyl peroxide in carbon tetrachloride was attempted. However, the solvent underwent reaction under the conditions employed so benzene was substituted in place of carbon tetrachloride. The reaction yielded, besides succinimide and N-phenylsuccinimide, colorless plates of a compound shown by nmr analogy to be 3,4-dibromo-7,8-dicarbomethoxytricyclo[4.2.2.$0^{2.5}$]deca-3,7-diene [81], the *trans*-dibromo addition product.



[81]



[82]



[83]

Evidence for this assignment was provided by some model compounds prepared by Farnum and Snyder.[70] The hydrogens labeled Ⓐ appeared at 5.81τ as a doublet and the Ⓑ hydrogens were found at 3.69τ as a triplet in the *cis*-dibromo compound **82**. In the *trans*-dibromo product **83** the Ⓐ hydrogens appeared as two quartets at 5.82 and 5.31τ. The Ⓑ hydrogens appeared as two triplets at 3.81 and 3.47τ.

In the dibromo ester **81** the protons labeled Ⓐ appeared as a quartet at 5.37τ and as part of a multiplet at 5.73τ. The Ⓑ hydrogens appeared as two triplets, each split further into a doublet, at 3.17 and 3.46τ. As a consequence of the non-identical nature of the Ⓐ protons, product **81** is assigned the *trans* structure.

Poutsma and Hinman have examined the solvent effects in radical reactions and have found that complex forming solvents, e.g. aromatic hydrocarbons, carbon disulfide (electron-rich solvents) favor addition over abstraction in the free radical chlorination of cyclohexene.[77]

The reaction of **80** with N-bromosuccinimide and benzoyl peroxide was repeated in chlorobenzene, which could be expected to be less of a complexing solvent than benzene, but the results were similar.

Other methods to effect an allylic halogenation were attempted. The COT-adduct 80 failed to react with t-butyl hypochlorite[78] under mild photolytic conditions; 80 also did not yield a product with N-chlorosuccinimide in refluxing methylene chloride or in carbon tetrachloride after 6o hours of reflux. When a 350-watt mercury lamp was used the solvent again entered into the reaction (the starting adduct 80 was inert under similar photolytic conditions).

When the *trans*-dibromo ester 81 was treated with one equivalent of sodium methoxide the reaction mixture turned red-brown but work-up of the organic phase yielded only starting material in less than one-half the initial amount. Some evidence that this system is quite base sensitive was provided by refluxing the COT-adduct 80 in dilute sodium hydroxide (0.2N) for 2-1/2 hours. The only product isolated was a high melting, apparently polymeric product.

It was our intention to eventually remove two equivalents of hydrogen bromide from the dibromo ester 81 and thus generate a cyclobutadiene, but the sensitivity of 81 precluded the success of this route.

Chapter 3

EXPERIMENTAL

Melting points were determined in soft glass capillary tubes using a Thomas Hoover apparatus. Both melting points and boiling points are uncorrected and are given in degrees centigrade.

Microanalyses were performed by the Micro-Tech Laboratories, Skokie, Illinois.

Infrared spectra were taken on Perkin-Elmer Model 237 B Spectrophotometer. Solution spectra were determined using 5-10 per cent chloroform or carbon tetrachloride solutions as indicated. Potassium bromide pellets were made using approximately 1.0 mg of compound : 100 mg of anhydrous potassium bromide. Peak positions are indicated in wave numbers and parenthetically in microns.

Ultraviolet spectra were taken in 95 per cent ethanol using a Bausch and Lomb Model 505 or a Cary Model 14 Spectrophotometer. Wavelengths for band maxima are indicated in millimicrons.

Nuclear magnetic resonance spectra were determined on a Varian Model A-60A Spectrometer. Chemical shifts are specified in tau units and the splitting constants, a first-order spectrum being assumed, are given in Hz. The following abbreviations are used: s refers to a singlet, d to a doublet, t to a triplet and q refers to a quartet. Letters are used in structural formulas in place of hydrogens and refer to the respective protons at those positions. Nmr solvents are as indicated; ten per cent solutions were ordinarily used.

Mass spectra were determined on an Associated Electrical Industries Model MS-9 Spectrometer.

Photochemical reactions, unless otherwise stated, were run in cylindrical reaction vessels containing a water-jacketed immersion well fabricated from quartz (Hanovia immersion well 19434) or pyrex. The well contained the mercury lamp and filter sleeve, when used.

1'-Keto-3'-carboxy-9,10-cyclopentenophenanthrene

[29]

A mixture of 19.89 g (0.1116 mol) of anthracene-free phenanthrene (see pp.40,85), 50.29 g (0.3799 mol) of anhydrous aluminum chloride in 225 ml of dry nitrobenzene and 10.95 g (0.1117 mol) of maleic anhydride was reacted as described by Schowalter.[32a] Work-up yielded a largely intractable brown solid which was extracted with a chloroform-methanol solution. The filtrate, upon standing a few days, yielded 400 mg of 29 as a tan solid, mp 199.5-200.0° [lit.: 200-201°[32a]]. The reaction was repeated on the same scale as the literature preparation as well as under a variety of changes in reaction time, temperature, solvent, and work-up conditions. While a more manageable product resulted when the reaction was run on a half-gram scale (for less than four hours below zero degrees in nitrobenzene), the yields remained discouragingly poor.

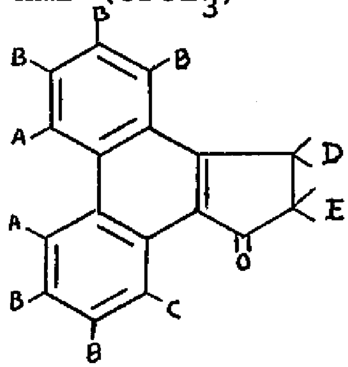
1'-Keto-9,10-cyclopentenophenanthrene [27]

Following Schowalter's procedure,[32a] 0.70 g (0.0013 mol) of potassium hydroxide was dissolved in 12.5 ml of warm ethylene glycol. The 0.1 N KOH solution was added to 0.285 g (0.00103 mol) of 1'-keto-3'-carboxy-9,10-cyclopentenophenanthrene [29] and the red solution was warmed to 130-140° over a period of 10 minutes and held there an additional five minutes.

Upon cooling to room temperature solids appeared. Acidification with HCl to a phenolphthalein end-point, filtering and then washing with distilled water gave 108 mg of light tan crystals, mp 162-165° [lit: 164°[54]; 170-171°[32a]], yield 45% [lit: 34%[32a]]. When the white solids were simply filtered and washed with water (acidification being dispensed with) a much poorer product resulted, mp 169-170°.

			Literature[36]	
	λ_m	log ε	λ_m	log ε
uv (95% ethanol)	242	(4.78)	242	(4.61)
	248	(4.49)	247	(4.62)
	262	(4.44)	262	(4.57)
	282	(4.32)	284	(4.01)
	313	(4.20)	312	(4.06)
	357	(3.36)	356	(3.32)

nmr (CDCl$_3$)



	τ	H	Assignment
(m)	0.72	1	C
(m)	1.50	2	A
(m)	2.29	5	B
(m)	6.80	2	D
(m)	7.32	2	E

ir (KBr) 3086 (3.24), 2941 (3.40), 1686 (5.93), 1610 (6.21), 1570 (6.37), 1499 (6.67), 1447 (6.91), 1401 (7.14), 749 (13.35), 723 (13.84).

12,13-Dichloro-2,3 dihydro-3a,11b-ethano-1*H*-cyclopenta[*l*]phenanthren-1-one

[30]

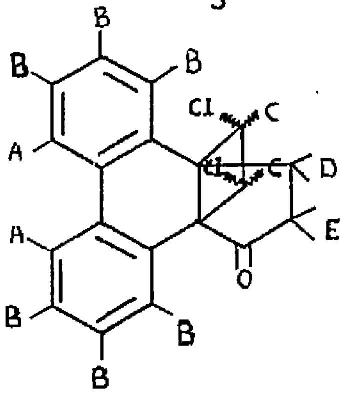
A solution of 1.0 g (0.00462 mol) of 1'-keto-9,10-cyclopentenophenanthrene [27] mp 171.3-171.8°, in 265 ml of distilled (50.5-55.0°) *cis*- and *trans*- dichloroethylene (Mathieson and Bell) was placed in a photolysis system described on pg. 57. A corex filter and a 200-watt mercury lamp were inserted. After deoxygenating with pre-purified nitrogen for 30 minutes, the light yellow solution was irradiated for 50 minutes. The reaction was monitored in the uv by examining the decrease in intensity of bands at 357, 313, 282 mμ and the appearance of new maxima at 278 and 271 mμ; 1.20 g of light tan needle bushes was isolated after removal of dichloroethylene. One recrystallization from *n*-propanol gave 0.8505 g, mp 165.0-166.0°. in 58% yield. A second crop yielded an additional 261 mg (18%) mp ≃162°. Further recrystallization gave the analytical sample as white crystals, mp 166.0-167.0°

Microanalysis:	C	H
Calc. for $C_{19}H_{14}OCl_2$ (329.25):	69.32	4.29
Found:	69.45	4.45

ir (KBr) cm^{-1} 3067 (3.26), 2950 (3.39), 1745 (5.73), 1625 (6.15), 1488 (6.72), 1447 (6.91), 1126 (8.88), 757 (13.21), 734 (13.62).

uv (95% ethanol)	λ_m	log ε
	229	4.41
	273	4.36
	278	4.37

nmr ($CDCl_3$)



	τ	H	Assignment
(m)	2.04	2	A
(m)	2.62	6	B
[J=7.5] (d)	5.40	1	C
[J=7.5] (d)	5.63	1	C
(m)	7.37	4	D + E

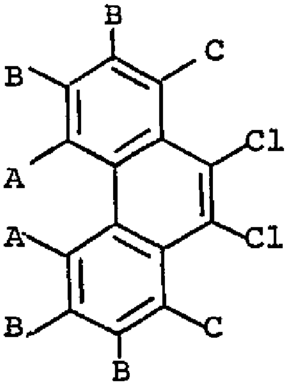
Mass Spectrum	m/e	Relative Intensity
70 electron volts	232	1000 (with 32% of total area)
inlet temp. 170°	233	210
	203	203.3
	202	196.5

All remaining ions have intensities less than 100.

