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I. THE PHOTOLYSIS OF 1,2-DIPHENYLCYCLOBUTENE.
II. THE SYNTHESIS OF 9,10-CYCLOBUTENOPHENANTHRENE FROM 9,10-DIMETHYLENE-9,10-DIHYDROPHENANTHRENE.
III. PYROLYSIS OF 2-METHYLENE-3,4,5,6,-DIBENZO-3',4'-(9-10-PHENANTHRO) SPIROBICYCLOHEXANE.
IV. THE DECOMPOSITION OF N-NITROSOKETIMINES.

The Johns Hopkins University, Ph.D., 1970
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I. The Photolysis of 1,2-Diphenylcyclobutene

II. The Synthesis of 9,10-Cyclobutenophenanthrene From 9,10-Dimethylene-9,10-Dihydrophenanthrene

III. Pyrolysis of 2-Methylene-3,4,5,6-Dibenzo-3',4'-(9-10-Phenanthro)spirobicyclohexane

IV. The Decomposition of N-Nitrosoketimines

by

John Paul Anhalt

A dissertation submitted to The Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy.

Baltimore, Maryland

1970

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Abstract

Part I

The synthesis of cis-3,4-dimethyl-1,2-diphenylcyclobutene (16) has been attempted. Two pathways, one starting with cis-3,4-dimethyl-1,2-diphenylcyclobutane (12), and one starting with cis-2-butene and diphenylacetylene were tried. 3,4-Dimethyl-1,2-diphenylcyclobutene (16) could not be obtained in pure form.

The possible wavelength effect in the photochemical formation of 9,10-cyclobutenophenanthrene (1) from 1,2-diphenylcyclobutene (2) and the cleavage of 2 to give diphenylacetylene and ethylene has been investigated. No wavelength effect has been found.

Part II

The synthesis of 9,10-cyclobutenophenanthrene (2) in four steps from 9,10-phenanthroquinone (5) is described. The intermediacy of 9,10-dimethylene-9,10-dihydrophenanthrene (4) is demonstrated.

Part III

The pyrolysis of 2-methylene-3,4,5,6-dibenzo-3'4'-(9,10-phenanthro)spirobicyclohexane (3) is shown to give principally tetrabenz(a,c,h,j)anthracene (4), ethane, and ethylene. The structure for the so-called 1,2,5,6-bis(9,10-phenanthro)cyclo-octa(1,5)diene (2), previously reported from the pyrolysis, is

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revised. Two possible mechanisms for the formation of the products in this reaction are discussed. One possible mechanism for the formation of 4 would involve an intramolecular ene reaction of 3 to give 4a,8a-ethano-10,10a-dihydrotetrabenz(a,c,h,j)anthracene (8). Loss of the ethano bridge from 8 by a reverse Diels-Alder reaction would then give 10,10a-dihydrotetrabenz(a,c,h,j)-anthracene (9). Another possible mechanism would involve a concerted loss of ethylene from 3 to give 9,10-dihydrotetrabenz-(a,c,h,j)anthracene (11). Both dihydroanthracenes would be expected to convert readily to 4.

Part IV

The formation of an electronically excited state in the thermal decomposition of an N-nitrosoketimine to a ketone and nitrogen has been examined. No excited state products have been detected.

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Acknowledgment

It is with sincere gratitude, that I would like to thank Dr. Emil H. White, for giving so generously of his time, counsel, and personal understanding.

I also wish to thank Mr. Joe Anhell, of this department, for taking the 100 mHz spectra and Mr. Eli Rapaport for taking the mass spectra.

I am grateful to Dr. D. O. Cowan for the use of his optical bench and light source and many helpful discussions.

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To Carol

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Part I.

The Photolysis of 1,2-Diphenylcyclobutene

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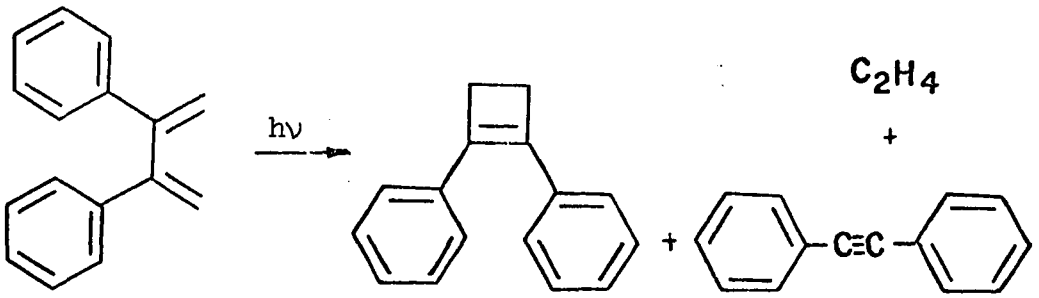
The photolysis of 2,3-diphenylbutadiene (1) in dilute solution gives 1,2-diphenylcyclobutene (2) as well as appreciable amounts of diphenylacetylene (3) and ethylene.[1] The formation of diphenylacetylene and ethylene is most easily explained through the intermediacy of 2 which also



1 2 3

gives high yields of these products on irradiation. Haller and Srinivason[2] have proposed cyclobutene-3,3,4,4-d_4 as an intermediate in the formation of acetylene and ethylene-d_4 in the vapor phase direct photolysis of 1,3-butadiene-1,1,4,4-d_4. These authors proposed that this cyclobutene decomposes to acetylene and ethylene from a vibrationally excited ground state since the decomposition does not occur in the condensed phase[3]. The possible formation of 3 from a vibrationally excited ground state of 2 would be difficult to rule out conclusively. The fact that irradiation of 2 in dilute solution gives principally diphenylacetylene and ethylene indicates that a vibrationally excited ground state is probably not involved. Furthermore, the conservation of orbital

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symmetry predicts that the concerted cleavage of 2 would occur from an electronically excited state[4].

The major photochemical reactions of 2 appear to be from a singlet state[5]. DeBoer and Schlessinger[5] found that the sensitized photolysis of 2 lead to no reaction with a quantum yield greater than 0.001; whereas, diphenylacetylene and ethylene were formed with a quantum yield of about 0.01 in the direct photolysis at 335 mμ[5]. In our work, we have obtained a quantum yield of the same order of magnitude for the decomposition of 2 to 3. Even sensitizers with triplet energies greater than 60 kcal/mole failed to cause appreciable reaction[5]. The transfer of triplet energy to 2 was not demonstrated; however, it appears quite probable, since stilbene ($E_T \sim 57$ kcal/mole[6]), which should be similar in triplet energy to 2, is known to quench sensitizers with triplet energies as low as 47 kcal/mole[7]. DeBoer and Schlessinger[5] have presented other evidence which characterizes the reactive state of 2 as a singlet. These authors observed a decrease in fluorescence quantum yield exactly parallel to an increase in the quantum yield for 1,2,5,6-tetraphenyltricyclo[4.2.0.$0^{2,5}$]-octane (4) formation with increasing concentration. This result indicates that formation of a collisional complex leading to formation of 4 or deactivation of the excited

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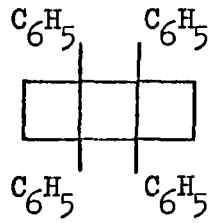

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state is the major process competing with fluorescence for deactivation of the singlet of 2, since the quantum yield for fluorescence of 2 at infinite dilution is 1.0 ± 0.05[5]. These authors also measured the intersystem crossing rates for 2 and found it to be negligible ($<10^{-2}$).

At about the same time as our work on the photolysis of 2,3-diphenylbutadiene (1)[1] was completed, Hoffmann and Woodward presented a theoretical interpretation of cycloaddition reactions[8]. This interpretation has been expanded upon in subsequent articles by these authors[4]. According to Woodward and Hoffmann, the cycloaddition of ethylene to ethylene to form cyclobutane is symmetry allowed if one ethylene is in an electronically excited state. The reverse reaction is also allowed if the cyclobutane is in an electronically excited state. The expansion of this concept to the cycloaddition of acetylene to ethylene to form cyclobutene in a symmetry-allowed process, presents no obvious problems, since the orbitals of acetylene perpendicular to the reaction

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plane can be considered as completely extraneous to what is basically the cycloaddition of two ethylenes. The reverse reaction does, however, present difficulties. The first excited state in cyclobutene would most likely involve the promotion of an electron in a π antibonding orbital.

The similarily of the photochemical cleavage of cyclobutane to the cleavage of cyclobutene is not clear from the original model. In cleavage of cyclobutane the excitation resides in the σ bonds, whereas in the cleavage of cyclobutene excitation is in a π bond. Coupling between the excited states of the π bond and the excited states of the σ bonds may explain this apparent discrepancy. In a purely physical picture, it would appear that any displacement toward formation of acetylene and ethylene in the lowest excited state of cyclobutene would lead to further displacement, since coupling between the π orbitals and the σ orbitals in the forming acetylene molecule would increase as the σ orbitals attain more π character.

The recent observation by Saltiel and Ng Lim[9] of the stereospecific cleavage of 5 and 6 to the respective cis and trans- cyclodeca-1-en-7-yne on direct irradiation supports the view that the photochemical decomposition of cyclobutenes is symmetry-allowed.

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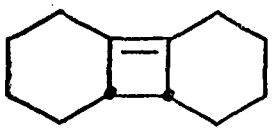

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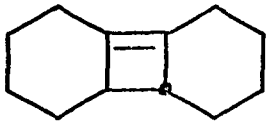

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In the photochemical cleavage of 2 to diphenylacetylene (3) and ethylene, the analogy to the cleavage of cyclobutane to ethylene is even more complicated. It is possible that the first transition in 2 would not involve a change in symmetry of the central ethylenic bond which is necessary for concerted (stereospecific) cleavage. In styrene, for example, the first excited state corresponds to the ^1L_b state of benzene and does not involve a change in symmetry of the olefinic double bond[10]. The first excited state of cis-stilbene, however, does show a node in the central double bond. This state corresponds to the ^1L_a states of the benzene rings and is shifted sufficiently to longer wavelength to become the first excited state in stilbene. This shift is due to the stronger coupling of the ethylenic states with the benzene states[10].

We initially set out to study the stereochemistry of the photolytic reactions of diphenylcyclobutene (2). Three reactions, in addition to dimerization, can be predicted to occur. In the absence of an oxidant, products arising from

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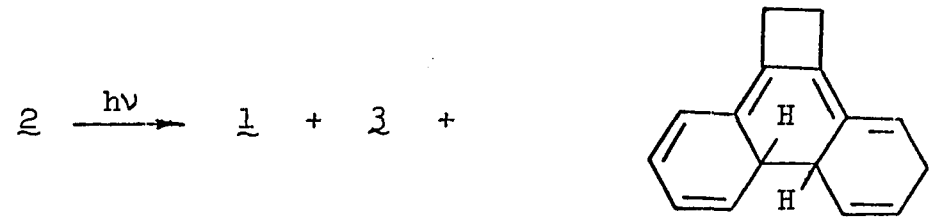
the dihydrophenanthrene (7) would not be expected.[11] The



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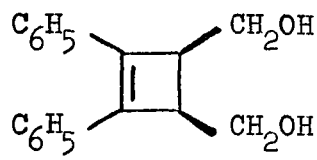
predicted course for the concerted formation of 1 is disrotatory; however, in the absence of substituents the stereochemical course of the reaction cannot be determined. Friend[12] attempted to solve this problem by photolysis of the cis-diol (8) and cis-ester (9). His results showed, however, that another product, possibly a phenanthrene, was formed in preference to 3.



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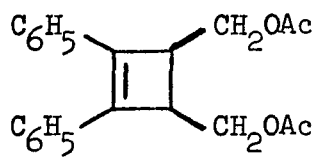

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We felt that the oxygens might be involved in this anomalous reaction. To test this hypothesis, we attempted the photolysis

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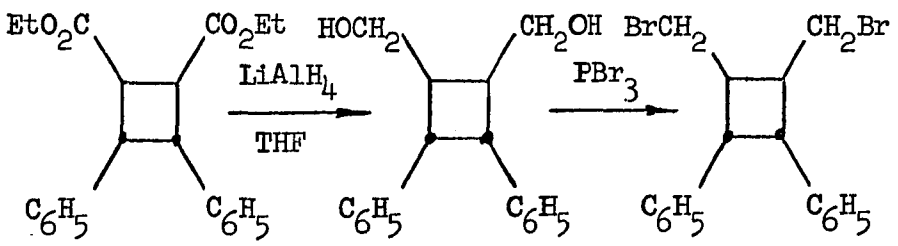
of cis-3,4-dimethyl-1,2-diphenylcyclobutene (16). Cis-3,4-bis(bromomethyl)-cis-1,2-diphenylcyclobutane (11) had previously been prepared by Blomquist and Meinwald[13] in two steps from diethyl β-truxinate (10). β-Truxinic acid was readily available from the photolysis of a suspension of freshly precipitated trans-cinnamic acid according to the method of Bernstein and Quimby[14]. Reduction of 11 with lithium



10 7 11

aluminum hydride gave an 87% yield of cis-1,2-diphenyl-cis-3,4-dimethylcyclobutane (12), mp 30-31°. We chose reduction of the dibromide (11) to avoid the possible formation of the cyclic oxide (13) which might occur in reduction of the ditosylate (14). The formation of a cyclic oxide in the reduction of 1,4-ditosylates has been reported in the synthesis of cantharidin[15]. Subsequently, 12 was prepared in an impure form by the lithium aluminum hydride reduction of 14[16]. It is interesting to note that the aromatic protons

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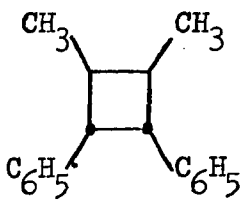

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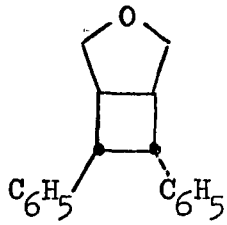

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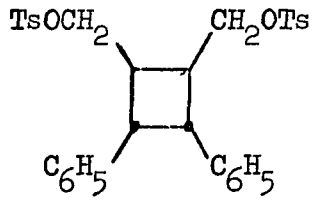

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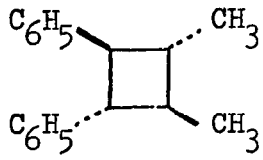
of 12 appear in the nmr as a rather broad singlet in contrast to the sharper singlet obtained for the all trans compound (15)[16]. Such a broadening of the phenyl resonance was reported



15

by Curtin, Gruen, Hendrickson, and Knipmeyer[17], and was explained on the basis of steric hindrance of rotation of the phenyl ring.