9,10-Dichlorophenanthrene

Repetition of the literature preparation [39] for 9,10-dichlorophenanthrene did not lead to a pure product. Distillation of the crude 9,10-dichlorophenanthrene gave a yellow solid that melted below 150° (lit: 160.0-160.5°[40]). It was found that a pure product could be obtained without a distillation if the crude material was washed with diethyl ether followed by two recrystallizations from a 2:1:1ethanol : benzene : acetic acid mixture. Pale yellow crystals melting between 162.8-163.5° were obtained. The uv (95% ethanol) closely resembled that in the literature (1,4 dioxane).[39]

nmr ($CDCl_3$)



	τ	H	Assignment
(m)	1.47	4	A, C
(m)	2.30	4	B

Attempted Trapping of Phenanthryne With Ethyl Vinyl Ether

Using a modification of Wittig's successful trapping of phenanthryne with anthracene[38] 1.145 g (0.00463 mol) of 9,10-dichlorophenanthrene[39] (mp 161.2-162.0°) was dissolved in 55 ml of tetrahydrofuran (distilled from $LiAlH_4$). The apparatus consisted of a 250-ml three-necked, round-bottomed flask fitted with a stirrer and motor, a condenser topped with a pressure-equilibrated addition funnel, gas inlet adaptor and a nitrogen bubbler. A few ml of the dichloride solution was added under nitrogen to 0.262 g (0.0108 mol) of magnesium in 25 ml of THF at room temperature; a drop or so of dibromoethane was added as an initiator. After approximately 20 minutes a grey darkening of the clear solution was noted and 10 ml of distilled ethyl vinyl ether was added. The solution was brought to reflux and the remaining dichlorophenanthrene solution was added slowly. The reaction was stirred and refluxed throughout the day, but after 12 hours little change was observed. Refluxing was continued overnight and by morning most of the magnesium was used up giving a clear, tan solution.

The solution was filtered from the remaining magnesium and the solvent was removed and replaced by 75 ml of methylene chloride. The solution was extracted with 15-ml portions of distilled water precipitating, as a major product, a cream-colored solid which was filtered, washed with dilute hydrochloric acid, water, and dried. Melting did not occur by 390° (lit: 380° for the trimer of phenanthrene[39]).

The yellow organic phase was dried over $MgSO_4$ and, after removal of solvent, yielded 0.83 g of a tan oil-solid.

nmr ($CDCl_3$): (m) 1.45 τ, (m) 2.30 τ, (s) 8.68 τ, (m) 9.06 τ.

The region from 2.47-8.68 τ was completely blank, eliminating a phenanthryl cyclobutenyl ether as one of the products in the oily-solid fraction.

The reaction was repeated and all organic products were chromatographed on neutral alumina and eluted with benzene and ether. A light tan solid was obtained that had a surface melt at 380° and charred at 390°.

ir (KBr)	3067 (3.26), 2976 (3.36), 2924 (3.42), 1629 (6.14), 1499 (6.67), 1425 (7.02), 1053 (9.50), 869 (11.51), 745 (13.35), 712 (14.05).

The uv (before chromatography) was shifted approximately 3 mμ to shorter wavelengths compared with 9,10-dichlorophenanthrene and it resembled the published uv spectrum of the trimer of phenanthrene.[39]

A yellow gum containing three components was also obtained and gave an nmr spectrum identical to that reported above.

Attempted Addition of Maleic Anhydride to 9-Bromophenanthrene

A solution of 28.0 g (0.109 mol) of 9-bromophenanthrene,[79] 20.0 g (0.203 mol) of freshly distilled maleic anhydride and

8.0 g (0.044 mol) of benzophenone in 650 ml of purified acetone[80] was added to the reaction vessel. The system was fitted with a condenser, magnetic stirrer and a 200-watt Hanovia high-pressure mercury lamp encircled with a pyrex filter. The system was deoxygenated with and subsequently kept under pre-purified nitrogen. The photolysis chamber was irradiated for 18-1/2 hours and the reaction was monitored in the ultraviolet, samples being taken every two hours for 10 hours and again after 18 hours. No spectral changes occurred.

Photolysis of Phenanthrene and Maleic Anhydride

In a procedure patterned after that of Bryce-Smith[43] 17.3 g (0.0971 mol) of phenanthrene, 13.0 g (0.133 mol) of distilled maleic anhydride and 4.3 g (0.021 mol) of benzil were added to 650 ml of purified hexane;[81] the system was deoxygenated and irradiated through pyrex for 4-3/4 hours in a photolysis setup described on pg. 57. The reaction was followed by uv but no change was detected; the pyrex filter was removed and the mixture was irradiated for an additional 17 hours through the quartz probe, but not change was observed in the ultraviolet spectrum. The quartz probe contained a thin layer of a brown solid which did not show aromatic absorption in the infrared spectrum and was not investigated further.*

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*In attempting to increase the solubility of material, the

In order to achieve homogeneity, the reaction was repeated at the same concentration in purified acetone. A clear yellow solution resulted which remained unchanged throughout the 20 hours of irradiation at room temperature. The reaction was again followed by uv, but no change was observed. The solvent was removed and the residual solids were mixed with 250 ml of water-ethanol containing 15 g (0.27 mol) of KOH and the solvent was refluxed for 2-1/2 - 3 hours. After removal of ethanol, the aqueous phase was extracted with benzene. Acidification of the water layer with hydrochloric acid gave 1.5 g of a brown, gummy solid, which melted over 119-190°.

A portion of the gum, 0.5 g, was dissolved in 1.3 ml of benzene and 2 ml of acetic anhydride on a steam bath and heating was continued for 45 minutes. The red solution was cooled and the solid was precipitated with diethyl ether. After filtering, washing and drying, the solid did not melt by 320°.

The reaction was repeated under a variety of conditions including changes in concentration and irradiation time, in acetone, hexane-acetone or tetrahydrofuran. A crude product, melting over a broad range, always resulted, and chromatography, sublimation, recrystallization, etc. all proved ineffective in giving a manageable product.

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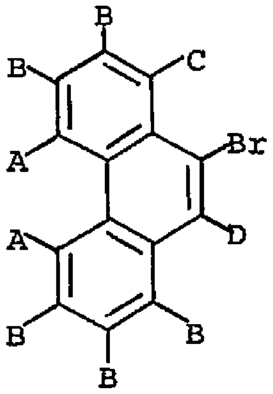
temperature was kept just below reflux by adjusting the rate of flow of the water coolant. The photolysis setup above differed from Bryce-Smith's which contained brushes to keep the well clean of deposited polymer films.[82]

9-Bromophenanthrene

Following an "Organic Synthesis" procedure,[79] 9-bromophenanthrene was prepared from 98% commercial phenanthrene (Henley & Co.). It was found that a tedious distillation could be avoided (but with some sacrifice in yield) provided that the more volatile materials, bromine, carbon tetrachloride, etc. were removed under reduced pressure and the product then purified by recrystallization from methanol. This gives a compound melting between 59-60° (lit: 54-56°; 65-66°[79]).

nmr ($CDCl_3$)



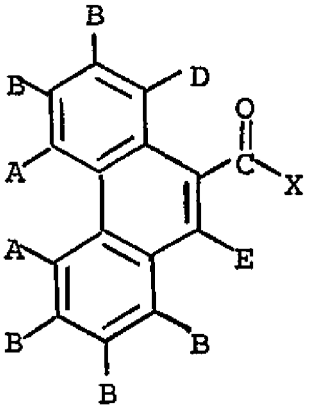
	τ	H	Assignment
(m)	1.40	3	A & C
(s)	1.88	1	D
(m)	2.28	5	B

9-Phenanthrenecarboxaldehyde

[47]

9-Phenanthrenecarboxaldehyde was prepared using an "Organic Synthesis" procedure[83] from 9-bromophenanthrene via reaction of the derived Grignard reagent with ethyl orthoformate to give the acetal which was hydrolyzed with sulfuric acid. The 9-phenanthryl aldehyde was purified (i.e. separated from anthracene-9-aldehyde) by forming the sodium bisulfite addition product. It was not necessary to distill the 9-phenanthrenecarboxaldehyde as reported; one recrystallization from glacial acetic acid followed by one recrystallization from absolute alcohol gave white crystals, mp 102.2-103.2° (lit: 100-101°[83]).

nmr ($CDCl_3$)



τ	H	Assignment
(s) -0.20	1	X
(m) 0.72	1	D
(m) 1.48	2	A
(s) 1.97	1	E
(m) 2.31	5	B

Ethyl α-Cyano-β-(9-phenanthryl)acrylate

[48]

In a reaction analogous to one in the tetrahydronaphthalene series,[51a] 103.0 g (0.541 mol) of 9-phenanthrenecarboxaldehyde [47] was warmed with 20 ml of piperidine, 40 ml of pyridine, and 200 ml of absolute ethanol to 70° in a 1-liter, three-necked, round-bottomed flask fitted with an addition funnel, condenser and a thermometer. The heat source (steam bath) was removed and 62.0 g (0.548 mol) of ethyl cyanoacetate (Eastman) was added rapidly; and exothermic reaction brought the solution to reflux where it was held for 3 minutes (at appreciably longer times, side reactions dominate the reaction). Slight cooling resulted in an exothermic precipitation of bright yellow crystals; the vessel was then thoroughly cooled in an ice bath. The crystals were filtered, washed with cold ethanol and air dried to give 133.4 g, mp 142.3-143.4°, in an 89% yield. An analytical sample was prepared by recrystallization from 95% ethanol and had a mp 143.5-144.0°.

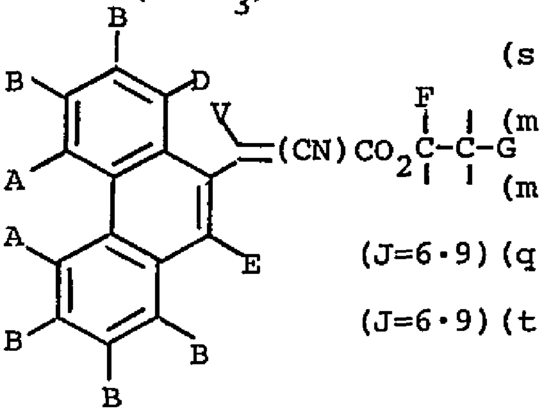
Microanalysis:	C	H
Calc. for $C_{20}H_{15}NO_2$(301.35)	79.71	5.02
Found:	79.94	5.07

ir ($CHCl_3$) 2222 (4.51), 1724 (5.80), 1608 (6.24), 1580 (6.33), 1490 (6.71), 1449 (6.90), 1383 (7.23), 733 (13.64).

uv (95% ethanol)

λ_m	log ε
250	4.57
267	4.45
285	4.23
299	4.07
362	4.24

nmr $(CDCl_3)$



	τ	H	Assignment
(s)	1.00	1	V
(m)	1.41	3	A&D
(m)	2.23	6	B&E
(J=6·9) (q)	5.57	2	F
(J=6·9) (t)	8.56	3	G

α-Cyano-β-(9-phenanthryl)acrylic Acid

[50]

A mixture of 200 mg (0.843 mol) of ethyl α-cyano-β-(9-phenanthryl)acrylate [48] and 10-15 ml of concentrated hydrochloric acid was brought to reflux; a few ml of glacial acetic acid was added at reflux to affect solution. Refluxing was continued overnight and yellow crystals were deposited by morning. The mixture was cooled in an ice bath, filtered, washed with distilled water and dried to give beautiful yellow needle crystals, mp 255° (dec). An analytical sample was prepared by recrystallizing twice from nitromethane followed by sublimation at 140-180°/0.1 mm.

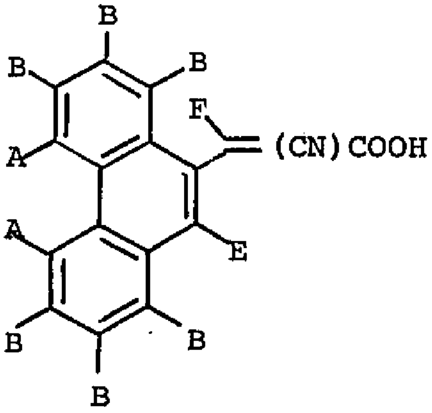
Microanalysis:	C	H
Calc. for $C_{18}H_{11}O_2N$ (273.29):	79.11	4.05
Found:	78.49	4.10

ir (KBr) 3086-2825 (3.24-3.54), 2591-2525 (3.86-3.96), 2217 (4.52), 1686 (5.93), 1600 (6.25), 1586 (6.33), 1490 (6.71), 1441 (6.94), 1389 (7.20), 1205 (8.30), 796 (12.57), 743 (13.45), 719 (13.90).

uv (95% ethanol)

λ_m	log ε
250	4.38
265	4.36
336	4.14

nmr (DMSO-d_6)



	τ	H	Assignment
(s)	1.19	≃1	F
(m)	1.32	≃2	A
(s)	1.79	≃1	E
(m)	2.24	≃6	B

Attempted Reduction of α-Cyano-β-(9-phenanthryl)acrylic Acid [**50**]

Utilizing a reported procedure[52] for the reduction of an α,β-unsaturated acid to a saturated acid 74.6 mg (0.273 mmol) of α-cyano-β-(9-phenanthryl)acrylic acid [**50**], 4.5 mg (0.069 mmol) of potassium cyanide, 3.3 mg (0.014 mmol) of nickel chloride hexahydrate and 10.3 mg (0.272 mmol) of sodium borohydride in 2 ml of water and 5 ml of ethanol were stirred for 3 hours. A black residue collected in the reaction vessel but an ultraviolet spectrum showed no change in the starting cyano-acid. Stirring overnight produced more black residue.

Ethyl α,β-Dicyano-β-(9-phenanthryl)propionate [51]

A solution of 133.4 g (0.4427 mol) of ethyl α-cyano-β-(9-phenanthryl)acrylate [48] and 28.84 g (0.4430 mol) of potassium cyanide in 783 ml of 95% ethanol was stirred for 1/2 hour at 65-70°. The solution became pale yellow and was acidified with dilute hydrochloric acid. A heavy white precipitate was filtered, washed with distilled water and dried, mp 121-123°. One recrystallization from 95% ethanol gave 115.7 g (79.6% yield) of beautiful white needles, mp 128.5-131.0°. Further recrystallization from the same solvent gave an analytical sample, mp 132.0-133.0°.

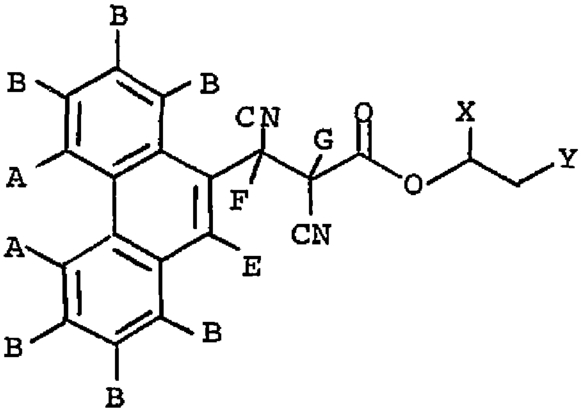
Microanalysis:	C	H
Calc. for $C_{21}H_{16}N_2O_2$ (328.37):	76.81	4.91
Found:	76.86	4.96

ir (KBr) 3058 (3.27), 2976 (3.36), 2833 (3.53), 2242 (4.46), 1742 (5.74), 1618 (6.18), 1493 (6.70), 1445 (6.92), 1366 (7.32), 1250 (8.00), 1012 (9.88), 765 (13.07), 748 (13.37), 727 (13.75).

uv (95% ethanol)

λ_m	log ε
246	4.73
254	4.75
276	4.24
286	4.17
297	4.18

nmr ($CDCl_3$)



	τ	H	Assignment
(m)	1.31	2	A
(s)	1.79	1	E
(m)	2.17	6	B
(d)	4.69	1	F
(q)	5.67	2	X
(d)	5.93	1	G
(t)	8.63	3	Y

9-Phenanthrylsuccinic Acid

[52]

A mixture composed of 115.7 g (0.383 mol) of ethyl α,β-dicyano-β-(9-phenanthryl)propionate [51], 500 ml of concentrated hydrochloric acid and 250 ml of glacial acetic acid was stirred and further diluted at reflux with the acid solution until solution was effected. Refluxing was continued overnight and a cream-white solid was deposited by morning. The mixture was cooled in an ice bath and additional solids precipitated. After filtering, washing with distilled water and drying, the white solids were used directly in the next experiment for the preparation of 9-phenanthrylsuccinic anhydride. The acid, when isolated in a separate experiment, was obtained in 81% yield, mp 218.5-221.5°. One recrystallization from 95% ethanol gave fine white needles (91% recovery), mp 128.5-131.0°.

Neutralization equivalent:

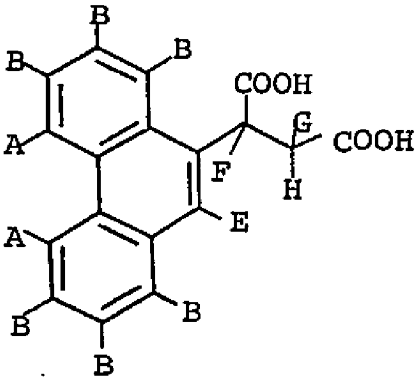
Calc.:	147
Found:	148

ir (KBr) 2703-2597 (3.70-3.85), 1706 (5.86), 1618 (6.18), 1493 (6.10), 1443 (6.93), 1393 (7.18), 1163 (8.60), 763 (13.10), 743 (13.46), 721 (13.87).

uv (95% ethanol)

λ_m	log ε
247	4.50
254	4.51
278	4.09
286	4.04
297	4.13

nmr (DMSO-d_6)



	τ	H	Assignment
(m)	1.27	2	A
(m)	2.10	7	B & E
($J_{GF(HF)}$ = 9) (q)*	5.17	1	F
($J_{GH(GF)}$ =16) (q)*	6.72	1	G or H
($J_{HF(GH)}$ = 5) (q)*	7.07	1	G or H

(q)* - indicates doublet of doublets

9-Phenanthrylsuccinic Anhydride

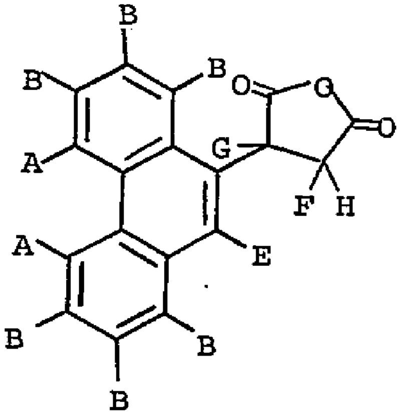
[38]

The phenanthrylsuccinic acid **52** obtained in the previous experiment was mixed with 250 ml of acetyl chloride and refluxed for two hours. The excess acetyl chloride was partially distilled and the solution was brought slowly to room temperature where crystallization took place. Some anhydrous diethyl ether was added and the mixture was chilled, filtered, washed with cold anhydrous diethyl ether and dried to give 74.3 g of solid, mp 144.3-145.0°. One recrystallization from a 5:4 carbon tetrachloride : benzene solution gave tiny white needles in an almost quantitative recovery, mp 144.5-145.0°, in an overall 70% yield from the dicyanoester 51.