The conversion of 12 to 16 met with difficulty. Benzylic bomination of 12 with N-bomosuccinimide (NBS) presumably gave

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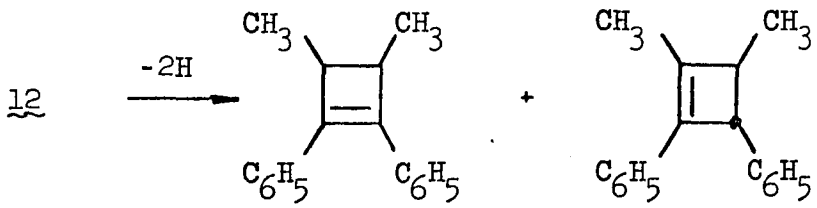
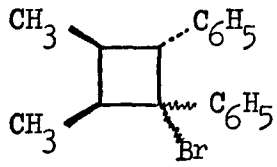


16 17

a monobromide (18). This bromide apparently eliminated



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spontaneously. The olefins from this elimination reacted further under the reaction conditions to give a complex mixture. In one run, a partial separation of two major components was obtained by tlc on silica gel impregnated with silver nitrate. These two compounds appeared to be 16 and 17 by comparison of their ultraviolet spectra with the ultraviolet spectrum of the parent hydrocarbon (2) and the published spectrum of 17[13a]. By analogy, Bloomquist and Meinwald obtained two isomers from the base promoted

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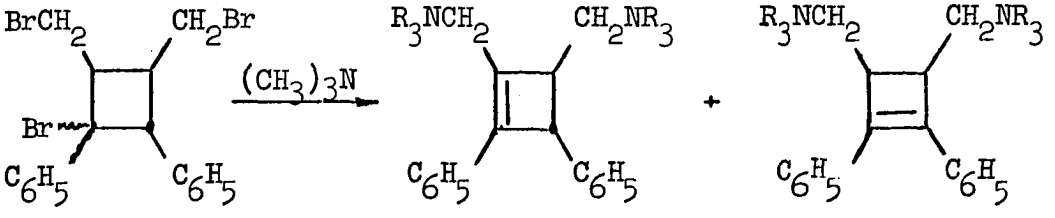
elimination of 19[13a].



19 R= CH_3

Separation of 16 and 17 by chromatography on silica gel impregnated with silver nitrate, athough applicable on a small scale, would be more difficult on a larger scale, since resolution would be poorer. In addition, the long contact time required by a preparative scale chromatography might allow decomposition catalyzed by silver ion to occur. Merk and Pettet have shown catalysis by silver ion in the thermal ring opening of cyclobutenes[18].

In an attempt to force the elimination in the desired direction, 6,7-diphenyl-3-thiabicyclo[3.2.0]heptane (20) was prepared. A single attempt to form 6,7-diphenyl-3-thiabicyclo-[3.2.0]hept-6-ene (21) by benzylic bromination with NBS apparently gave a mixture of products. This pathway was abandoned in favor of shorter alternatives.

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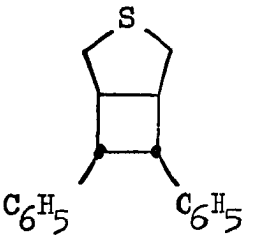

20

The report by Chapman and Adams[19] of the synthesis of of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene in 30% yield by photolysis of diphenylacetylene and tetramethylethylene indicated that 16 might be synthesized by irradiation of cis-2-butene and diphenylacetylene. Although the cis stereochemistry in the product would be reasonably certain it would be necessary to prepare a small sample by another method in order to confirm that no isomerization occurred. Irradiation of diphenylacetylene and cis-2-butene followed by chromatography of the reaction mixture on silca gel impregnated with 2,4,7-trinitro-9-fluorenone[20] gave an oil in low yield. The ultraviolet spectrum of this oil was completely consistent with the structure 16.

The tribromide 19 was prepared by the method of Blomquist and Meinwald[13a]. Solvolysis of this bromide in 95% ethanol gave a solution, the ultraviolet spectrum of which was

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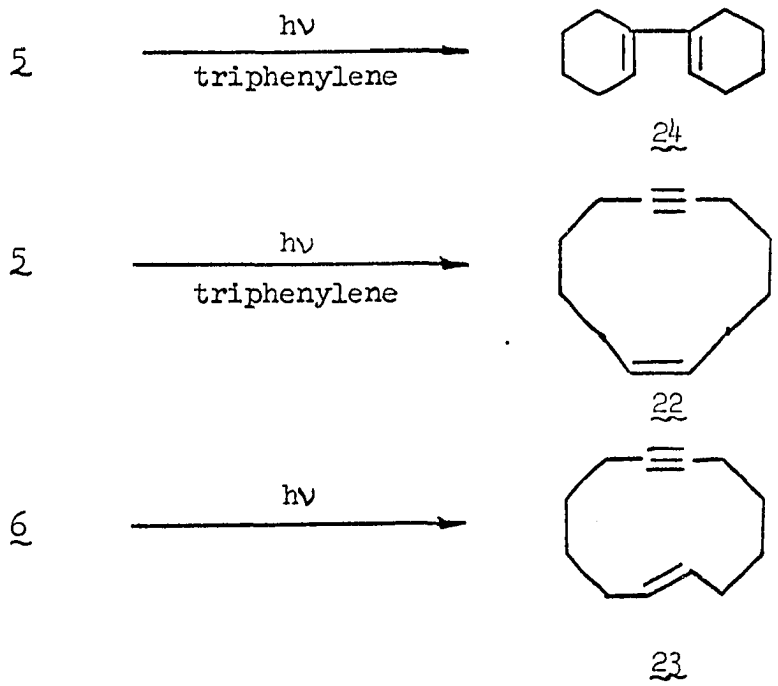
consistent with the formation of a 1,2-diphenylcyclobutene.

At this point in our work, when the synthesis of 16 finally appeared certain, Saltiel and NgLim[9] reported their results from the irradiation of 5 and 6. These authors found that not only was cleavage of 5 and 6 stereospecific to give cis-cyclododeca-1-en-7-yne (22) and trans-cyclododeca-1-en-7-yne (23), but that photoinduced ring opening to give 1,1'-bicyclohexenyl (24) was stereospecific and disrotatory. The triphenylene functioned to sensitize the



conversion of 24 to 5. The reactions of 5, however, were not sensitized by triphenylene.

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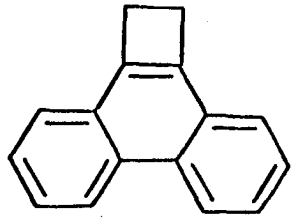
The report by Saltiel and Ng Lim proved what we were attempting to show by the photolysis of 1,2-diphenyl-3,4-dimethylcyclobutene (16). We subsequently abandoned this phase of our work.

The results (Table 1) from a set of preliminary irradiations of 1,2-diphenylcyclobutene (2) indicated that the formation of 9,10-cyclobutenophenanthrene (25) occurred in the absence of



25

oxidants with irradiation below 230 mμ. This result was surprising. The well known formation of phenanthrene by the photolysis of cis-stilbene has been found to occur in solution only in the presence of an oxidant[11]. Srinivasan and Powers[21] have been able to photochemically convert cis-stilbene to phenanthrene in the absence of an oxidant, but only in the vapor phase. Srinivasan and Powers proposed cis-4a,4b-dihydrophenanthrene (26) as a plausible intermediate[21]. In solution, trans-4a,5a-dihydrophenanthrene has been proposed as an intermediate[11,22]. This intermediate, however, may not

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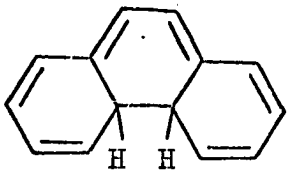
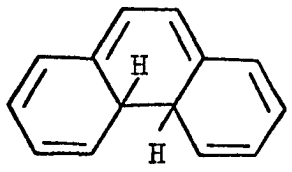
Table 1. Preliminary Photolysis of 1,2-Diphenylcyclobutene (2).

Wavelength of irradiation	Time (hr)	% (moles/liter x 10^5)					
		2		3		25	
230 mμ	35	28	(2.3)	21	(1.2)	51	(1.0)
270 mμ	0.7	71	(3.2)	27	(0.09)	1.9	(1.2)
300 mμ	1[a]	1.5	(0.06)	93	(4.2)	5.5	(0.25)

[a] Further irradiation at this wavelength caused no change.



26



27

be the only intermediate involved in the conversion of cis-stilbene to phenanthrene in solution[23].

These early predictions for the stereochemistry of the dihydrophenanthrene(s) formed in the photolysis of cis-stilbene were made without benefit of the concept of conservation of orbital symmetry proposed by Woodward and Hoffmann[24] in 1965. According to this concept, the first excited state of cis-stilbene should give trans-dihydrophenanthrene (27)[4]. As stated above, the first excited state of stilbene is related to the ^1L_a state of the benzene rings[25]. The ^1L_a state of benzene has nodes through the bonds. This state gives the same symmetry for the closure to dihydrophenanthrene as the simple HMO model gives for the excited state closure of 1,3,5-hexatriene to 1,3-cyclohexadiene (Figure 1). In each case, symmetry about a C_2 axis is maintained. The predicted product from the photochemical closure of cis-stilbene is 27.

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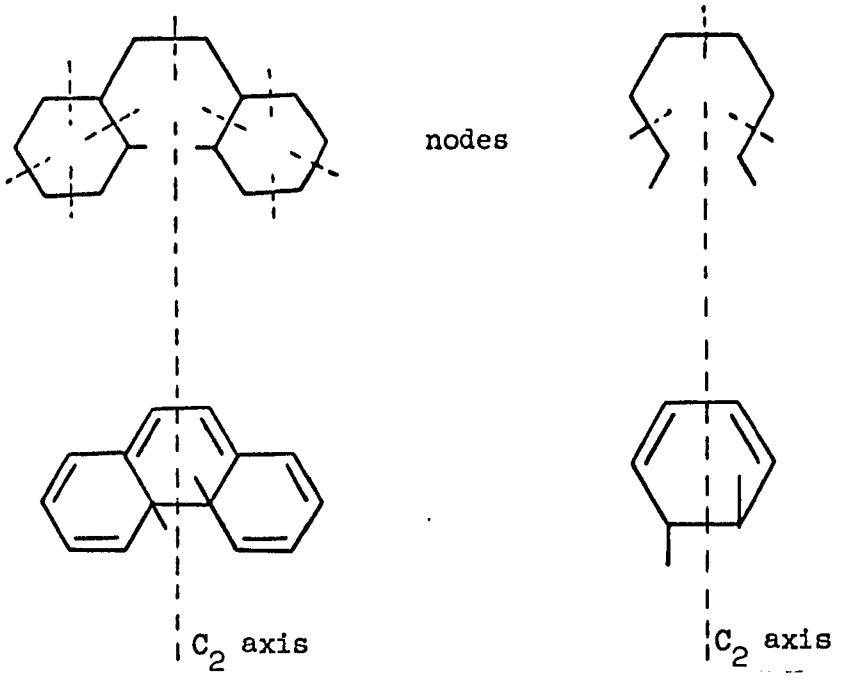

Figure 1.

The second excited state of cis-stilbene, which is related to the ^1L_b state of the benzene rings, would be predicted to give conrotatory closure to 26 (Figure 2). A similar argument

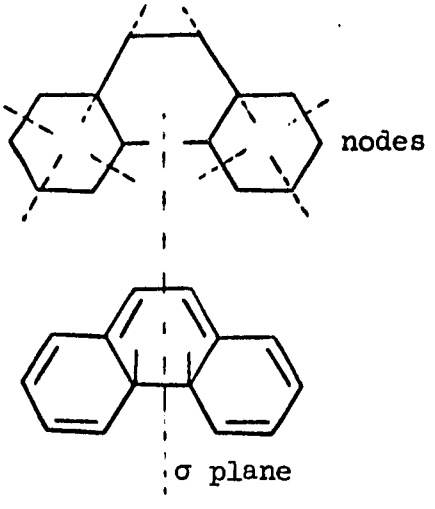

Figure 2.

based on the ^1L_a and ^1L_b states of benzene has been used by Quinkert, Finke, Palmowski, and Wiersdorff to explain the

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lack of stereospecificity in the photochemical opening of 7,8-diphenylbenzocyclobutene.

The ultraviolet spectrum of 2 shows two, well defined maxima at 226 mμ (log ε 4.33) and 297 mμ (log ε 4.24). Because these maxima are well separated (λ_{min} 246 mμ, log ε 3.26), the possibility existed that formation of 25 was from a higher excited state, or ground state, via a cis-4a,4b-dihydrophenanthrene, which could eliminate molecular hydrogen. We measured the quantum yield for formation of products in the photolysis of 2 as a function of the wavelength of exciting light (Table 2). We found no significant difference to occur at the two wavelengths of light used. The apparent discrepancy between the results in Table 1 and Table 2 cannot be explained at present. The possible formation of a 4a,4b, dihydrophenanthrene in the photolysis of 2 is indicated by the formation of an orange color, which fades in the dark, during the irradiation. The visible spectrum of a reaction solution immediately after irradiation showed a broad maxima centered at 440 mμ. Degassed solutions of irradiated cis-stilbene show a similar maxima at 450 mμ[23].