Microanalysis:	C	H
Calc. for $C_{18}H_{12}O_3$ (276.29):	78.25	4.38
Found:	77.89	4.36

ir (CHCl$_3$) 1859 (5.38), 1779 (5.62), 1600 (6.25), 1493 (6.70), 1449 (6.90), 1410 (7.09), 1079 (9.27), 1064 (9.40), 912 (10.97),

nmr (DMSO-d$_6$)



	τ	H	Assignment
(m)	1.22	2	A
(m)	2.15	7	B & E
(t)	*4.46	1	G
(8 peak m)	6.29	2	F & H

*or overlapping (q)

Anhydride formation from 9-phenanthrylsuccinic acid could also be effected by heating with polyphosphoric acid and phosphorous pentoxide or with phosphorus pentachloride and stannic chloride; neither reaction showed any accompanying ring closure onto the phenanthrene part of the molecule as evidenced by a lack of absorption beyond 300 mμ in the ultraviolet spectrum.

9-Phenanthrylmaleic Anhydride

[37]

In a reaction analogous to the conversion of phenylsuccinic anhydride to phenylmaleic anhydride,[55] 1.32 g (0.00478 mol) of the phenanthrylsuccinic anhydride **38**, 1.78 g (0.0100 mol) of N-bromosuccinimide and a few mg of benzoyl peroxide were heated with 50 ml of dry carbon tetrachloride for 12 hours under nitrogen. The starting anhydride was not soluble initially but went into solution, which turned red, as the reaction progressed. N-Bromosuccinimide, which had settled to the bottom, was almost completely depleted being replaced by a floating white solid, shown later to be succinimide. The mixture was filtered hot and the succinimide was washed with hot benzene. The filtrate was cooled to 0-5°, precipitating a yellow solid which was filtered, washed with cold carbon tetrachloride, and dried. A small amount of impurities was sublimed at 110°/0.1 mm during a 2-1/2 hour period. The residue was recrystallized twice from a 1:1 mixture of benzene : hexane to give 671 mg of deep-yellow rectangular plates in a 51 per cent yield. The crystals decomposed at 152.2°, showed only one spot on tlc (chloroform) and gave a negative halogen test in a sodium fusion test.

Microanalysis:	C	H
Calc. for $C_{17}H_{11}OBr$ (311.20):	65.61	3.56
Found:	66.19	3.60

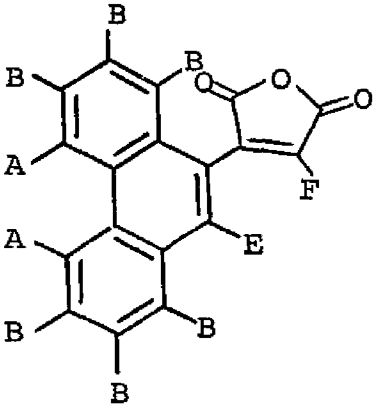
ir (KBr) 3086 (3.24), 1835 (5.45), 1764 (5.67), 1610 (6.21), 1490 (6.71), 1443 (6.93), 1222 (8.18), 907 (11.03), 772 (12.96), 747 (13.38), 726 (13.77).

uv (95% ethanol)

λ_m	log ε
225	4.25
254	4.49
299	4.19

tailing to 355 mμ

nmr ($CDCl_3$)



	τ	H	Assignment
(m)	1.39	2	A
(s)	1.91	1	E
(m)	2.15	6	B
(s)	2.99	1	F

Photolysis of 9-Phenanthrylmaleic Anhydride

[37]

In the same photochemical set-up that was described on pg. 57, 0.2278 g (0.839 mmol) of 9-phenanthrylmaleic anhydride **[37]** and 0.0395 g (0.188 mmol) of benzil were dissolved in 650 ml of anhydrous diethyl ether. The system was deoxygenated by bubbling pre-purified nitrogen through the solution, which was then irradiated for 4-1/2 hours with a 450-watt high-pressure mercury lamp through a pyrex filter. In a separate experiment it was found that a similar irradiation through corex without a sensitizer gave only starting material after 5 hours. The solution became decidedly less yellow as the reaction progressed. At the end of the irradiation the ultraviolet spectrum showed a loss of absorption beyond 299 mμ and the appearance of the typically well-defined phenanthrene-like spectrum. Removal of the solvent left a yellow oil which was triturated with a little diethyl ether to give a grey solid as the major product. The solid was washed with ether, dried and had a mp between 240.5 and 243.0°. Its infrared spectrum, although related to phenanthrene, showed no anhydride absorption. The filtrate showed a small amount of anhydride at 1862 and 1779 cm^{-1} that was not starting anhydride, but because of the small yield was not investigated further.

ir (KBr)	3021 (3.31), 2915 (3.43), 1709 (5.85), 1451 (6.89), 1134 (8.82), 764 (13.09), 747 (13.39), 722 (13.86).
uv (95% ethanol)	$\underline{\lambda_m}$ 226, 256, 271, 279, 289, 301.

Photolysis of Ethyl α-Cyano-β-(9-phenanthryl)-acrylate [**48**]

A saturated solution (approximately 6 mg/ml of ethyl α-cyano-β-(9-phenanthryl)acrylate in anhydrous diethyl ether was deoxygenated in a photolysis apparatus described on pg 57.

The solution was irradiated with a 450-watt high-pressure lamp and the progress of the reaction was monitored in the ultraviolet. Samples were taken periodically and the strong absorption at 3600 Å disappeared after 36 hours. The resulting spectrum contained the well-defined absorptions of a phenanthrene molecule. The solvent was removed, leaving a yellow oil which was chromatographed on neutral alumina and gave largely one product, a yellow glass, 50 mg of which was refluxed in a mixture of 5 ml of concentrated hydrochloric acid, 1 ml of glacial acetic acid for 12 hours. The glass was not soluble at reflux; only starting material was recovered. A 1:1 mixture of concentrated hydrochloric acid : glacial acetic acid also did not effect complete solution at reflux. Basic hydrolysis with ethanolic potassium hydroxide liberated a gas (presumably ammonia) which turned red litmus blue. The residue after work-up gave a resinous product which was not investigated further.

A similar irradiation through pyrex using benzil as a photosensitizer was found after 7-2/3 hours to have produced no change in the ultraviolet spectrum.

ir (of the chromatographed product) ($CHCl_3$):

2237 (4.47), 1736 (5.76), 1597 (6.26),
1497 (6.68), 1449 (6.90), 1366 (7.32),
1093 (9.15).

uv (95% ethanol) λ_m

223, 250, 266, 276, 288, 299.

Attempted Schmidt Reaction of 9,10-Dicarboxyphenanthrene Anhydride

[**54**]

The anhydride **54**,[57] 0.5384 g (0.00215 mol), was heated in 200 ml of concentrated sulfuric acid to 160-165° to effect solution and was then cooled to 35° without any precipitation occurring. Sodium azide, 0.492 g (0.00757 mol), was added in one batch with stirring.[84] No gas evolution was apparent through a nitrogen bubbler. Care was taken to keep the temperature below the boiling point of HN_3 (37°). Stirring was continued for 2 hours after which time an additional 1.06 g of sodium azide was added, with no apparent change. The solution was poured onto ice water; yellow solids were filtered, washed with H_2O and dried to give only starting material.

The reaction was repeated using hydrazoic acid in 1,4-dioxane.[85] Hydrazoic acid (0.70 N) was prepared and standardized with 0.02 N sodium hydroxide. Solution of 0.5197 g (0.00209 mol) of anhydride **54** in 125 ml of purified dioxane (distilled from $LiAlH_4$)[86] was effected by warming on a steam bath. Some precipitation occurred when cooled to room temperature in a 250-ml three-necked round-bottomed flask equipped with a 10-ml pressure-equilibrated addition funnel, reflux condenser, thermometer, magnetic stirrer and nitrogen bubbler. An excess of hydrazoic acid was added with no evolution of gas being observed; a total of 45 ml was used. The mixture was refluxed for 5 hours, cooled, poured onto distilled water, filtered and dried to give only starting anhydride.