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Table 2. Quantum Yields for the Photolysis of 2

Wavelength of light used (mμ)	$\varphi^{a}_{formation} \times 10^{5}$ 1	$\varphi^{a}_{formation} \times 10^{5}$ 3	$\varphi^{a}_{formation} \times 10^{5}$ Total	$\varphi^{a}_{disappearance} \times 10^{5}$ 2
270	1.11 ± 0.13	25.5 ± 2.7	26.6 ± 2.8	31.0 ± 4.4
230	0.41 ± 0.02	15.3 ± 0.4	15.7 ± 0.4	15.2 ± 0.9

[a] Each value is the average of two determinations. The cited range is the deviation from this mean.

Experimental Section

Melting points, except where noted, were taken with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were preformed by Mr. Joseph Walters in this department.

Infrared spectra were determined on Perkin-Elmer Model 337 or 521 infrared spectrometers, and were calibrated against known absorption bands of polystyrene. Ultraviolet spectra were determined on a Cary Model 14 spectrometer. Proton magnetic resonance spectra (nmr) were determined on Varian Associates A-60 or HA-100 spectrometers using tetramethylsilane as an internal standard.

Thin-layer chromatography (tlc) was performed on Eastman Chromatogram sheets containing a fluorescent indicator. Visualization was with 2537 Å light.

GLC analysis of photolysis mixtures was performed using a 18 x 0.085 in. column packed with 0.70 g of 1% of 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on 100/120 mesh Gas-Chrom Q[26]. Product yields were determined by using phenanthrene as an internal standard.

β-Truxinic Acid. β-Truxinic acid was prepared by a modification of the method of Bernstein and Quimby[14]. Sodium cinnamate (510 g, 3.0 moles) dissolved in 8 l. of water

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was placed in a 12 l. pyrex flask. Hydrochloric acid (6N) was slowly added to pH 2. The mixture became homogeneous at this point. Aqueous sodium hydroxide was added to pH 4 and the volume was increased to 12 l. by addition of water. The resulting suspension was mechanically stirred and irradiated with five 275 W General Electric sunlamps for 98 hr. During this irradiation, the suspension temperature was kept at 6 ~ 12° by circulating ice-water over the reaction vessel. After the irradiation, the suspension was filtered. The damp solid was digested with 2 l. of ethyl ether and filtered. The solid from this treatment was crystallized from 1.2 l. of 95% ethanol to give 157 g (35%, 0.53 mole) of β-truxinic acid, mp 208-210° (lit.[14] 206-208°). TLC on cellulose (pyridine-petroleum ether 1:2) gave a single spot of Rf 0.37. A sample of cinnamic acid gave Rf 0.68 . Infrared spectrum (KBr) 1699, 1410, 1250, and 845 cm^{-1}. Infrared absorptions at 925 (broad) and 580 cm^{-1}, which are present in α-truxillic acid, were absent.

Diethyl β-Truxinate(10)[27]. Concentrated sulfuric acid (3 ml) was added at room temperature to a stirred slurry of β-truxinic acid (74 g, 0.25 mole) in 350 ml of absolute ethanol and 150 ml of toluene. The mixture was heated until all the solid had dissolved. After refluxing for 4 hr, the apparatus was modified for distillation. Distillation proceeded for 1 hr (250 ml of distillate). Ethanol (200 ml) and toluene

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(100 ml) were added to the reaction mixture, and 300 ml of additional distillate was collected over a period of 1.5 hr. The reaction mixture was cooled in an ice-bath and then transferred to a 2 l. separatory funnel. Cold water (1 l.) and 10% sodium carbonate solution (250 ml) were added, and the organic layer was separated. The aqueous layer was then extracted with a mixture of benzene (100 ml) and ether (200 ml). The organic layers were combined and extracted with 500 ml of water. The organic layer was then filtered through sodium sulfate to give a clear filtrate which was concentrated on a rotary evaporator to a viscous oil. Ethanol (50 ml) was added and the solution was placed in a refrigerator. After 2 days, a solid mass had formed in the flask. The mass was crushed with a stirring rod and separated from the mother liquor by vacuum filtration to give 87.5 g (0.23 mole, 92%) of 10, mp 29-35° (lit.[27] 50°). This product was recrystallized from aqueous ethanol to give 79 g (0.22 mole, 90%) of 10, mp 29.5-31.5°; ir (KBr) 1730, 1200, 1065, and 695 cm^{-1}; nmr ($CDCl_3$) δ 6.80 (m, 10 H), 4.32 (A_2B_2 multiplet, 2.0 H), 4.06 (q, 4.0 H, J= 7 Hz), 3.67 (A_2B_2 multiplet, 1.9 H), and 1.23 (t, 6.0 H, J= 7 Hz). Small samples of the product were recrystallized from an ether-isooctane mixture or sublimed with no change in the melting point.

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1,2-Bis-(hydroxymethyl)-3,4-Diphenylcyclobutane. (7)[13a]. Diethyl β-truxinate (70.4 g, 0.20 mole) dissolved in 100 ml of anhydrous ether was added over a 1 hr period to a stirred suspension of lithium aluminum hydride (16.7 g, 0.44 mole) in 500 ml of anhydrous ether. The mixture was refluxed for 12 hr under nitrogen. The reaction vessel was then cooled in an ice-bath and 60 ml of water was slowly added. The mixture was allowed to stir 1 hr and was then vacuum filtered. The solid from this filtration was mixed with 4 N hydrochloric acid and extracted with ethyl acetate. The ethyl acetate and ether solutions were combined and evaporated under vacuum to give a white solid. This material was recrystallized from a mixture of 300 ml of methanol and 100 ml of water to give 48.1 g (0.18 mole, 90%) of 7, mp 110-111° (lit.[13a] 110-111°); ir (KBr) 1014 and 699 cm^{-1}. A second crop of 7 (3.24 g, 12 mmoles, 6%) was obtained by addition of water to the mother liquor.

1,2-Bis(bromomethyl)-3,4-diphenylcyclobutane (11)[13a]. 1,2-Bis(bromomethyl)-3,4-diphenylcyclobutane (11) was prepared by the method of Blomquist and Meinwald[13a] from 1,2-bis (hydroxymethyl)-3,4-diphenylcyclobutane (26.8 g, 0.100 mole) and phosphorus tribromide (27.4 g, 0.102 mole). The product from this reaction was recrystallized from carbon tetrachloride to give 33.7 g (0.086 mole, 86%) of 11, mp 95.5 - 96.5°

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(lit.[13a] 95.5-96.5°); nmr (CCl_4) δ 6.96 (m, 10.0 H) and two overlapping multiplets at δ 3.70 and 3.42 (7.9 H).

1,2-Dimethyl-3,4-diphenylcyclobutane (12). 1,2-Bis (bromomethyl)-3,4-diphenylcyclobutane (3.94 g, 10.0 mmoles) was placed in an addition funnel attached to a 100 ml three neck flask containing lithium aluminum hydride (3.04 g, 0.08 mole). The apparatus was flushed with nitrogen. Tetrahydrofuran (THF) was then distilled directly from $LiAlH_4$ into the addition funnel (20 ml) and the reaction flask (30 ml). It was necessary to warm the solution in the addition funnel in order to dissolve all of the dibromide (11). The warm solution of 11 was then added with stirring to the $LiAlH_4$ in THF. After stirring for 30 min at room temperature, the reaction mixture was heated to reflux for 2.5 hr. Excess $LiAlH_4$ was then destroyed by addition of ethyl acetate (50 ml) to the cool reaction mixture. The mixture with ethyl acetate was allowed to stir for 30 min at room temperature. It was then filtered. Ether (300 ml) was added to the filtrate and the mixture was extracted with water. The ethyl acetate-ether layer was dried with sodium sulfate, filtered, and evaporated to an oil (2.3 g) on a rotary evaporator. This oil was sublimed at 50° and 5×10^{-3} torr to give 2.26 g (9.60 mmoles, 96%) of 12, mp 30.2-31.8°; nmr (CCl_4) δ 6.92 (s, 10.0 H), 3.48 (m, 2.0 H), 2.87 (m, 2.0 H) and 1.20 (m, 5.9 H); ir (KBr) 1077, 1031, and 699 cm^{-1}.

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Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.36; H, 8.45.

Attempted Preparation of 1,2-Diphenyl-cis-3,4-dimethyl-cyclobutene (16).

A. 1,2-Diphenyl-3,4-dimethylcyclobutane (59 mg, 0.25 mmole) and N-bromosuccinimide (45 mg, 0.25 mmole) were placed in a reaction vessel constructed from a 19/38 $\overset{T}{S}$ joint. Seven crystals of dibenzoylperoxide were added. The vessel containing the mixture of dry reagents was attached to a water cooled cold-finger condenser which was attached to a vacuum system and evacuated to 5×10^{-3} torr. Carbon tetrachloride (3 ml) which had been dried over phosphorus pentoxide and degassed by one freeze-pump-thaw cycle was distilled into the reaction vessel through the vacuum system. Nitrogen was then admitted to the system and the reaction mixture was heated to reflux for 30 min. After 15 min of reflux, the solution became reddish-brown and then the color suddenly faded. The formation of a reddish-brown color during reactions with NBS has been explained by the formation of bromine, caused by reaction of hydrogen bromide with the NBS[28]. The formation of hydrogen bromide would indicate that spontaneous elimination of the bromide from 12 was occurring.

After the reflux period, the carbon tetrachloride solution was poured onto a column of basic alumina (10 g). The products

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were then eluted with deoxygenated isooctane (50 ml), and the column and receiver were continuously flushed with nitrogen. The solvent was distilled from the eluent under vacuum to give an oil. TLC of this oil on silica gel (ethyl acetate-benzene 1:3) gave a single fluorescent spot of Rf 0.62 which did not correspond to 12. Ultraviolet spectrum (n-hexane) maxima at 293 (rel intensity 0.65), 285 (0.64), 270 sh (0.90) and 262 mμ (1.00) indicated that this oil could be a mixture of 1,2-diphenyl-3,4-dimethylcyclobutene (16) and 1,4-diphenyl-2,3-dimethylcyclobutene (17). Blomquist and Meinwald[13a] report $\lambda_{max}^{isooctane}$ 255 (4.06), 261 (4.10), and 270 sh (3.90) for 1,4-diphenyl-2,3-bis(dimethylaminomethyl)cyclobutene dimethobromide. The oil was sublimed at 40° and 5 x 10^{-3} torr. The nmr (CCl_4) of the sublimate showed a multiplet at δ 7.25 with a superimposed singlet at δ 7.15, low level multiplets between δ 3.00 and 3.70 and multiplets at δ 2.07 and 1.25. The absence of a peak at δ 6.92 confirmed that no 12 was present. TLC of the sublimate on silver nitrate impregnated silica gel using n-hexane gave two bands of material which were extracted with hexane. The ultraviolet spectrum of the faster moving material showed $\lambda_{max}^{n\text{-hexane}}$ 254 sh (rel intensity 0.93), 260 (1.00), and 270 sh mμ (0.70). This material was probably 17. The ultraviolet spectrum of the slower moving material showed

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$\lambda_{max}^{n\text{-hexane}}$ 225 (rel intensity 1.00) and 293 mμ (0.64). This material was almost certainly 16. Brief irradiation of a nondegassed solution of this material with 2537 Å light gave a spectrum similar to that of phenanthrene. Attempts to obtain the same separation on a preparative scale failed.

B. The procedure used in A was repeated using 23.6 mg (0.10 mmole) of 12 and 39 mg (0.21 mmole) of NBS. The reaction product was not chromatographed on alumina; instead, the reaction solution was evaporated to dryness and the residue triturated with hexane and carbon tetrachloride. The residual material was soluble in water. TLC of the organic fractions on silica gel (benzene-hexane 1:3) showed practically no material in the carbon tetrachloride fraction. The hexane fraction showed six spots. The ultraviolet spectrum of the hexane fraction was similar to the spectrum of material obtained after chromatography on alumina in A.

C. The results from A and B indicated that spontaneous elimination of hydrogen bromide occurred under reflux conditions. Therefore, the bromination was attempted at -72° using light as the initiator instead of dibenzoyl peroxide.

1,2-Dimethyl-3,4-diphenylcyclobutane (19.2 mg, 81.4 μmoles) and NBS (14.6 mg, 81.4 μmoles) were placed in a tube made of 14 mm Pyrex glass. Methylene chloride (2 ml) was added and the solution was degassed by two freeze-pump-thaw cycles at

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5×10^{-3} torr. After warming to room temperature to complete solution, the mixture was immersed in a Dry Ice-ethanol bath and irradiated with a G.E. Sunlamp for 1 hr. The reaction was observed constantly for the first 15 min and at 5 min intervals thereafter. No color change occurred, however, a white precipitate formed on the vessel walls. The reaction mixture was then warmed to room temperature, at which time the solution and the precipitate turned slightly yellow. The sample was frozen in liquid nitrogen and opened. The methylene chloride was completely removed under high vacuum, during which time, temperature of the vessel was controlled by the evaporation of the methylene chloride. After evaporation of the methylene chloride, a yellowish residue remained. This residue was extracted with hexane. The ultraviolet spectrum of the hexane extract had a maxima at 291 mμ. Fine structure at 253, 260, and 272 mμ was present; however, it was of low intensity and barely resolved. TLC on silica gel (benzene-hexane 1:3) gave one major fluorescent spot (Rf 0.66). The lower portion of the spot quenched the fluorescence of the silica gel sheet. Three minor spots near the origin were also present. Attempts to resolve the major spot into fluorescent and nonfluorescent spots on silver nitrate impregnated silica gel and alumina failed.

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6,7-Diphenyl-3-thiabicyclo[3.2.0]heptane (20). 1,2-Bis-(bromomethyl)-3,4-diphenylcyclobutane (1.97 g, 5.0 mmoles) dissolved in 87 ml of absolute ethanol was added with stirring to a solution of sodium sulfide nonahydrate (6.0 g, 25 mmoles) in 50 ml of 30% aqueous ethanol. After addition of the dibromide was complete (30 min), 23 ml of water was added. The dibromide was present as a fine suspension. The reaction mixture was placed under a nitrogen atmosphere and warmed to reflux. At reflux temperature, the reaction mixture was just perceptibly cloudy. After refluxing 3 hr the solution was clear. The reaction was followed by tlc on silica gel (benzene-hexane 1:2). The reaction refluxed an additional 5 hr. The solvent from the reaction mixture was removed on a rotary evaporator and the residue was taken up in a mixture of water and benzene. The benzene layer was separated and the water layer was extracted with two additional portions of benzene. The benzene extracts were combined and filtered through sodium sulfate and then evaporated to an oil which solidified after being placed under high vacuum overnight. This solid dissolved in 35 ml of hot, absolute ethanol. The filtered solution was flushed with nitrogen and allowed to cool in the refrigerator. An amorphous precipitate formed on cooling. The clear supernatant was decanted and the precipitate was washed with 5 ml of ethanol. Water was added

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to the combined ethanol solutions to give crystallization. A total of 1.10 g (4.15 mmoles, 83%) of 20 was obtained, mp 66.2-67.4°. This material was recrystallized from ethanol followed by sublimation at 100° and 5 x 10^{-3} torr to 897 mg (3.37 mmoles, 68%) of 20, mp 66.2-67.0°; nmr (CCl_4) δ 6.95 (m, 9.9 H), 3.67 (m, 2.0 H), 3.45 (m, 2.0 H), and 2.86 (m, 3.9H); ir (KBr) 1215, 1076, 761, 750, 722, and 700 cm^{-1}.

Anal. Calcd for $C_{18}H_{18}S$: C, 81.15; H, 6.81; S, 12.03. Found: C, 81.11; H, 6.86.

Reaction of 6,7-Diphenyl-3-thiabicyclo[3.2.0]heptane (20) with N-Bromosuccinimide (NBS). 6,7-Diphenyl-3-thiabicyclo [3.2.0]heptane (21.3 mg, 80 μmoles) and NBS (14.7 mg, 82 μmoles) were added to a reaction vessel consisting of a section of 14 mm glass tubing about 5 cm long which was sealed at one end and had a length of 8 mm glass tubing attached to the other end. The 8 mm tubing was terminated with a 10/30 ground glass joint for attachment to the vacuum system. Carbon tetrachloride (2 ml) was added, the mixture was degassed by two freeze-pump-thaw cycles at 1 x 10^{-2} torr, and the tube was sealed off. The mixture was irradiated for 15 min with a G.E Sunlamp at room temperature and there was no change in color. The mixture was then irradiated for 1.5 hr in a bath of refluxing carbon tetrachloride. At the end of this additional irradiation period, a precipitate had formed on the vessel

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walls, and the solution had become darker in color. The vessel was cooled and opened. The solvent was evaporated with a stream of nitrogen to give an oily residue. Hexane was added to the residue; however, very little dissolved. A few drops of carbon tetrachloride were then added and the mixture was warmed to complete solution. TLC on silica gel (benzene-hexane 1:3) showed two spots very near the origin, and a third spot at Rf 0.32.

Photolysis of Diphenylacetylene (3) and cis-2-Butene. Diphenylacetylene (166 mg, 0.93 mmole) and spectral grade n-hexane (2 ml) were placed in a reaction vessel constructed from an 18 mm quartz to Pyrex graded seal. The bottom of a Dewar condenser was attached to the Pyrex portion of the graded seal. When filled with Dry Ice this condenser allowed for reflux of the 2-butene used in a run. This condenser had a vent near the upper rim to which was attached a calcium chloride filled drying tube. A side arm, also attached to the Pyrex portion of the graded seal, terminated near the bottom of the quartz portion. Gases could be introduced through this side arm and allowed to bubble through the reaction solution. A short length of Tygon tubing was used to attach the side arm to a gas cylinder. A long stainless steel needle was inserted through the wall of the Tygon tubing to the bottom

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of the quartz portion for removal of samples throughout the reaction. Dry Ice was placed in the reflux condenser and approximately 4 ml of cis-2-butene were condensed into the reaction mixture. Dry nitrogen (99.7% pure) was bubbled through the solution for 10 min before beginning irradiation with a 450 W Hanovia medium pressure lamp using a Vycor filter. The reaction mixture was irradiated for 7 hr. During the irradiation, samples were withdrawn through the syringe needle for tlc. TLC after 1 hr irradiation on alumina (hexane) showed three spots for the reaction mixture. The center spot (Rf 0.35) corresponded to diphenylacetylene and quenched the fluorescent background of the tlc plate. Fluorescent spots at Rf 0.17 and 0.43 were present. The appearance of the tlc did not change from that of the tlc taken after 1 hr.

After irradiation, the Dry Ice was removed from the condenser and the cis-2-butene was evaporated by a slow stream of nitrogen. The remaining hexane solution was diluted to about 10 ml with hexane and added to 1 g of silica gel (60-200 mesh) coated with 5% of 2,4,7-trinitro-9-fluorenone (TNF). This mixture was evaporated to dryness on a rotary evaporator. A column (40 cm x 1 cm) was dry-packed with 5% TNF coated silica gel (15 g). The reaction material was chromatographed on this column using hexane. Two major colored bonds were observed and collected using a continuous

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nitrogen flush of the receivers. The first band eluted (red band) showed λ_{max}^{hexane} 225 mμ (rel intensity 1.51) and 292 mμ (1.00) This material was probably the desired product (12). On evaporation of the hexane, this fraction yielded a colorless oil (about 10 mg) which failed to crystallize. An attempt to form a TNF or 2,4,5,7-tetranitro-9-fluorenone[29] complex gave only a red solution from which no solid complex could be isolated. The second band (yellow-orange) gave 50 mg of a crystalline material identified as diphenylacetylene.

cis-1,2-Bis(bromomethyl)-trans-3-phenyl-4-bromo-4-phenylcyclobutane (19). 1,2-Bis(bromomethyl)-3,4-diphenylcyclobutane (0.788 g, 2.00 mmoles) was converted to the title compound by the method of Blomquist and Meinwald[13a]. The product (0.183 g, 0.387 mmole, 19.3%) was obtained after fractional crystallization from ether-hexane mixtures, mp 101.8-102.2° dec (lit.[13a] 105-105.5° dec). Treatment of 19 with ethanol overnight at room temperature gave a solution with λ_{max} 224 (rel intensity 1.00) and 288 mμ (0.44).

1,2-Dibenzoylethane. The procedure of Bailey and Lutz[30] was followed for the preparation of the title compound. Dibenzoylethylene (35.4 g, 0.15 mole) was reduced with stannous chloride (33.9 g, 0.15 mole) and hydrochloric acid (100 ml of 8 N) to give 34.6 g (0.145 mole, 97%) of crude product, mp 126-132° (lit.[30] 145-147). This product was

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recrystallized from ethanol to give 29.9 g (.126 mmole, 84%) of dibenzoylethane, mp 143-145° (lit.[30] 145-147°).

DL-1,4-Diphenylbutane-1,4-diol.[31] Dibenzoylethane (23.63 g, 0.099 mole) was reduced by the method of Dodson and Zielske[32] using sodium borohydride (3.78 g, 0.10 mole) in aqueous ethanol to give, after crystallization from a mixture of chloroform and isooctane, 22.84 g (.094 mole, 95%) of the title compound, mp 88.5-90° (lit.[32] 89-90°).

1,2-Diphenylcyclobutene (2). A solution of sodium amide was prepared by slowly adding sodium metal (2.07 g, 0.089 g-atom) to 350 ml of liquid ammonia containing a few crystals of ferric nitrate. To this solution, meso-1,4-dichloro-1,4-diphenylbutane (4.830 g, 0.0173 mole) dissolved in anhydrous ether (100 ml) was added over a period of 0.5 hr. The apparatus was purged with nitrogen and allowed to stir for 5.5 hr under reflux. After this time, ether (100 ml) and ammonium chloride (3.16 g, 0.059 mole) were added with stirring. A slow stream of nitrogen was passed over the reaction mixture overnight to remove the excess ammonia. After evaporation of the ammonia was complete, ether (100 ml) was added followed by a small amount of ammonium chloride. No additional reaction occurred. The solution was stirred under a nitrogen flow for an additional 0.5 hr, or until there was no more odor of ammonia. The solution was washed into a separatory funnel with 200 ml of ether and

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150 ml of water (a water soluble precipitate was present). The ether layer was separated and washed with an additional 100 ml of water. The ether layer was separated and filtered. Evaporation of the ether on a rotary evaporator gave 3.52 g (0.0171 mole, 96%) of crude, crystalline product. Recrystallization from ethanol (flushed with nitrogen and argon) failed. The ethanol solution was evaporated to a solid which was chromatographed on silica gel (125 g) using only isooctane as eluent. The isooctane fractions (400 ml) yielded a nicely crystalline material which was recrystallized from aqueous ethanol to give 2.80 g (0.0136 mole, 79%) of 1,2-diphenylcyclobutene, mp 52.5-53.1°.

This material was recrystallized twice more from aqueous ethanol and once from hexane. All manipulations were performed under an argon atmosphere using solvents which had been previously flushed with argon. GLC analysis on 1% TCEP at 90° showed no 2,3-diphenylbutadiene or other impurities. The product obtained showed: mp 52.3-53.0°; ir (KBr) 1215, 925, 908, and 750 cm^{-1}; uv max (n-hexane) 226 (4.36), 236 sh (4.10), 297 (4.24), 305 sh (4.23), and 320 i mμ (3.99); uv min (n-hexane)210 (4.13) and 246 mμ (3.26).

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.21; H, 6.93.

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Exploratory Photolysis of 1,2-Diphenylcyclobutene (2).

A 4.5×10^{-5} M solution of 1,2-diphenylcyclobutene (2) in hexane was prepared. To each of three identical reaction vessels, 3 ml of this solution was added. Each reaction vessel consisted of a 10 mm i.d. Pyrex to quartz graded seal attached by a length of 8 mm glass tubing to the bottom of a Dewar condenser (48 mm o.d.). The condenser was attached to a vacuum system by a $\overset{T}{S}$ glass joint. The quartz end of the graded seal was closed off 5 in below the graded portion of the seal. In a run, the quartz portion of the apparatus containing the sample was cooled in liquid nitrogen. The apparatus was evacuated to 1×10^{-5} torr and then closed off with a stopcock. Liquid nitrogen was added to the Dewar condenser and the solvent was allowed to sublime onto the cold finger. After sublimination was complete, the apparatus was again evacuated to 1×10^{-5} torr and closed off. The liquid nitrogen was removed from the cold finger and the sample portion of the graded seal was cooled in liquid nitrogen. After transfer of the solvent was complete, the apparatus was evacuated to 1×10^{-5} torr. The samples were then sealed off at the 8 mm glass tubing. Each of the three reaction solutions were degassed in this way. Satisfactory ultraviolet spectra could be obtained through the quartz portion of these sample tubes.

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A Bausch and Lomb high intensity monochromator with the appropriate light source was used for the following irradiations. For the 230 mμ irradiation, a deuterium lamp source and a 9.6 mμ band pass were used. For the 270 mμ and 300 mμ irradiations, a 200 W high pressure short arc mercury lamp source and a 2.4 mμ band pass were used.

The results from the photolyses of 2 are given in Table 1. The compositions of the reaction mixtures were calculated from the extinction coefficients of 2, 3, and 25 at three wavelengths. The assumption was made, and later justified (vida infra), that only these three compounds are present in the reaction mixture in sufficient quantity to affect the optical density of the mixture at the three wavelengths used. The concentration of 25 was obtained from the intensity of its maxima at 357 mμ (ε 2,190). With the concentration of 25 determined, the portion of the observed intensity at 320 mμ due to 25 was determined (ϵ_{320}500). This small correction was substracted from the observed intensity at 320 mμ to give the intensity due to 2 (ϵ_{320}9,700). From this value, the concentration of 2 was calculated. The concentration of 3 was taken to be the difference between the initial concentration of 2 and the final concentration of 2 and 25.

Preparative Photolysis of 2. The photolysis of 2 was

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performed on a preparative scale in order to identify at least the major products rigorously.

A. Photolysis of 2 Using a Pyrex Filter. 1,2-Diphenylcyclobutene (204.3 mg, 0.9903 mmole) was dissolved in hexane (1 l.) and placed in a 1 l. quartz flask. The solution was deoxygenated by a steady stream of nitrogen (prepurified) introduced into the solution through a gas dispersion tube. Vigorous stirring was maintained with a magnetic stir-bar throughout the deoxygenation and irradiation steps. After 6 hr, irradiation was begun using a Pyrex filtered ($\lambda \geq 270$ mμ) 450 W medium pressure mercury lamp. The course of the reaction was followed by glc on 1% TCEP at 90°. After 7 hr of irradiation, approximately 60% of 2 had decomposed and the irradiation was stopped. After standing for 6 hr, the reaction solution was transferred to a volumetric flask and diluted with hexane to 1.000 l. Three aliquots of 5, 300, and 600 ml were withdrawn. To the 5 ml aliquote, 0.688 mg of phenanthrene was added. The glc analysis of this aliquot is given in Table 3. The other two aliquots were evaporated to dryness on a rotary evaporator equipped with a Dry Ice cooled condenser. Heat was not applied to the evaporating solutions. As a result, the temperature of the solutions was maintained below 0° during the evaporation. The ultraviolet spectrum of the distillate

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Table 3. GLC Analysis of Photolysis Products[a]

Run	Composition (μmoles, % yield)					
	1	2	3	25	Total dimer[b]	Total 2 accounted for
A	20.6 (2.1)	240 (24.3)	482 (48.8)	7.0 (0.7)	81.6 (16.5)	912.8 (92.4)
B	7.9 (1.3)	256 (42.1)	267 (44.1)	1.5 (0.3)	36.6 (12.1)	605.6 (99.9)

[a] GLC analyses were performed on 1% TCEP at 90°. Each value reported was the average of the values obtained from three injections. The spread of values for each component was no greater than ± 2% of its mean value, except for 25 in which the spread was ± 10%. [b] Calcd from weight of sublimination residue.