Preparation of Sodium 10-carbomethoxyphenanthrene-9-carboxylate

A solution of sodium methoxide in methanol was prepared by adding 0.250 g (0.0109 mol) of sodium to 8 ml of absolute methanol (dried by refluxing over and distilling from magnesium turnings). The anhydride **54**, 1.31 g (0.00531 mol), which had been dried for 12 hours at 105°, was added to 50 ml of 1,4-dioxane (purified by refluxing and distilling from calcium hydride followed by refluxing for 20 hours over sodium and distilling from the metal). Half of the above solution of sodium methoxide in methanol was added under nitrogen to the anhydride in dioxane and stirred at room temperature. A bright yellow solution was effected in approximately 10 minutes. An ir (neat) showed a peak at 1715 cm^{-1} and a complete loss of the characteristic carbonyl doublet of the anhydride. If the solution was not kept completely anhydrous and the starting anhydride was not pre-dried, a white solid, presumably the sodium salt of the acid, precipitated. It lacked both the anhydride and ester carbonyl functions but exhibited a strong broad peak at 1579 cm^{-1} in the ir (KBr).

The half-ester itself could not be isolated. Acidification with an ammonium chloride solution gave a yellow solid which, after filtering, washing and drying, yielded only starting anhydride.

Attempted Synthesis of 9,10-Dicarbomethoxyphenanthrene [56]

Following the literature report,[57] 0.6367 g (0.00257 mol) of 9,10-dicarboxyphenanthrene anhydride [54] was added to 4.41 g (0.0786 mol) of potassium hydroxide in 6.5 ml of methanol and 13.0 ml of distilled water. Solution was effected almost immediately and heating was continued for one hour on a steam bath. Ten ml of dimethyl sulfate (from a newly opened bottle) was added slowly over a 45 minute period. It was necessary to occasionally add potassium hydroxide (same concentration as above) to keep the solution basic. The solution was cooled, but the expected yellow crystals did not materialize. After refrigeration produced no crystals, the solution was refluxed for one hour but only a small amount of solid was produced upon cooling and trituration with water. Because of the small yield, the solids were not worked up.

Attempted Photolysis of Phenanthrene and Dimethyl Acetylenedicarboxylate

A solution of 9.8 g (0.055 mol) of phenanthrene, 10.65 g (0.0749 mol) of distilled dimethyl acetylendicarboxylate and 2.1 g (0.0012 mol) of benzophenone in 650 ml of purified hexane[81] was deoxygenated with pre-purified nitrogen and irradiated for 5-1/3 hours through pyrex using a photolysis apparatus described on pg. 57. The well became coated with a small amount of a tan solid that lacked aromatic absorption in the infrared spectrum and was not investigated further. After removal of solvent and starting ester, a higher boiling, minor fraction distilled at 95°/0.6 mm. It exhibited aromatic absorption (due probably in part to co-distilled phenanthrene) as well as several carbonyl peaks in the infrared spectrum. This oil was not investigated since the desired photoadduct would not be expected to have such a low boiling point.

Thermal Reaction of Phenanthrene and Tetracyanoethylene

Anthracene-free phenanthrene (see pp.40,85), 2.764 g (0.0155 mol) and 2.50 g (0.0128 mol) of recrystallized (from chlorobenzene) TCNE (mp 197.5-198.2°)[61] were dissolved in 9 ml of dimethoxyethane (which had previously been passed through basic alumina until a test showed that it was free of peroxides). The deep burgundy-colored solution was refluxed for six hours, cooled and poured onto distilled water. The solids were filtered, taken up in diethyl ether, dried and the solvent was evaporated to give a mixture that was nearly identical in the ir with the starting mixture. The mixture melted at 85° (phenanthrene melts at 100°); the temperature was taken higher looking for the sublimation of TCNE. At approximately 180° a violent reaction took place within the capillary tube.

Removal of Anthracene from Commercial Phenanthrene

Phenanthrene (98%, Henley & Co.), 40.0 g, was dissolved in 1200 ml of purified hexane and placed in a 2-liter pyrex round-bottomed flask and irradiated for 28-1/4 hours with a G.E. 275-watt sunlamp. After filtering and washing with acetone, 1.03 g (2.7%) of a white crystalline solid was obtained. It melted at 267.8-269.0° after one recrystallization from chlorobenzene and showed a base peak of 178 in the mass spectrum. When heated above 270° under vacuum (0.15 mm) a highly fluorescent white solid was obtained, mp 208-210°, whose ir and uv spectra were identical to those of anthracene (mp 213°). The photolysis product was therefore the dimer of anthracene.

Attempted Photolysis of Dimethyl Maleate and Phenanthrene

To 6.35 g (0.0356 mol) of anthracene-free phenanthrene was added 8.2 ml (0.067 mol) of dimethyl maleate (Eastman). The reaction vessel consisted of an air cooled quartz tube fitted with a condenser and a nitrogen bubbler. The system was deoxygenated with pre-purified nitrogen and a G.E. 350-watt mercury lamp was set approximately six inches from the quartz tube which was irradiated for 12 hours (refluxing did not occur). The solution turned dark brown during this time. After removal of 9.97 g of starting ester and phenanthrene (which co-distilled at 50°/0.1 mm), 5.89 g of residue was hydrolyzed after the method of Cargill.[62] To the residue was added 75 ml of an 8% sodium hydroxide solution which was heated for 21 hours at 95° (at reflux temperatures a solid, presumably phenanthrene, collected in the condenser). The deep-red solution was cooled, some solids filtered, and the aqueous phase was extracted three times with diethyl ether. The solution was acidified with 1.5 N hydrochloric acid until just acid to litmus paper. The reddish-brown solid was washed with water, acetone and dried. It gave 110 mg of material that melted between 145-210°.

An attempted esterification after Bryce-Smith's method[43] using 5 ml of refluxing methanol with one drop of sulfuric acid gave, after work-up, a high-melting apparently polymeric product.

Attempted Reaction of Phenanthrene with Diethyl Fumarate

Phenanthrene, 4.00 g (0.0224 mol), 5.27 g (0.0306 mol) of diethyl fumarate and 0.867 g (0.00476 mol) of benzophenone were dissolved in 265 ml of purified hexane.[81] The solution was deoxygenated by purging with pre-purified nitrogen and was then photolyzed through a corex filter for 6 hours using a 200-watt high-pressure mercury lamp. The photolysis vessel was similar to that previously described on pg. 57.

The solvent was removed and a white solid shown by infrared analysis to be phenanthrene was filtered from a yellow oil. The oil was heated to 175° at 35-40 mm, but did not distil (diethyl fumarate boils at 132° at 22 mm). After removing a fraction at 87-90°/0.13 mm, the residual oil (0.74 g) was hydrolyzed after the method of Bryce-Smith[43] by refluxing with 0.54 g of sodium hydroxide in 30 ml of water for six hours. The mixture was extracted with diethyl ether and then acidified to a congo-red end-point to give a product melting between 225-245°. The uv showed typical phenanthrene-type absorption out to 299 mμ. Absorption beyond 277 mμ is inconsistent with the desired photoadduct.[43]

1'-Keto-3'-carboxy-9,10-cyclopentenophenanthrene [29] from 9-Phenanthrylsuccinic Anhydride

A solution of 910 mg (3.29 mmol) of 9-phenanthrylsuccinic anhydride [38] in 5 ml of dry nitrobenzene was cooled to 0-5°C with an ice bath; 1.5 mg (0.011 mol) of aluminum chloride was dissolved in 15 ml of dry nitrobenzene at the same temperature. The anhydride was added dropwise with stirring to the aluminum chloride solution and the reaction temperature was kept at 0-5° for 2 hours. It was then allowed to warm to room temperature over a period of 2-1/2 hours; a suspension of crystalline solids dissolved as the temperature rose. The deep-red solution was poured onto a 1:4 mixture of concentrated hydrochloric acid and water precipitating a white solid which could be isolated by filtration. The product was washed with water and dried, mp 184 ≈200°. An extraction with 200 ml of chloroform and 100 ml of carbon tetrachloride yielded 100 mg of a white crystalline solid, mp 197 ≈200° (lit: 200-201°[32a]), from the filtrate.

When the reaction was carried out on a larger scale, the extraction was done via a Soxhlet extractor using a 2:1 chloroform : benzene solution as solvent. The extracted material came out of solution, as it filtered back to the pot; the extraction was periodically interrupted for a filtration whenever 100 mg or so of solid had collected. It was found that after a forerun was taken the early fractions were the richest in the five-membered keto-acid.

The product was decarboxylated with potassium hydroxide in ethylene glycol as described on pg. 58. Before acidification the solution was cooled in a refrigerator. White crystalline solids precipitated and were filtered, washed with water, and dried to give 40 mg of product (5.6% yield from the anhydride), mp 171.5-172.0° (lit: 170-171°[32a]). The spectral data, ir, uv and nmr, were identical to 1'keto-9,10-cyclopentenophenanthrene prepared from the Friedel-Crafts reaction of phenanthrene and maleic anhydride (see pg. 58.).

9-Carboxy-2,3-benzperinaphth-[7]-one [61]

The basic filtrate in the decarboxylation reaction above was acidified with dilute hydrochloric acid to give, after filtering, washing with water and drying, very fine pale yellow needles, mp 192-194°. The unextracted material in the above experiment was treated in a similar fashion, i.e. subjected to decarboxylation, filtration and acidification. The combined yield based on reacted starting material was 94%.