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obtained from this low temperature evaporation showed that a negligible quantity of the photolysis products (< 1.0 μg) had been codistilled with the solvent.

The residue resulting from the 600 ml aliquot was chromatographed under argon on 40 g of 60/200 mesh silica gel (2 cm x 30 cm) impregnated with 5% 2,5,7-trinitro-9-fluorenone using n-hexane as the eluent. Each fraction was collected under argon and then passed through 4 g of basic alumina in a 12 mm O.D. column. This second chromatography on alumina was found necessary in order to remove traces of trinitrofluorenone which bled off the silica gel column. Nine fractions of 50 ml each were collected. Each fraction was analyzed by glc on 1% TCEP at 90°. Fractions which were essentially one compound were further identified by physical methods. The first two fractions (1.0 mg) contained a mixture of 2,3-diphenylbutadiene (1) and 1,2-diphenylcyclobutene (2). The third fraction (7.6 mg) was essentially pure 2, mp 48.5-50°. The infrared spectrum of this material was identical to the spectrum of 2. Fractions four (19.6 mg) and five (17.7mg) contained mixtures of 2 and diphenylacetylene (3). Fraction six (34.5 mg) contained diphenylacetylene (3), mp 57.0 - 58.0°. The infrared spectrum of this material was identical to the spectrum of 3. Fraction seven (5.6 mg) gave a single spot by tlc on silica gel (cyclohexane) corresponding to

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tricyclooctane (4). Fraction eight (12.9 mg) gave by tlc on silica gel (cyclohexane) a major spot corresponding to 4 and minor spots corresponding to 1,2,5,6-tetraphenyl-1,5-cyclooctadiene and an unknown. The infrared spectra of both fractions were identical to the spectrum of 4. The ninth fraction (6.4 mg) appeared by tlc on silica gel (cyclohexane) to be pure 1,2,5,6-tetraphenyl-1,5-diene (28); however, the infrared spectrum showed a small amount of impurity. Recrystallization of this fraction from hexane gave material which had an infrared spectrum identical to the spectrum of 28. The total material recovered from this chromatography was 105 mg. The calculated amount, correcting for the mass loss of ethylene in the formation of diphenylacetylene, was 115 mg. Thus, within experimental error, all of the starting material in the reaction has been accounted for.

A small sample of pure tricyclooctane (4) was absorbed onto a silica gel tlc sheet. Irradiation with 2537 Å light for a few seconds and subsequent development (cyclohexane) gave two spots which were identified as 4 and 28 by position and behavior with ultraviolet light. Cyclooctadiene 28 turns immediately orange when irradiated with 2537 Å light, tricyclooctane 4 turns orange on longer irradiation (probably due to formation of 28).

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The residue from the 300 ml aliquot was dissolved in carbon tetrachloride and transferred to a sublimer. The solvent was evaporated by a slow stream of nitrogen. Additional carbon tetrachloride was added and similarly evaporated. The residue was sublimed onto a Dry Ice cooled cold finger at 5×10^{-3} torr and 60° for 4 hr. Sublimation was continued for 1 hr at 80°. A colorless crystalline (10 mg) remained in the sublimer pot. TLC on silica gel (cyclohexane) of this residue showed only two spots. These spots corresponded to tricyclooctane 4 and cyclooctadiene 28. The nmr spectrum of this material showed two singlets at δ 2.94 and 2.52. These peaks were in the ratio of 1:3.1 (Table 4) and corresponded to 28 and 4 respectively. The tlc of the subliminate on 5% TNF impregnated silica gel (hexane) showed only three spots. These spots corresponded to diphenylcyclobutene (2), diphenylacetylene (3), and cyclobutenophenanthrene (25). A small amount of 2,3-diphenylbutadiene (1) could not be detected under these conditions, since it is poorly resolved from 2. The nmr spectra, however, indicated that a small amount of 1 was present. The analysis of this subliminate as determined from the nmr spectrum is given in Table 4. The similarity of the two analyses serves as a check on the validity of each. A small sample of the sublimate used in this analysis was resublimed under the same conditions. The analysis of the

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Table 4. NMR Analysis of Photolysis Products

Run	Composition (μmoles, % yield)					
	1	2	3	25	4	28
A	25.8 (2.6)	246 (24.9)	546 (55.3)	6.9 (0.7)	61.7 (12.5)	19.9 (4.0)
B	7.1 (1.2)	280 (46.2)	316 (52.1)	3.2 (0.5)	10.2 (3.4)	26.4 (8.7)

[a] The analysis of the mixture was based on the assumption that only the six compounds in the table were present and that their sum should account for all of 2 present initially.

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resublimed material by glc was unchanged.

B. Photolysis of 2 Using Unfiltered Light from a Medium Pressure Mercury Lamp. 1,2-Diphenylcyclobutene (125.3 mg, 0.6074 mmole) was dissolved in hexane (1 l.) and placed in a 1 l. quartz flask. The solution was flushed for 6 hr with nitrogen and then irradiated with the unfiltered light from a 450 W medium pressure mercury lamp. The reaction was followed by glc on 1% TCEP at 90°. After 1 hr, approximately 60% of the diphenylcyclobutene had decomposed. The reaction mixture was transferred to a 1 l. volumetric flask and diluted to 1.000 l. with hexane. To a 10 ml aliquot of this solution, 1.0 ml of a 0.2414 mg/ml solution of phenanthrene in hexane was added. The glc analysis of this aliquot is given in Table 3. The change in the relative yield of 1 with respect to 3 can be explained by its increased absorption in this region ($\lambda_{max}^{cyclohexane}$ 243, log ε 4.26)[33].

A 980 ml aliquot of the remaining reaction mixture was evaporated to dryness and the volatile products were sublimed from the residue at 5 x 10^{-3} torr as is described in A. A nonvolatile residue of 14.8 mg remained. TLC on silica gel (cyclohexane) of this residue showed mainly tricyclooctane 4 and cyclooctadiene 28. Two light spots corresponding in position to 2 and 3 were also present. The nmr of this

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residue confirmed the presence of a small amount of 2 (≤ 6%). The analysis of this mixture from the nmr spectrum is given in Table 4. The predominance of cyclooctadiene (28) over 4 (2.6:1) in this instance, probably reflects the fact that the longest wavelength absorption of tricyclooctane 4 is at 272 mμ (log ε 2.86)[1].

The sublimate from the 980 ml aliquot showed by tlc on silica gel (hexane) or 5% TNF impregnated silica gel (cyclohexane) major spots corresponding to diphenylcyclobutene (2) and diphenylacetylene (3). A faint spot corresponding to cyclobutenophenanthrene (25) was also present. The composition of this faction was determined by analysis of its nmr spectrum. The results from this analysis are given in Table 4.

The close agreement that was obtained between compositions determined from the nmr spectrum and by glc, indicates that glc analysis of the photolysis mixtures from 2 would be sufficient alone when insufficient material exists for other analytical methods.

Analytical Photolysis of 2. Two light sources were used for the photolyses described in Table 5. For most of the photolyses a collimated beam of light from a 1000 W Hg-Xe short arc lamp[34] was focused on the entrance slit of a Bausch and Lomb high intensity monochrometer[35]. The construction and

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Table 5. Analytical Photolysis of 2

Wavelength of light used (mμ)	Source	Intensity[a] x10^9 (einsteins/sec)	Time (hr)	Total light x10^5 (einsteins)	Moles 2 x10^6	Concentration 2 x10^3
270	Hg	6.44	3	8.04	5.76	1.44
270	Hg-Xe	4.63	4	6.67	5.76	1.44
230	Hg-Xe	1.15	4	1.65	0.983	0.246
230	Hg-Xe	1.15	4	1.65	0.983	0.246

[a] The quantum yield for formation of Fe^{2+} at 230 mμ was assumed to be equal to the quantum yield at 254 mμ (1.25). The quantum yield for formation of Fe^{+2} at 270 mμ was taken to be 1.24. See: C. A. Parker, "Photoluminescence of Solutions", Elsevier Publishing Co., New York, New York, 1968, pp 208-210.

full description of this light source has been given by Baum[36]. A 9.6 mμ band pass was used. A cell compartment was attached to the exit side of the monochrometer. Attached to this cell compartment was a RCA-935 photodiode for periodically monitoring the incident and transmitted light intensities. A 1.0 meg ohm resistor was used in series with the photodiode and a 180 V battery. Voltage across this resistor was measured with a model 4470 Dana digital voltmeter[37]. The light intensity was determined by ferrioxalate actinometry before and after each run and in most cases at least once during the run. The light intensity in the cell compartment was found not to vary by more than 3% in a run.

A Bausch and Lomb 250 W superpressure mercury light source[35] was used for one run. The light intensity with this source varied by 20% during a run. The intensity was measured by actinometry every 30 min throughout this run. The average of the values obtained was used in subsequent calculations.

Two photolysis vessels were constructed from 1 cm quartz cuvettes which were attached through graded seals to 10 mm Pyrex tubing. The end of this tubing was closed and expanded to form a bulb of 5 ml capacity. A side arm was attached midway on the stem and bent so as to be parallel to the long axis of the cell. In a run, the solution of 2 was added to the bulb portion of the photolysis vessel, and the side arm

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was attached to a vacuum system with a Veeco quick coupling[38]. The reaction solution was degassed by six freeze-pump-thaw cycles at 1 x 10^{-6} torr.

Four photolyses were performed, two at each wavelength. The conditions for these photolyses are given in Table 5. The quantum yields calculated from these photolyses are given in Table 2. In general, 2-3 ml of a freshly prepared solution of 2 in pentane was added to the cell. Additional pentane was then added to give 4 ml of solution. The addition of this pentane also served to wash any residual 2, left on the vessel walls by evaporation, into the bulb. The solution was then degassed and the vessel was sealed off. During this degassing, about 0.5 ml of pentane was lost. The calculated optical densities of the degassed solutions at the wavelength of irradiation ranged from 3 to 12.

During irradiation, the two concentrated samples were mixed by shaking the vessel every 15 min. The more dilute samples were mixed every 30 min.

After irradiation, each photolysis mixture was allowed to stand at room temperature for 6 hr in order to allow any 4a,4b-dihydrophenanthrene present to convert back to 2. The photolysis vessels were then opened and the contents transferred to volumetric flasks. Each sample was then diluted to a known volume. Aliquots of these solutions were diluted further to

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obtain ultraviolet spectra. From the total optical density at the wavelength of irradiation and the calculated optical density of 2 at that wavelength after irradiation (calculated from the known dilution factor and the concentration of 2 obtained from glc analysis), the fraction of light absorbed by 2 and the quantum yields for diphenylbutadiene (1) and diphenylacetylene (3) were determined (Appendix). The results from these calculations are given in Table 2.

The two solutions from each run were combined and an amount of phenanthrene equal to one-fourth the weight of 2 present initially was added. The vessel containing this solution was immersed in a Dry-Ice-acetone bath and the solvent (pentane) was removed under vacuum. The residue was analyzed by glc (Table 2) on 1% TCEP at 90°. Pentane (6 ml) was added to one residue from a 270 mμ run, and the entire process was repeated. GLC analysis of the resulting residue showed no change in composition after this treatment. TLC of the residues from each run on silica gel (hexane) and 5% TNF impregnated silica gel (cyclohexane) indicated that only diphenylacetylene (3) and diphenylcyclobutene (2) were present. GLC showed, in addition to these two compounds, a small amount of 2,3-diphenylbutadiene (1). No cyclobutenophenanthrene (25) was found in any of these analytical runs.

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PART II

THE SYNTHESIS OF 9,10-CYCLOBUTENOPHENANTHRENE FROM 9,10-DIMETHYLENE-9,10-DIHYDROPHENANTHRENE

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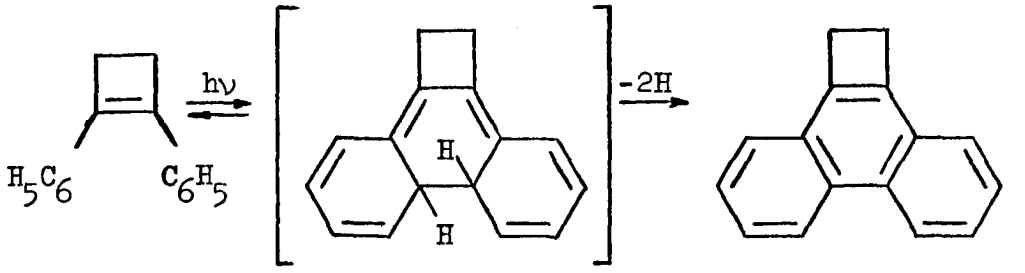
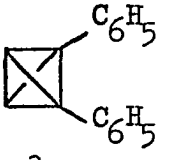
Our interest in 9,10-cyclobutenophenanthrene (2) was first aroused during a study of the photochemistry of 1,2-diphenylcyclobutene (1) in which it is a possible product (equation 1).



(1)

1 2

We were stimulated to the synthesis of 2 by the subsequent report by Masamune and Kato of diphenyltetrahedrane (3)[2,3]. This report drew our attention because of our interest in 3 and because the physical properties attributed to 3 by Masamune and Kato appeared to match better the predicted properties of 2[3].



3

We wish now to report the full synthesis and characterization of 2.