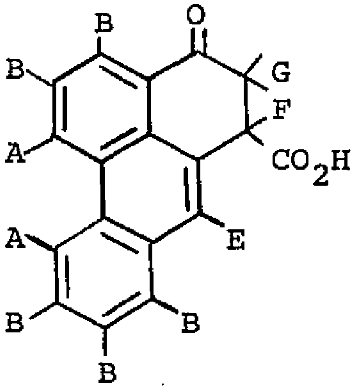
ir (KBr)	3086 (3.24), 2959 (3.38), 2740-2551 (3.65-3.92), 1724 (5.80), 1689 (5.92), 1598 (6.27), 1493 (6.70), 1449 (6.90),

ir (KBr) (continued) 1401 (7.14), 1381 (7.24), 1183 (8.45), 769 (13.0).

uv (95% ethanol)

λ_m	log ε	λ_m	log ε
244	4.48	284	4.27
251	4.46	319	4.10
263	4.40	367	3.52

nmr (DMSO-d_6)



	τ	H	Assignment
(m)	1.17	2	A
(m)	2.17	6	B & E
(J=4) (t)	5.53	1	F
(J=4) (d)	6.89	2	G

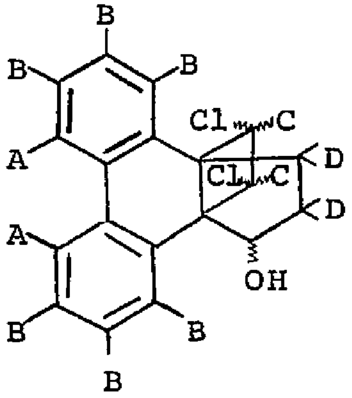
12,13-Dichloro-2,3-dihydro-3a,11b-ethano-1*H*-cyclopenta[*l*]phenanthren-1-ol [**64**]

The cyclopentanophenanthrene photoadduct **30**, 329 mg (1.05 mmol), was sirred with 70 mg (1.8 mmol) of sodium borohydride in 5.0 ml of absolute ethanol at 0-5°. After an hour all of the ketone went into solution. The progress of the reaction was followed by tlc and within one hour and fifty minutes all starting ketone (R_f 41/50-benzene) was depleted and a new spot appeared (R_f 20/54-benzene). The solution was acidified to a pH 6 giving a white precipitate and the mixture was extracted with diethyl ether. After drying the ether phase over magnesium sulfate and filtering, the solvent was removed on a rotary evaporator to give tan crystals, mp 200°, in 89 per cent yield. Two recrystallizations from ethanol-water raised the melting point to 204.8-206.0°. Further recrystallization gave the analytical sample as white needles, mp 207.0-207.4°.

Microanalysis:	C	H
Calc. for $C_{19}H_{16}OCl_2$(331.25):	68.89	4.87
Found:	68.95	4.87

ir (KBr)	3584 (2.79), 3077 (3.25), 2959 (3.38), 2874 (3.48), 1486 (6.73), 1443 (6.93), 766 (13.05), 738 (13.55), 727 (18.76),
($CHCl_3$)	3400

nmr($CDCl_3$ CD_3COCD_3)	τ	H	Assignment
(m)	1.77	2	A
(m)	2.53	6	B
[J=7.6] (d)	4.87		C
[J=7.6] (d)	5.57		C
(m)	7.03		D
(m)	7.85		D



The absorptions of the hydrogen on the carbon containing the alcohol as well as the hydrogen of the hydroxyl group were obscured by the other hydrogens present.

Mass Spectrum	m/e	Relative Intensity
70 electron volts,	234	1000 (with 26% of total area)
inlet temp 170°	233	315.1
	217	219.2
	216	145.2
	215	178.1
	202	164.4
	191	137

All other ions have intensities of less than 100.

Attempted Elimination Reactions on 12,13-Dichloro-2,3-dihydro-3a,11b-ethano-1*H*-cyclopenta[*l*]phenanthren-1-ol

A solution of 100 mg (0.317 mmol) of the dichloro-alcohol **64** in 8 ml of anhydrous diethyl ether was combined with a freshly prepared zinc-copper couple[87] and the ether solution was refluxed for 16 hours with vigorous stirring under nitrogen. Thin layer chromatography indicated only starting material (R_f 20/54-benzene). The ether was removed and 4 ml of dry methanol was added; refluxing and stirring were continued for 5-1/2 hours. The couple assumed a bright copper color. The solution was acidified with 0.2 N hydrochloric acid giving a white solid which was filtered, washed with water until the washings were neutral, and dried to give only starting material.

The reaction was repeated with 46 mg of 64 dissolved in 10 ml of anhydrous diethyl ether and 0.13 ml of acetic acid. Activated zinc[88] (200 mg) was added and the mixture was stirred under nitrogen at room temperature for 12 hours and at reflux for 7 additional hours, but no change was observed (tlc). The diethyl ether was replaced by dry tetrahydrofuran which was refluxed for 4-5 hours but the starting material remained unreactive.

A similar reaction was performed on the corresponding ketone 30. Refluxing with activated zinc and acetic acid for 15 hours in dry tetrahydrofuran gave only starting material.

Reaction of 12,13-Dichloro-2,3-dihydro-3a,11b-ethano-1*H*-cyclopenta[*l*]phenanthren-1-ol with Sodium in Liquid Ammonia

The dichloro-alcohol 64 was heated in a drying pistol at 100°/0.1 mm for 2-1/2 hours; 50 mg was then dissolved in 4 ml of anhydrous diethyl ether in a three-necked round-bottomed flask equipped with a magnetic stirrer, dry ice condenser and a soda-lime exit trap. Pre-purified nitrogen was passed through the system which had been pre-dried. Ammonia was double-distilled into the system and excess sodium was added. Within a few minutes a deep blue color pervaded the mixture. Stirring was continued for 1.75 hours. Solid ammonium chloride was added until the blue color disappeared. Water was added carefully and the ammonia was allowed to evaporate. Additional diethyl ether was added; the organic phase was separated and extracted three times with water and dried over anhydrous magnesium sulfate. The desiccant was filtered and a tlc showed no starting material (R_f 20/54-benzene); a new spot appeared at R_f 14/53-benzene. The ether was removed to give an oil which did not solidify. Chromatography on silica using hexane, benzene-ether, as elutents gave, as a main fraction, a dark-colored gummy-solid. The product appeared polymeric and purification was not continued.

ir ($CHCl_3$)	3200-3400 (3.12-2.94), 1715 (5.83), 1600 (6.25), 1450 (6.90). No absorption was noted at 1555 cm^{-1}.[69]

Attempted Dehalogenation of Alcohol $\underset{\sim}{64}$ and Ketone $\underset{\sim}{30}$ by Means of Lithium Aluminum Hydride

A tetrahydrofuran solution (4 ml) containing 82 mg (0.26 mol) of the ketone $\underset{\sim}{30}$ was refluxed under nitrogen for 12 hours with 6.6 mg (0.18 mmol) of lithium aluminum hydride.[70]

The reaction mixture was cooled, one drop of water was added and the mixture was stirred overnight. The solids (inorganic) were filtered, washed with THF and the filtrate was reduced in volume. The residual crude green oil was taken up in chloroform and dried over magnesium sulfate. Filtration and removal of solvent gave an oil whose ir (neat) showed a hydroxyl group at 3425 cm^{-1} and two weak-to-moderate absorptions at 1770 and 1724 cm^{-1} (the ketone absorbed at 1745 cm^{-1}). The oil was dissolved in 4-5 ml of dry THF and approximately 15 mg of lithium aluminum hydride was added and the solvent was refluxed for 12 hours under nitrogen. After work-up, a crude oil was obtained whose ir was similar to that cited above except the peaks at 1770 and 1724 cm^{-1} were reversed in intensity, the 1770 cm^{-1} peak was now the stronger one. There was no indication of any absorption at 1555 cm^{-1}.[69]

A reaction with lithium aluminum hydride and the dichloro-alcohol **64** in dry THF was attempted. After 2-1/2 hours the ir showed the appearance of peaks at $1730_{(w-m)}$ and $1712_{(sh)}$ cm^{-1}.

The crude nature of the products, the anomalous peaks in the 1700 region, and the lack of an absorption at 1550 cm^{-1} characteristic of a cyclobutene carbon-carbon double bond did not prompt further work on these products.

Preparation of the Ketal 68 of 12,13-Dichloro-2,3-dihydro-3a,11b-ethano-1*H*-cyclopenta[*l*]-phenenthren-1-one

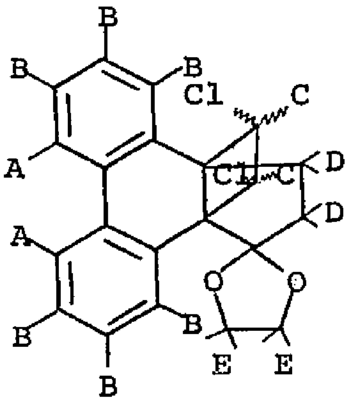
A solution of 397 mg (1.27 mmol) of the ketone 30 in 17 ml of ethylene glycol was heated with a few mg of *p*-toluenesulfonic acid for one half hour at 168°. The solution was cooled, mixed with benzene and aqueous sodium carbonate and shaken. The benzene layer was separated and extracted with water; the aqueous phase was extracted once with benzene. The organic phase, after drying over magnesium sulfate, filtering and, after removing the solvent, yielded 388 mg (82% yield) of a cream-colored solid, mp 175-180°, R_f 37/53.5 (benzene). One recrystallization from benzene-hexane gave white plates, mp 184-185°. An analytical sample melted between 185.1-186.0°.