During the progress of this synthesis, we were able to demonstrate the intermediacy of 9,10-dimethylene-9,10-dihydrophenanthrene (4). Previously, this compound had been reported as a reactive intermediate and its presence was inferred only

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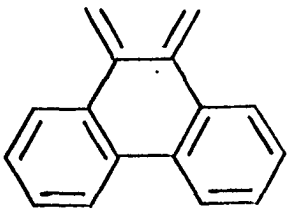

4

by trapping with various dienophiles[4]. The instability of 4 with respect to dimerization and polymerization prevented our complete characterization of it; however, we were able to obtain its ultraviolet spectrum in dilute solution. The direct observation of 4 in the ultraviolet is to our knowledge the first such observation of an o-quinodimethane not substituted in the terminal methylene positions[5].

9,10-Cyclobutenophenanthrene (1). The synthesis of 2 was achieved in four steps starting with the readily available 9,10-phenanthroquinone (5). The sequence of synthesis to trimethyl (10-methyl-9-phenanthrylmethyl) ammonium chloride (10) is to be found in the literature[4]; however, certain steps in this sequence warrant special comment (equation 2).

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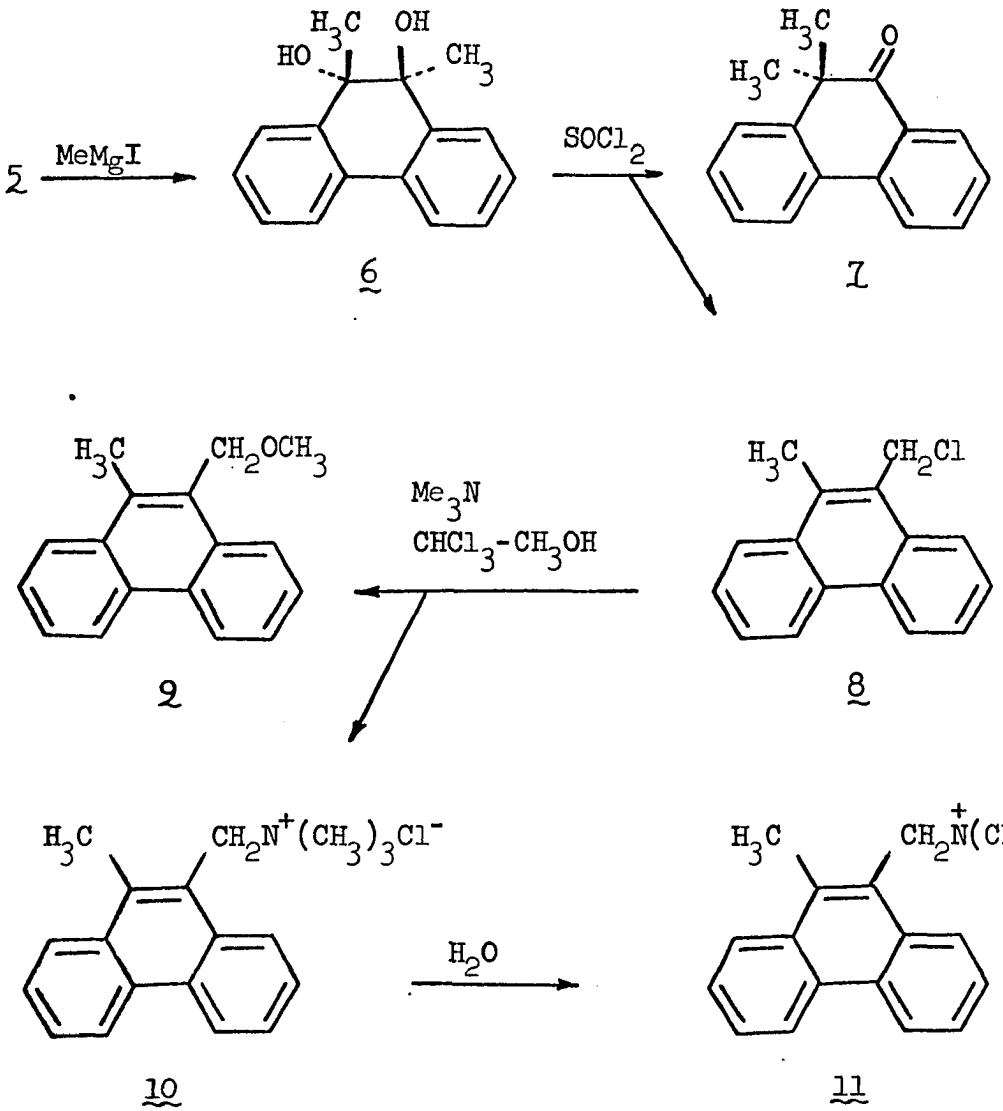

The conversion of trans-9,10-dimethyl-9,10-dihydroxy-phenanthrene (6) to 9-chloromethyl-10-methylphenanthrene (8) is reported to go smoothly and to give no 10,10-dimethyl-9(10H) phenanthrone (7)[6]. In our work, however, a 24% yield of 7 was realized. The production of 7 may have been due to the somewhat more vigorous conditions employed.

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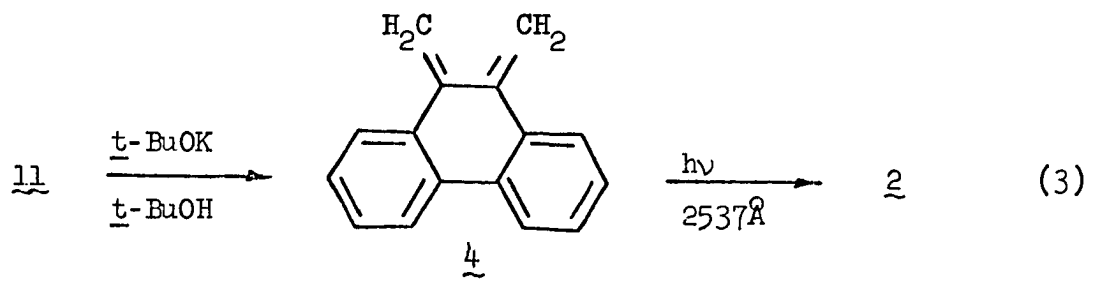
The conversion of 8 to 10 also met complication. The solvent system employed was that recommended in the literature[4a], and in addition to 10, 20% of 9-methoxymethyl-10-methylphenanthrene (9) was obtained. In retrospect, it would probably have been advisable to use benzene as a solvent to avoid formation of this ether (9). Benzene has been used in the preparation of the quaternary bromide from 9-bromomethyl-10-methylphenanthrene without complication[4c].

The conversion of the monohydrate (11) to cyclobutenophenanthrene (2) was straight forward (equation 3). It was found



(3)

that best yields are obtained when dry t-butyl alcohol is used, and when both steps in the reaction are carefully monitored (see experimental section). Early irradiation of 11 before elimination is completed appeared, at least qualitatively, to give more complicated reaction mixtures. In addition, compound 2 is photodecomposed by prolonged irradiation.

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The physical data found for the product are completely consistent with the assigned structure of 2. The methylene protons of 2 at δ 3.35 (s, 4.0 H) in the nmr spectrum are shifted 0.70 ppm downfield from the methyl protons of 9,10-dimethylphenanthrene. This shift is consistent with the formation of the cyclobutene ring (Table 1). Similarly, the 1,8 protons of 9,10-dimethylphenanthrene are shifted downfield from the 2,3,6,7 ring protons at δ 7.46 by the methyl groups and appear in the spectrum as an isolated multiplet centered at δ 7.97; whereas, in 2, the 1,8 protons form a multiplet centered at δ 7.65. This upfield shift toward the 2,3,6,7 protons at δ 7.45 is consistent with formation of the cyclobutene ring[7]. The ultraviolet spectrum of 2 ($\lambda_{max}^{n\text{-hexane}}$ 255 mμ, log ε 4.83) is similar to that of 9,10-dimethylphenanthrene, and clearly indicates a phenanthrene chromophore.

The mass spectrum of 2 shows apparent successive losses of 15, 13, 13, and 13 mass units. This pattern of fragmentation may be explained by two parallel processes (equation 4).

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Table 1. Position of Benzylic Protons as a Function of Ring Size in Benzocycloalkenes

	Benzylic protons (δ)
o-Xylene[a]	2.23
Tetralin[a]	2.76
Indane[a]	2.91
Benzocyclobutene[b]	3.14
9,10-Dimethylphenanthrene	2.65
Cyclobutenophenanthrene	3.35

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[a] N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "NMR Spectra Catalogue", Vol. II, Varian Associates, Palo Alto, California, 1963. [b] G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, Tetrahedron, 20, 1179 (1964).

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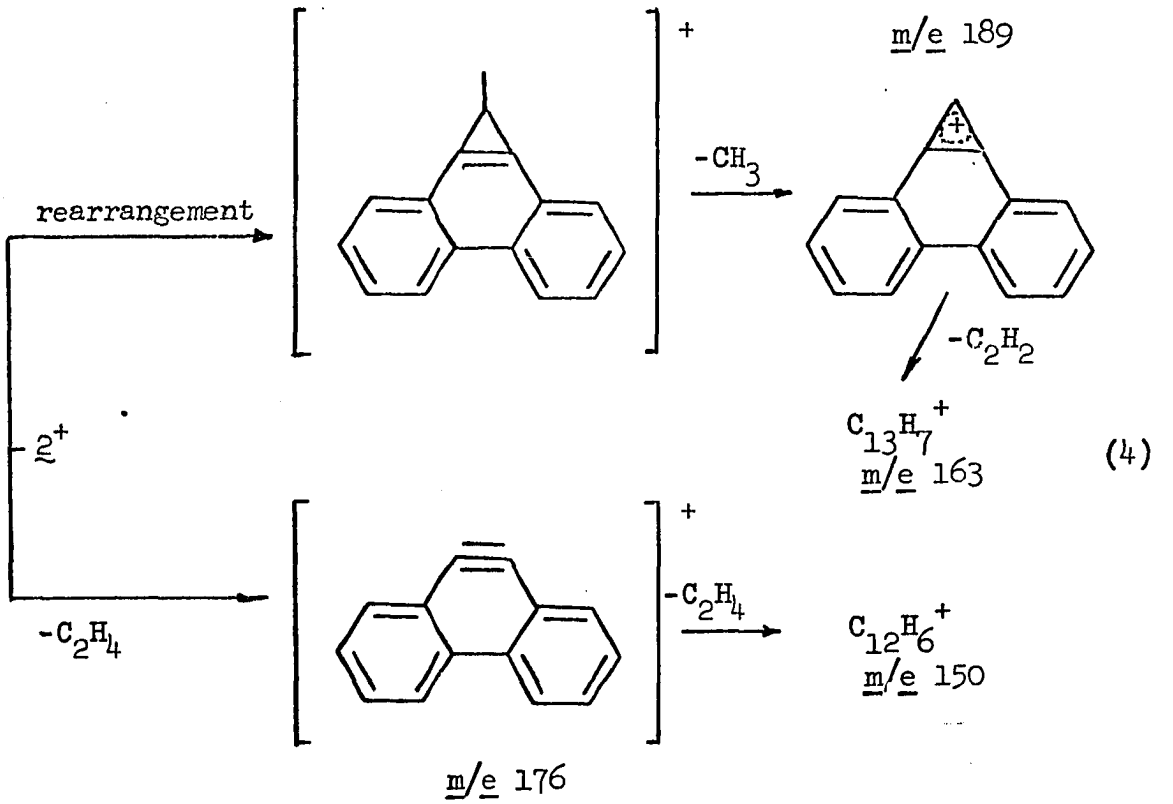

(4)

A weak metastable peak at m/e 128 supports the m/e 176 → 150 transition[8].

9,10-Dimethylene-9,10-dihydrophenanthrene (4). The intermediacy of 4 was demonstrated by the addition of maleic anhydride to a reaction solution prepared in exactly the same manner as in the synthesis of 2 before irradiation. The addition of acetic acid to this solution served to prevent continued elimination of the quaternary chloride (10) after addition of the maleic anhydride. Thus, the nearly quantative yield of

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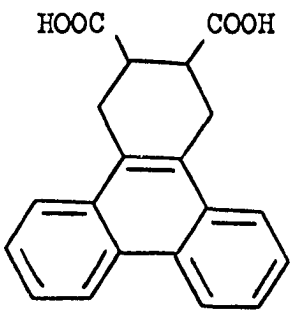
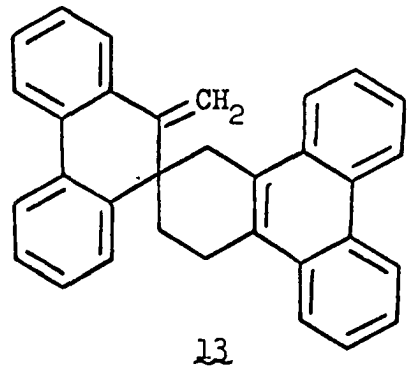
1,2,3,4-tetrahydro-2,3-triphenylene-cis-dicarboxylic acid (12) indicates that the almost complete conversion of 10 to 4 had occurred (Table 2). The small amount of dimer (13)[4c] found may have formed after addition of maleic anhydride. The formation of 13 was not evident in the ultraviolet spectrum when the



12



13

reaction was quenched with acetic acid; however, it is not certain that such a small quantity would be detected. The results from the formation of the maleic anhydride adduct indicate that the quinodimethane (4) has a half-life of about 8 hr at room temperature and 10^{-3} M in t-butyl alcohol. Comparison of the ultraviolet spectrum of this reactive intermediate with model systems (Table 3) indicates that the spectrum is consistent with structure 4. Each of the model compounds in Table 3 show some evidence of long wavelength absorption between 280 mμ and 300 mμ. The presence of a well defined maxima at 300 mμ in 4 may be the expression of a relatively rigid structure.

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Table 2. Product Yield for the Reaction of 9,10-Dimethylene-9,10-Dihydrophenanthrene with Maleic Anhydride

Aliquot	Time, hr[a]	Compound 13			Compound 12		
		(mg;	mmole;	%[b])	(mg;	mmole;	%[b])
A_1	0.1	0.7	0.0017	3.4	29.0	0.091	91.0
A_2	0.1	0.5	0.0012	2.4	29.9	0.093	93.0
B	8.0	10.3	0.025	50.0	12.3	0.038	38.0
C	103.0	17.1	0.042	84.0	2.8	0.0087	8.7

[a] After ultraviolet spectrum indicated complete conversion to 4.

[b] Based on 0.20 of the total reaction, or 0.100 mmole.

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Table 3.

	λ_{max} mμ (log ε)
9,10-Dimethylene-9,10-dihydrophenanthrene (4)	216 sh (4.56); 244 (4.42); 260 sh (4.25); 300 (3.79)[a]
2,3-Diphenylbutadiene[d]	243 (4.26); 280 sh (3.22); 287 sh (2.70)[b]
2,3-Diphenyl-13-cyclooctadiene[c]	247 (4.41); 295 sh (3.00)[b]
Styrene[c]	203 (4.38); 246 (4.11); 282 f (2.90)[c]
Calcd. for 4[f]	203 (4.68); 246 (4.41); 282 f (3.20)

[a] In t-butanol. [b] In cyclohexane. [c] In heptane. [d] A. C. Cope and D. S. Smith, J. Amer. Chem. Soc., 74, 5136 (1952). [e] P. P. Shorygin, M. F. Shostakovskii, E. N. Prilezhaeva, T. N. Shkurina, L. G. Stolyarova, and A. P. Genich, Izv. Acad. Nauk USSR, Ser. Khim., 61, 1571 (1961); "Organic Electronic Spectra", Vol. V., John Wiley and Sons, Inc., New York, 1969. [f] Calcd. value is twice the value of styrene. This assumption is based on two nonconjugated styrene chromophores.

Experimental Section

Melting points, except where noted, were taken with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were preformed by either Mr. Joseph Walters in this department or Galbraith Laboratories, Inc., Knoxville, Tennessee.

Infrared spectra were determined on Perkin-Elmer Model 337 or 521 infrared spectrometers, and were calibrated against known absorption bands of polystyrene. Ultraviolet spectra were determined on a Cary Model 14 spectrometer. Proton magnetic resonance spectra (nmr) were determined on Varian Associates A-60 or HA-100 spectrometers using tetramethylsilane as an internal standard for nonaqueous solutions and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) for aqueous solutions. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-6 mass spectrometer.

Thin-layer chromatography (tlc) was performed on Eastman Chromatogram sheets containing a fluorescent indicator. Visualization was with 2537 Å light.

9,10-Dimethyl-9,10-dihydroxy-9,10-dihydrophenanthrene (6). 9,10-Phenanthraquinone was purified *via* the sodium bisulfite addition product according to the method of Graebe[9]. Recrystallization from glacial acetic acid afforded fine plates, mp 207-8° (lit.[9] 205°); ir (KBr) 1674, 1281, and 759 cm^{-1}.

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A solution of methylmagnesium iodide was prepared by the addition of methyl iodide (27 ml, 61.5 g, 0.43 mole) in ether (100 ml) to magnesium turnings (9.72 g, 0.40 g-atom) in ether (30 ml). The mixture was stirred at room temperature until the magnesium was completely consumed. The solution was then diluted with ether (50 ml) and cooled in an ice-bath. The small crystals of purified 9,10-phenanthraquinone (20.67 g, 0.0995 mole) were then added in several portions. Each portion (2 g) was allowed to dissolve before addition of the next portion. The mixture was stirred for 1.0 hr at room temperature and then heated to reflux for 11 hr. Following the reflux period, the reaction mixture was treated as described by Gardner and Sarrafizadeh[4c]. Recrystallization of the crude product from benzene gave 18.1 g (0.075 mole, 76 %) of the title compound, mp 167.5 - 163.8° (lit.[4c] 163-164°); ir (KBr) 3439, 1180, 947, 760, and 730 cm^{-1}. The mother liquor on concentration yielded an additional 0.70 g (3.4 mmoles, 3.5%) of product, mp 160.5-167.5°.

9-Chloromethyl-10-methylphenanthrene (8). 9-Chloromethyl-10-methylphenanthrene was prepared by a modification of the method of Millar and Wilson[4a]. To a suspension of 6 (10.58 g, 44.0 mmoles) in ether (60 ml), thionyl chloride (12.7 mg, 21.0 g, 0.18 mole) was added with stirring. The reaction mixture was protected from atmospheric moisture with a drying tube. After stirring for 1.5 hr the mixture was heated to reflux for 5.5 hr at which time the

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reaction mixture became homogenous. Reflux was allowed to continue for 2 hr, afterwhich, the ether was allowed to distill off until stirring became impossible and hydrogen chloride evolution commenced. The mixture was then placed under aspirator vacuum and heated on a steam-bath until hydrogen chloride evolution ceased (1 hr). Ethyl acetate (100 ml) was added and the mixture was heated to reflux overnight. The nearly homogenous hot solution was filtered and allowed to cool to give 4.25 g of 8 (17.7 mmoles, 40%), mp 152.5-154° (lit.[4c] 155-156°); ir (KBr) 1254, 780, 760, and 720 cm^{-1}. The ethyl acetate mother liquor was evaporated to dryness on a rotary evaporator and the residue was dissolved in hot benzene. Addition of an equal volume of isooctane gave nicely shaped, slightly colored crystals of 8 (1.40 g, 5.8 mmoles, 13%), mp 146-148.5°. TLC of each batch on silica gel (benzene-hexane 1:2) gave a single spot of Rf 0.48.

The benzene-isooctane mother liquor on evaporation gave a crystalline mass (4.52 g) which on tlc on silica gel (benzene-hexane 1:2) gave two spots of Rf 0.27 and 0.48. This material was chromatographed on silica gel (100 g) using a benzene-hexane mixture (1:2) as eluent. The fractions containing the slow moving material were evaporated to crystalline solids and combined. Recrystallization from hexane gave 2.45 g (10.6 mmole, 24%) of 10,10-dimethyl-9(10H)phenanthrone(7) mp 72.0-73.5°

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(lit.[10] 75°). The infrared spectrum (KBr) was identical to that reported in the literature for 7[11] with prominent bands at 1675, 982, 783, 756, and 732 cm^{-1}; uv (hexane) 238 (log ε 4.39), 248 (4.33), 267 (3.99), 276 (4.05), 292 sh (3.74) and 320 mμ (3.50); nmr (CCl_4) δ 7.92 (m, 3.2 H), 7.38 (m, 5.2 H), and 1.50 (s, 6.0 H). The fraction containing the faster moving material gave a crystalline solid after evaporation. TLC on silica gel (benzene-hexane 1:2) of this material was identical to that of 9-chloromethyl-10-methylphenanthrene.

Trimethyl (10-methyl-9-phenanthrylmethyl)ammonium chloride monohydrate (11). The procedure of Millar and Wilson[4a] for the synthesis of trimethyl(10-methyl-9-phenanthrylmethyl)ammonium chloride (10) was followed. Trimethylamine generated by stirring the corresponding hydrochloride (9.6 g, 0.10 mole) with barium oxide (26 g, 0.27 mole) was bubbled into a stirred suspension of 9-chloromethyl-10-methylphenanthrene (3.000 g, 12.45 mmoles) in a mixture of chloroform (210 ml) and absolute methanol (70 ml). After stirring for 1.5 hr at room temperature, the reaction mixture was heated to reflux for 1.0 hr at which time the solution was homogeneous. The reaction mixture was allowed to cool with stirring for an additional 3 hr. TLC on silica gel (benzene-hexane 1:2) showed the presence of considerable starting material. Additional trimethylamine generated by adding dropwise a solution of the hydrochloride (14.4 g, 0.150

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mole) in water (50 ml) to a huge excess of sodium hydroxide (200 g) was bubbled through the reaction mixture for 1.0 hr at room temperature. TLC under the same conditions no longer showed starting material; however, a new spot at Rf 0.18 was present in addition to the expected spot at the origin corresponding to the title quaternary chloride. The reaction mixture was then heated to reflux for 2.0 hr, after which time the tlc was unchanged. The solvents were removed from the reaction mixture on a rotary evaporator and the resulting solid was placed under high vacuum overnight. The solid was then dissolved in absolute ethanol and the solution was filtered. Addition of ether gave 1.958 g of material which gave only a very faint spot at Rf 0.20 in addition to the spot at the origin. The nmr ($CDCl_3$) of this material showed a doublet at δ 2.93 (J= 5 Hz) attributable trimethylamine hydrochloride[12]. The only other peaks in the spectrum were attributable to the quaternary chloride at δ 8.72 (m, 2.94 H), 8.17 (m, 1.25 H), 7.70 (m, 4.67 H), 5.82 (broad doublet, 1.71 H, $\underline{CH_2}$)[13], 3.50 (s, 9.00 H), 3.02 (s, 3.6 H). From this spectrum, 9.0% (31 mol %) trimethylamine hydrochloride was indicated. When the spectrum was taken using deuterium oxide as solvent the doublet attributed to trimethylamine hydrochloride coalesced to a singlet at δ 3.17[14]. This peak represented the same amount of trimethylamine hydrochloride as was found using chloroform-d as solvent. The presence of

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trimethylamine hydrochloride was further confirmed by weak infrared bands (nujol) at 2515, 2470, and 987 cm^{-1}. The quaternary chloride (10) readily formed a chloroform insoluble hydrate. The impure quaternary chloride (10) was crystallized twice from water to give 1.103 g (3.47 mmoles, 28%) of analytically pure trimethyl(10-methyl-9-phenanthrylmethyl)-ammonium chloride monohydrate (11): uv max (t-butyl alcohol) 224 (log ε 3.38), 250 (4.63), 257 (4.69), 272 sh (4.11), 278 sh (3.99), 292 (3.96), 303 (3.93), 334 (2.53), 340 sh (2.26), and 350 mμ (2.26); ir (nujol) 3430, 3350, 875, and 760 cm^{-1}; nmr (D_2O) δ 8.21 (m, 2.0 H), 7.91 (m, 1.9 H), 7.68 (m, 3.8 H), 4.82 (d, 1.7 H), 2.98 (s, 8.9 H), and 2.52 (s, 3.1 H).

Anal. Calcd for $C_{19}H_{22}NCl \cdot H_2O$: C, 71.80; H, 7.61; N, 4.41. Found: C, 71.81; H, 7.36; N, 4.22.

The mother liquor from the initial precipitation of the quaternary ammonium chloride with ether was evaporated to a crystalline solid (1.638 g) which gave a principal spot on tlc on silica gel (benzene-hexane 1:2) of Rf 0.20. This material was dissolved in carbon tetrachloride (10 ml) and filtered. The clear solution was then evaporated to give a crystalline solid which was recrystallized from ethanol to give 0.598 g (2.54 mmoles, 20%) of 9-methoxymethyl-10-methylphenanthrene, mp 108.7-111.0° (lit.[4c] 113-114°); ir (KBr) 1099, 953, 755, and 720 cm^{-1}; nmr ($CDCl_3$) δ 8.67 (m, 2.2 H), 8.15 (m, 2.2 H), 7.61

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(m, 4.0 H), 4.96 (s, 2.0 H), 3.48 (s, 2.8 H), and 2.76 (s, 3.0 H).

9,10-Dimethylene-9,10-dihydrophenanthrene (4). A freshly prepared solution of potassium t-butoxide (0.10 ml of 0.37 M, 37 μmoles) was added to 5 ml of a 5.25×10^{-4} M solution of 11 (2.63 μmoles) in t-butyl alcohol. The solution was mixed well and then placed in an ultraviolet cell of 0.5 mm path-length. The disappearance of the fine structure and maxima characteristic of 11 and the appearance of maxima at 244 and 300 mμ (characteristic of 4) were observed. After 21 min there was no longer any evidence of 11, and the maxima at 244 and 300 mμ showed no further decrease in intensity (the decrease results from the low extinction of 4 relative to 11). After an additional 8 min the spectrum was unchanged. The ultraviolet spectrum of this solution showed max (log ε) 216 sh (4.56), 244 (4.42), 260 sh (4.25), and 300 mμ (3.79). Since the quinodimethane (4) could not be isolated, concentration of solutions of 4 leading to dimer (13) and polymer, the ε values we report are approximate and are calculated by assuming the concentration of 4 to be the same as the initial concentration of 11 (5.25×10^{-5} M). This assumption is justified since high yields (93%) of the maleic anhydride adduct (12) were obtained (Table 2). Other justification of a substantive nature follows from assuming these ε values. The ultraviolet spectra of solutions of 4 briefly irradiated with a 4 w germicidal lamp were interpretable as the sum of

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just the two components 2 and 4 (vida infra). Since the reactant (11) and known products (2 and 13) have greater extinction coefficients at the position of maxima for 4, the presence of small amounts of these compounds would lead to an increase in the calculated ϵ values for 4. The absence of these compounds in the reaction mixture after apparent complete conversion of 11 to 4 is evident from the constant ϵ values obtained for 4 over a range in concentrations from 2.0×10^{-5}M to 5.3×10^{-4}M.

A portion of this reaction solution was diluted with t-butyl alcohol to 3.17×10^{-5}M and placed in a 1 cm path-length cell. After irradiation for 2 min with a 4 W germicidal lamp, the ultraviolet spectrum showed maxima at positions identical to 9,10-cyclobutenophenanthrene (2). The intensities corresponded to a mixture comprised of 56% 2 (1.76×10^{-5}M) and 44% 4 (1.41×10^{-5}M). Further irradiation caused a net decrease in the concentration of 2.

The Adduct of 9,10-Dimethylene-9,10-dihydrophenanthrene with Maleic Anhydride. Trimethyl (10-methyl-9-phenanthrylmethyl)ammonium chloride monohydrate (159 mg, 0.500 mmole) was dissolved in t-butyl alcohol (500 ml, Baker Analyzed) and protected from atmospheric moisture by a drying tube. A freshly prepared solution of potassium t-butoxide (27 ml of 0.34 molar, 7.5 mmoles) was then injected. After stirring for 2 min a sample was withdrawn and placed in an ultraviolet cell of 0.5 mm path-length.