Microanalysis:	C	H
Calc. for $C_{21}H_{18}O_2Cl_2$(373.28):	67.57	4.86
Found:	67.07	4.86

When the reaction was run in benzene and refluxed for 18-1/2 hours, only starting material was recovered; a 1:1 mixture of refluxing ethylene glycol : benzene yielded the same results. When ethylene glycol was used as solvent and heated from 100-140° for 1/2 hour, the starting material was still present in the reaction medium.

ir (KBr) 3058 (3.27), 2959 (3.38), 2882 (3.47), 1623 (6.16), 1486 (6.73), 1441 (6.94), 1152 (8.58), 1041 (9.61), 944 (10.59), 758 (13.20), 735 (13.60).

nmr ($CDCl_3$)



		τ	H	Assignment
	(m)	1.82	2	A
	(m)	2.44	6	B
(J=8)	(d)	5.01	1	C
(J=8)	(d)	5.56	1	C
	(m)	5.72-8.5	8	D, E

Reaction of a Zinc-Copper Couple with the Ketal **68** of 12,13-Dichloro-2,3-dihydro-3a,11b-ethano-1*H*-cyclopenta[*l*]phenanthren-1-one

A dry diglyme solution containing 114 mg (0.305 mmol) of ketal **68** was stirred overnight at room temperature under nitrogen with 360 mg of a zinc-copper couple.[87] Thin layer chromatography showed that the ketal was still unreacted. The mixture was then heated from 110-120° for an hour, filtered and the couple was washed with benzene. The filtrate was concentrated using a vacuum pump; the white solid residue showed two spots on tlc, starting material, R_f 43/59 (benzene), and a new spot, R_f 25/59 (benzene). The solid was recrystallized from absolute ethanol to give colorless plates whose tlc showed only a small amount of the slower moving spot. An ir was almost identical to starting ketal and the white crystals showed surface melting at 171°, solidification and then melting at 184° (starting ketal, mp 183.5-184.0°). The filtrate from the recrystallization was taken to dryness but gave only a small amount of a gum whose ir lacked definition and the gum was not investigated further.

Attempted Formation of the Tosylate of 12,13-Dichloro-2,3-dihydro-3a,11b-ethano-1*H*-cyclopenta[*l*]phenanthren-1-ol.

A cold solution (0-5°) of 50 mg (1.5×10^{-4} mol) of the dichloro-alcohol **64** in 2.5 ml of pyridine (distilled from barium oxide) was combined with 57.3 mg (3.0×10^{-4} mol) of purified *p*-toluenesulfonyl chloride.[89] The temperature was maintained for 24 hours; no evidence of the formation of the pyridinium hydrochloride salt was found even after 24 hours at room temperature. Thin layer chromatography showed only starting material, R_f 16/52 (benzene). The solution was refluxed[90] for 23 hours but the starting alcohol remained intact (tlc).

The reaction was repeated using 2,6-lutidine instead of pyridine. The solution was heated to reflux over a twenty-minute period with the concurrent formation of white crystals. The mixture was cooled and white needles were filtered and found to be soluble in water. The filtrate was acidified with dilute hydrochloric acid and chloroform was added. The organic phase was extracted three times with water, dried over magnesium sulfate, filtered, and the chloroform was removed to give only the starting alcohol.

Preparation of the Acetate of 12,13-Dichloro-2,3-dihydro-3a,11b-ethano-1*H*-cyclopenta[*l*]phenanthren-1-ol

Using a procedure for the dehydration of an alcohol,[91] a solution of 20 mg of the dichloro-alcohol 64 in one or two ml of acetic anhydride was refluxed for one hour with 12 mg of potassium acid sulfate. The reaction was followed by thin layer chromatography which showed the disappearance of the starting alcohol. The mixture was cooled, diethyl ether and a dilute sodium carbonate solution were added and the ether layer was separated and washed three times with water. A yellow oil was obtained after drying over magnesium sulfate, filtering and removing the ether. An infrared spectrum showed the loss of the alcohol function at 3584 and 3400 cm^{-1}, but the desired dehydration product was not obtained; the acetate (1742 cm^{-1}) was formed from the alcohol and acetic anhydride.

ir ($CHCl_3$) 1742 (5.74), 1484 (6.74), 1443 (6.93), 1372 (7.29), 1057 (9.46), 760 (13.15), 733 (13.63).

1'-Keto-3'-bromo-9,10-cyclopentenophenanthrene

[71]

A dry carbon tetrachloride solution containing 232 mg (0.001 mol) of 1'-keto-9,10-cyclopentenophenanthrene [27], 178 mg (0.001 mol) of N-bromosuccinimide and a few mg of benzoyl peroxide was refluxed for 1/2 hour under nitrogen. The NBS had reacted completely. Succinimide at the surface was filtered, washed three times with cold carbon tetrachloride, and once with warm carbon tetrachloride. The filtrate was extracted three times with water, dried over magnesium sulfate and, after removal of solvent, gave a tan solid in good yield, mp 148-152° dec. An analytical sample, as deep yellow rectangular plates, mp 152.2°, R_f 39/57 (benzene), was prepared by recrystallization from benzene-hexane.

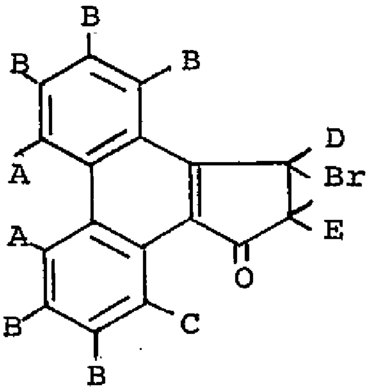
Microanalysis:	C	H
Calc. for $C_{17}H_{11}OBr$ (311.20):	65.61	3.56
Found:	66.19	3.60

ir (KBr) 3086 (3.24), 2942 (3.42), 1709 (5.85), 1610 (6.21), 1570 (6.37), 1502 (6.66), 1447 (6.91), 1401 (7.14), 758 (13.20), 726 (13.73).

uv (95% ethanol)

λ_m	log ε
247	4.56
263	4.55
285	4.18
324	4.13

nmr ($CDCl_3$)



		τ	H	Assignment
	(m)	1.29	2	A
	(m)	1.63	1	C
	(m)	2.19	≈5	B
[J=2.5]	(d)	4.12	* 1	D
[J=2.5]	(d)	4.03		
	(d)	6.41	** 2	E
	(d)	6.67		

*) Apparent coupling constants

**) Apparently overlapping doublets.

1'-Keto-9,10-cyclopentadienophenanthrene Dimer

[77]

Triethylamine (2 ml) and 50 mg (0.16 mmol) of 1'keto-3'-bromo-9,10-cyclopentenophenanthrene [71] were stirred for one hour at room temperature under nitrogen. The triethylamine was purified by distillation followed by a redistillation from a 2% solution of phenylisocyanate.[92] The tan crystals of the bromoketone were replaced by a pale yellow suspension as the reaction progressed. A cream-colored solid precipitated upon the addition of 4 ml of water and was filtered, washed with 0.1 N hydrochloric acid and dissolved in chloroform. The chloroform layer was washed with water until neutral, dried over magnesium sulfate, filtered and, after removal of solvent, yielded a cream-tan solid (R_f 12/57 as the only spot in benzene), mp 200° dec.

ir (KBr) 3049 (3.28), 3012 (3.22), 2907 (3.44), 2841 (3.52), 1773 (5.64), 1686 (5.93), 1610 (6.21), 1570 (6.37), 1499 (6.67), 1447 (6.91), 1401 (7.14), 755 (13.24), 728 (13.73).

uv (95% ethanol) $\underline{\lambda_m}$

249, 259, 288, tailing to 364.

Photolysis of 1'-Keto-3'-bromo-9,10-cyclopenteno-phenanthrene[**71**] in Dichloroethylene

The irradiation of 95 mg (0.305 mmol) of the bromo-ketone **71** was carried out with a 250-watt mercury lamp through a corex filter using 250 ml of cis- and trans-dichloroethylene in an apparatus described on pg. 57. The solution turned red during the photolysis (65 minutes) and samples were taken for ultraviolet analysis. The absorption band at 324 mμ in the starting bromo-ketone was shifted to 317 mμ accompanied by a loss of definition and a broadening of the band. Absorption at 285 mμ was not shifted but was broadened. The solvent was removed, leaving a red glass that decomposed below 130°. A tlc showed that almost all of the starting bromo-ketone had reacted (R_f 32/55 benzene). The ir resembled starting material; the carbonyl was intact at 1689 cm^{-1} and there was a slight shift from 749 to 758 cm^{-1} and from 723 to 726 cm^{-1} in the red product. The uv data indicated that the 9,10-photoadduct had not formed and the nature of the red solid was not pursued further.

Attempted Photolysis of 9,10-(1'-Keto)cyclopentenophenanthrene with Maleic Anhydride

A hexane solution (265 ml) containing 116 mg (0.536 mmol) of the ketone 27 and 56 mg (0.57 mmol) of maleic anhydride was photolyzed using a 450-watt mercury lamp with a corex filter in an apparatus described on pg. 57. After 16 hours of irradiation the 9,10-double bond of the cyclopentenophenanthrene was still intact as shown by the ultraviolet absorption of the unsaturated ketone beyond 300 mμ. The photolysis probe was coated with a tan solid which did not appear in the ir to be a phenanthrene derivative, i.e. it lacked aromatic absorption.

7,8-Dicarbomethoxytricyclo[4.2.2.$0^{2.5}$]deca-3,7,9-triene [80]

In a modification of Reppe's[76] procedure, 27.9 g (0.268 mol) of distilled cyclooctatetraene, 37.8 g (0.266 mol) of distilled dimethyl acetylenedicarboxylate and 0.033 g (0.0030 mol) of hydroquinone were heated under nitrogen in a 100-ml round-bottomed flask containing an immersion well (to measure internal temperature) and a reflux condenser. The temperature was taken up slowly to 160° (vigorous refluxing started at 140°) and was maintained between 160-170° for 4 hours. The vigorous refluxing eventually subsided as the reaction proceeded. Distillation gave 16.5 g of a colorless liquid, bp 110-112°/0.15 mm (lit: 138-145°/2 mm[76]).

3,4-Dibromo-7,8-dicarbomethoxytricyclo[4.2.2.0$^{2.5}$]deca-3,7-diene [81]

The COT-acetylenic ester adduct 80, 0.6364 g (0.002585 mol), 1.031 g (0.005792 mol) of N-bromosuccinimide and 0.0545 g (0.225 mmol) of benzoyl peroxide were dissolved in 8 ml of dry benzene and set to reflux. After one hour all solids were in solution (yellow). Refluxing was continued for a total of 9-2/3 hours. The resulting red solution was chilled in a refrigerator for 4 hours. Tan solids were filtered off, washed three times with cold benzene and once with diethyl ether to give 0.2389 g of a water soluble product shown by ir to be succinimide.

Anhydrous diethyl ether (7 ml) was added to the filtrate and the mixture was placed in the refrigerator overnight giving 0.2193 g of a cream-colored solid, mp 147-151°. Two recrystallizations from hexane/benzene gave material of mp 154-155°.

ir ($CHCl_3$) 1709, 1597, 1499, 1456, 1383 cm^{-1}.

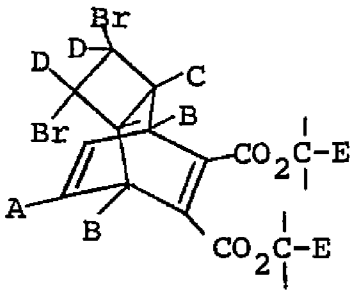
nmr ($CDCl_3$) (m) 2.6τ (5H)

(s) 7.2τ (4H)

Structure Assignment: N-Phenylsuccinimide (lit: mp 155-156°).

The solvent was removed from the filtrate and 10-15 ml of diethyl ether was added, depositing 0.7802 g of a cream-colored solid melting between 105-120°. Four recrystallizations from benzene/hexane gave beautiful colorless plates, mp 133.4-134.1°. An additional 0.3925 g (mp 127-128° - after one recrystallization) was obtained by seeding and cooling the mother liquor.

nmr ($CDCl_3$)



	τ	H	Assignment
(triplet with each peak a doublet)	3.17	2	A
"	3.46		
(q)	5.37	1	D
(m)	5.75	3	D & C
(s)	6.20	6	E
(m)	6.90	2	B

ir (CCl_4) 3033 (3.33), 2958 (3.38), 2841 (3.52), 1718 (5.82), 1639 (6.10), 1608 (6.22), 1456 (6.89), 1433 (6.98), 1433 (7.41),

ir (CCl_4)(continued) 1333 (7.50), 1314 (7.61), 1064 (9.40),
1072 (9.33), 1124 (8.90), 1134 (8.82).

Attempted Dibromination of 7,8-Dicarbomethoxytricyclo-[4.2.2.0$^{2.5}$]deca-3,7,9-triene [80] in Carbon Tetrachloride

A solution of the COT-acetylenic ester adduct 80, 0.5188 g (0.00211 mol), and 0.8205 g (0.00461 mol) of N-bromosuccinimide in 8 ml of dry carbon tetrachloride was refluxed for 88 hours. No reaction was apparent; NBS remained on the bottom of the reaction vessel. Five mg of benzoyl peroxide was added and reflux was continued for three hours. The N-bromosuccinimide underwent reaction and yielded an amber, oily residue which formed a gum upon cooling in a freezer. Chromatography on silica gave an oil (related to starting ester) whose ir and nmr showed loss of vinyl protons (no product was found corresponding to that obtained when benzene was used as solvent. See pg.105.). The solvent apparently entered into the reaction as is shown below.

Reaction of Carbon Tetrachloride, N-Bromosuccinimide and Benzoyl Peroxide

The reaction described above was repeated without the COT-acetylenic ester adduct. After one hour's time NBS began to react and an oily solid was deposited on the top and sides of the reaction vessel and the mixture became amber in color, effects similar to that described in the experiment above.

Reaction of 3,4-Dibromo-7,8-dicarbomethoxytricyclo-$[4.2.2.0^{2.5}]$deca-3,7-diene[81] with Sodium Methoxide

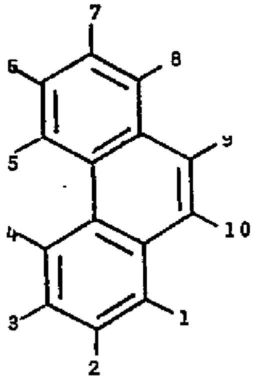
The dibromide 81, 0.499 g (0.00123 mol) and 0.0589 g (0.00128 mol) of sodium hydride (53.5% as a mineral oil dispersion) were added to 3 ml of dried benzene and the suspension was warmed. Two drops of a 10% solution of absolute methanol in benzene was added to initiate reaction. As the reaction became self-sustaining and a gas was evolved the mixture turned pink (occasionally, as the gas evolution subsided, a few drops of methanol solution were added). The solvent was taken to reflux for one hour. Additional methanol was added to the red mixture and, after the addition of some diethyl ether, the mixture was acidified with a 5% HCl solution. Solids which had collected on the bottom of the reaction vessel dissolved at this point. The organic phase was washed twice with Na_2CO_3 and once with water (the organic phase was colorless and the aqueous phase was yellow). After drying over $MgSO_4$, filtration and removal of solvent, 0.1706 g of a solid, mp 130-132°, was collected and shown by ir analysis to be identical to starting dibromo ester. No other product was isolated in the organic phase.

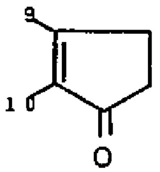
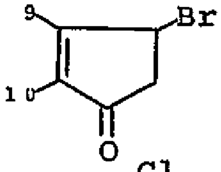
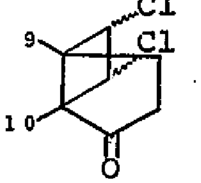
Work-up of the aqueous phase yielded only a negligible amount (other than salts) of a colorless, oily solid which was not investigated further.

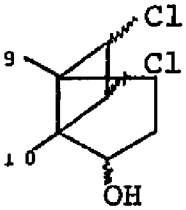
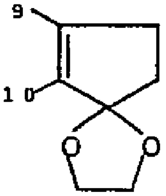
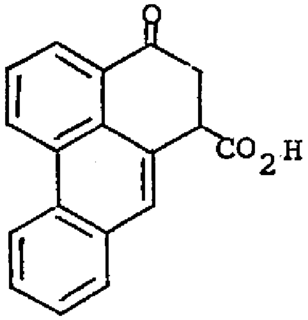
Hydrolysis of 7,8-Dicarbomethoxytricyclo-[4.2.2.$0^{2.5}$]deca-3,7,9-triene[80]

In order to determine the stability of the ester 80 in base, a solution of 0.5838 g (0.00237 mol) of 80 in 50 ml of 0.2 N sodium hydroxide was refluxed for 2 hours. Acidification with HCl yielded an apparently polymeric material that did not melt by 340°.

NMR(τ) CORRELATION TABLE OF PHENANTHRENE DERIVATIVES



		4-5	10	8	12367(8)
PHENANTHRENE		1.07	2.30 (s)	1.87	1.87-2.12
9=Br		1.40	1.88 (s)	1.40	2.28
9,10=Cl		1.47	-	1.47	2.30
9=CHO	[47]	1.48	1.97 (s)	0.72	2.31
9=CH=C(CN)CO_2Et	[48]	1.41	2.23 (s)	1.41	2.23
9=CH=C(CN)CO_2H	[50]	1.32	1.79 (s)		2.24
9=CH(CN)CH(CN)CO_2Et	[51]	1.31	1.79 (s)		2.17
9=Succinic Acid	[52]	1.27	2.07		2.10
9=Succinic Anhydride	[38]	1.22	2.15		2.15
9=Maleic Anhydride	[37]	1.39	1.91 (s)		2.15
	[27]	1.50	-	0.72	2.29
	[71]	1.29	-	1.63	2.19
	[30]	2.04	-		2.62

		4-5	10	8	12367(8)
	[64]	1.77	–		2.53
	[68]	1.82	–		2.44
	[61]	1.17	2.17		2.44

SUMMARY

The synthesis of the non-isomerizable Dewar benzene 23 and a study of its chemistry remains an intriguing problem. Prof. Goldman's group is pursuing the synthesis of 1'-keto-9,10-cyclobutenophenanthrene [39] by means of Wittig reactions on 9,10-phenanthrenequinone. The irradiation of the phenanthrocyclobutenone and dichloroethylene would be expected to give a compound, analogous to the one prepared from the phenanthrocyclopentenone 27, which would lead to the Dewar benzene 23. Work is also planned on other routes to the synthesis of 9-amino-10-carboxyphenanthrene [55] which would serve as another phenanthryne precursor which, as in the benzyne case, would be expected to give phenanthrocyclobutene derivatives in addition reactions.

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AUTOBIOGRAPHICAL STATEMENT

John P. Burke was born in New York City in 1936. He attended a parochial elementary school in Queens and was graduated from Power Memorial High School in Manhattan in 1954. That same year he entered Iona College in New Rochelle, New York, and majored in chemistry receiving a bachelor's degree in 1958. In April of 1959 he married the former Rita Egan. They have one daughter, Maura, age 6. After service with the United States Army at the Quartermaster Corps' chemical laboratory, Fort Lee, Virginia, he taught in high schools in Virginia and New York. In 1963 he returned to school to do graduate work at Queens College from which he received a master's degree in chemistry in 1965. While pursuing his doctoral work at the City University of New York he continued teaching as a part-time lecturer at Queens College. In June of 1969 he joined the faculty of Pace College, New York City, as an assistant professor of chemistry.