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The reaction was followed in the ultraviolet until no further decrease in the maximum at 244 mμ was observed. This occurred 14 min after addition of the potassium t-butoxide. Glacial acetic acid (0.5 ml, 8.7 mmoles) was then added to give a pH of about 7.0. The reaction was allowed to stir an additional 4 min, after which, four 100 ml aliquots were withdrawn. Twenty min after the addition of potassium t-butoxide, maleic anhydride (1.1 g, 11 mmoles) was added to each of two of the aliquots (A_1 and A_2). Upon addition of the maleic anhydride, a cloudy precipitate formed and the solution turned pink. After 8 hr at room temperature, the same amount of maleic anhydride was again added to A_1 and A_2 as well as to a third aliquot (B). After an additional 8 hr, A_1 and A_2 were worked-up as described below and additional maleic anhydride was added to B. This aliquot was worked-up after an additional 8 hr. The fourth aliquot (C) was treated exactly the same as the first three with addition of maleic anhydride commencing 103 hr after maleic anhydride was added to A_1 and A_2.

Sixteen hr after the initial addition of maleic anhydride, each aliquot was concentrated on a rotary evaporator until only a few milliliters of t-butyl alcohol remained. A solution of potassium hydroxide (5 g) in water (100 ml) was then added and the mixture heated to 80-90° for 2.5 hr. Upon cooling, the mixture was vacuum filtered through Whatman #50 filter paper

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and the precipitate was washed well with water and dried *in vacuo*. The clear filtrate was then acidified with 1 N hydrochloric acid. The precipitate was collected by vacuum filtration through a medium grade sintered glass filter and washed well with water followed by drying *in vacuo*. The base insoluble precipitates each melted at 234-7° dec. The literature values for 2-methylene-3,4,5,6-dibenzo-3',4'-(9,10-phenanthro)spirobicyclohexane (13) are 228.5-229° and 252-253° depending on the solvent for crystallization[15]. The infrared (KBr and CS_2), ultraviolet (ethanol), and nmr ($CDCl_3$) spectra of the combined base insoluble product were identical to those of 13 prepared by the method of Stille and Foster[16]. The tlc on silica gel (benzene-hexane 1:2) showed a large spot at Rf 0.38 identical to 13 and barely perceptible spots at Rf 0.19 and at the origin. A portion of this product after recrystallization from ethanol gave an ir (KBr) identical to the spectrum of the crude product, and melted at 245-247° dec. A second portion recrystallized from cyclohexane melted at 229-231° dec. The ir (KBr) of this sample showed a strong band at 913 cm^{-1} characteristic of the lower melting form of 13[4b]. TLC on silica gel (benzene-hexane 1:2) of both forms and authentic 13 gave a single spot of Rf 0.43.

The acid precipitated material sublimed readily upon melting. Material from the first two aliquots melted at

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280-290° dec (Kofler). Due to the small amount of sample, only the melting point of the sublimate could be determined for the second two aliquots. In each case, the sublimed material melted at 305-308°. The values reported for 1,2,3,4-tetrahydro-2,3-triphenylene-cis-dicarboxylic acid (12) are 279-282° dec (sublimate: 308-313°)[4b]. Recrystallization from an ethyl acetate-ethanol mixture (1:1) gave crystals which melted at 282-284° dec; ir (KBr) 1690 cm^{-1} [lit.[4b] (nujol mull) 1698 cm^{-1} (C=O str.)]; uv max (EtOH) 349 (log ε 2.90), 333 (2.76), 298 (4.05), 286 (4.03), 278 (4.15), 272 (4.19), 255 (4.79, lit.[13] 4.78), 247 (4.70), 224 (4.37), and 215 mμ (4.47). A small sample of this material sublimed in an 8 mm glass tube sealed at 20 mm Hg and heated to 275-300° to give very nice needles. The ir (KBr) was identical to that of authentic 1,2,3,4-tetrahydro-2,3-triphenylene-cis-dicarboxylic anhydride[17].

The yields of 12 and 13 for each aliquot are summarized in Table 2.

9,10-Cyclobutenophenanthrene (2). Trimethyl (10-methyl-9-phenanthrylmethyl)ammonium chloride monohydrate (239 mg, 0.75 mmole) and t-butyl alcohol (Baker Analyzed, 1.0 l.) were placed in a 1.0 l. quartz reaction round bottom flask with a single 24/40 $\overset{T}{S}$ joint. To the other member of this joint was attached a coarse porosity gas dispersion tube (Scientific Glass Apparatus Co., JG 8500) and a section of 8 mm O.D. glass tubing.

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The 8 mm tubing was closed with a rubber septum through which a long stainless steel needle was inserted. This needle normally functioned to allow the nitrogen being bubbled through the reaction solution to escape; however, the tip could be inserted below the surface of the liquid for the withdrawing of aliquots. The flask also contained a magnetic stir-bar.

The solution of 11 was then flushed for 8 hr with nitrogen (Airco Prepurified) dried by passage through a glass coil immersed in a Dry Ice-ethanol bath. During this period, a solution of potassium t-butoxide in t-butyl alcohol was prepared under argon and diluted with t-butyl alcohol to 0.76 N as determined by titration with hydrochloric acid. The clear, colorless solution of potassium t-butoxide (14.0 ml, 10.6 mmoles) was injected below the surface of the nitrogen flushed solution of quaternary chloride over a 5 min period. An aliquot was withdrawn and placed in an ultraviolet cell of 0.5 mm path-length. The formation of 9,10-dimethylene-9,10-dihydrophenanthrene (4) in this aliquot was monitored in the ultraviolet until no further change (decrease) in the maximum at 244 mμ was observed (20 min). Irradiation was begun using a Rayonet Photochemical Reactor[18] equipped with 2537 Å lamps. The photolysis was followed in the ultraviolet by periodically withdrawing aliquots. The concentration of cyclobutenophenanthrene appeared to reach a maximum after 25 min irradiation; irradiation was stopped

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after a total of 30 min. Glacial acetic acid (1.0 ml, 17.4 mmoles) was added to the cloudy reaction mixture to give a neutral solution. The t-butyl alcohol was then removed on a rotary evaporator at 40-50° to give a white solid which was dried at 5×10^{-3} torr overnight. This solid was stirred with a mixture of hexane (100 ml) and water (100 ml). The mixture was then filtered to give an amorphous solid (67.0 mg) which did not melt below 290°; however, it appeared to decompose slowly above 200°. This material did not contain any cyclobutenophenanthrene by tlc on silica gel (benzene-hexane 1:2). It was undoubtedly a mixture since it was only partially soluble in benzene. The residue which was insoluble in benzene was partially soluble in water.

The hexane solution on tlc on silica gel (benzene-hexane 1:2) gave a major spot at Rf 0.58 corresponding to authentic cyclobutenophenanthrene[3]. A minor spot at the origin as well as extremely light spots at Rf 0.47 and 0.27 were present. Evaporation of the hexane solution gave a semicrystalline mass. Attempted recrystallization of this material from ethanol-water mixtures kept under nitrogen gave solid products which on tlc showed that decomposition had occurred. From the tlc of the combined solids, cyclobutenophenanthrene was now estimated to constitute only one-half of the total. The combined solids were chromatographed on 12 g of silica gel using cyclohexane as eluent. The fractions were collected under argon and

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yielded 23 mg (0.113 mmole, 15%) of cyclobutenophenanthrene mp (Kofler) 135-137° (lit.[3] 130-131°). Recrystallization from hexane gave an analytical sample: mp 135.5-136° (Kofler); ir (KBr) 2955, 1204, 948, 942, 744, and 721 cm^{-1}; uv max[19] (EtOH) 220 (log ε 4.33), 247 (4.70), 255 (4.80), 270 (4.23), 279 (4.06), 289 (4.01), 301 (4.14), 324 (2.83), 339 (3.10), and 357 mμ (3.23); uv max (n-hexane) 220 (4.37), 247 (4.73), 255 (4.83), 270 (4.27), 278 (4.10), 288 (4.04), 301 (4.20), 324 (2.70), 332 (2.67), 339 (3.06), 343 (2.75), 348 (2.74), 352 (2.73), and 357 mμ (3.34); fluorescence max[20] (diethyl ether, 340 mμ excitation) 362 (rel intensity 1.29), 382 (1.55), and 398 sh mμ (1.00); nmr (CCl_4) δ 8.60 (m, 2.1 H), 7.65 (m, 2.0 H), 7.45 (m, 4.0 H), and 3.35 (s, 4.0 H); mass spectrum (70 eV) m/e (rel intensity) 204 (100), 203 (67), 202 (48), 201 (12), 200 (11), 189 (7.5), 176 (6.0), 163 (2.6), 150 (3.5), 102 (6.7), 101.5 (6.2), 101 (25), 100.5 (4.6), 100 (8.4), 89 (7.4), 88 (9.3), and 76 (5.7).

Anal. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92; Mol wt 204. Found: C, 94.03; H, 5.94; Mol wt 215 (Mechrolab Osmometer in chloroform); 204 (mass spectrum).

Unsuccessful Approach to the Synthesis of 9,10-Cyclobutenophenanthrene (2). Trimethyl (10-methyl-9-phenanthrylmethyl)-ammonium chloride monohydrate (108 mg, 0.34 mmole) dissolved in ethanol (10 ml) was converted to trimethyl (10-methyl-9-phenanthryl methyl)ammonium hydroxide by passage through a column of Amberlite

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IRA-400 (OH^-) resin according to the method of Millar and Wilson[4a]. The solution was diluted to 225 ml with additional ethanol and then placed in a cylindrical quartz vessel (5 cm x 18 cm). The solution was stirred and flushed with nitrogen (Airco Prepurified) for 30 min. So far, the procedure was performed in a refrigerated room at 5°. TLC on silica gel (benzene-hexane 1:2) showed a single spot at the origin. The reaction solution was then irradiated with stirring in a Rayonet Photochemical Reactor[18] at 2537 Å at 35°. The reaction was followed by tlc on silica gel (benzene-hexane 1:2). Irradiation was stopped after 30 min. TLC showed the absence of starting material. Spots were present at Rf 0.048, 0.25, 0.41, and 0.56. The spot at Rf 0.56 corresponded in position to both 9,10-dimethylphenanthrene and 9,10-cyclobutenophenanthrene. The reaction solution contained a fine precipitate and gave a strong odor of trimethylamine. The precipitate (27 mg) was separated by filtration. The solution was evaporated to dryness at 25° on a rotary evaporator. This residue was chromatographed on a preparative tlc plate (20 cm x 20 cm) prepared with 30 g of alumina using a benzene-hexane (1:2) mixture for development. During this chromatography, the products were protected from oxygen by an argon atmosphere. Five bands of material were evident; however, only the two apparently major bands were extracted and the material identified. One band (Rf 0.51-0.67) gave 7.0 mg (0.034 mmole, 10%) of

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dimethylphenanthrene: mp (Kofler) 138.5-141° (lit.[10] 139°). The ir (KBr) 1602, 1580, 1435, and 749 cm^{-1}; uv (Et_2O); and mass spectrum (70 eV) m/e (rel intensity) 206 (100) and 191 (97) were identical to authentic 9,10-dimethylphenanthrene. The second band (Rf 0.23-0.32) gave 2.0 mg (8 μmoles, 2.4%) of 9-ethoxymethyl-10-methylphenanthrene: mp (Kofler) 96.0-97.2° (lit.[4c] 91-92°); uv max (EtOH) 224 (log ε 4.25), 248 (4.56), 255 (4.63), 272 (4.04), 278 (3.94), 287 (3.83), 299 (3.83), 333 and 350 mμ; ir (KBr) 1120, 1097, 1010, and 755 cm^{-1}; nmr (CCl_4) δ 8.59 (m, 2.1 H), 8.09 (m, 2.1 H), 7.50 (m, 3.8 H), 4.94 (s, 1.9 H), 3.57 (q, 2.1 H, J= 7 Hz), 2.74 (s, 3.0 H), and 1.19 (t, 3.35 H, J= 7 Hz); mass spectrum (70 eV) m/e (rel intensity) 250 (0.76), 206 (14), 204 (13), 191 (15), and 44 (100).

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12. A nearly saturated solution of trimethylamine hydrochloride in $CDCl_3$ gave a singlet at δ 2.95; however, a dilute solution gave a doublet at δ 2.88 (J= 5 Hz).

13. The two methylene protons appear as a doublet (actually two unresolved singlets) due to hindered rotation caused by the bulky trimethylammonium group.

14. The nmr (D_2O) of trimethylamine hydrochloride gave a singlet at δ 2.91. Addition of trimethyl (10-methyl-9-phenanthrylmethyl)ammonium chloride (< 50 mol %) shifted this peak to δ 3.07.

15. The lower melting form was obtained by crystallization from cyclohexane by Stille and Foster[4b]. The higher melting form was obtained by crystallization from ethanol[4b,c]. The literature melting points are corrected. The melting points reported for the precipitates were taken on a Kofler hot-stage apparatus.

16. Gardner and Sarrafizadeh[4c] report uv max (EtOH) 245 (log ε 4.44), 256 (4.46), and 272 mμ (4.44) for 13. In our hands, compound 13 prepared by the method of Stille and Foster[4b] gave uv max (EtOH) 215 (log ε 4.72), 225 (4.71), 247 (4.81), 256 (4.81), 268 (4.46), 272 (4.45),

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278 (4.39), 287 (4.32), 300 (4.19), 336 (2.83), 342 (2.63), and 351 mμ (2.85).

17. We wish to thank Professor Stille for a generous sample of this material.

18. The Southern New England Ultraviolet Company, Middletown, Connecticut.

19. The low intensity absorptions (log ε less than 2.80) between 320 and 360 mμ are not reported for the ethanol spectrum because of the low solubility of cyclobutenophenanthrene (2) in this solvent.

20. Fluorescence spectrum and molecular weight (osmometer) as reported by E. W. Friend, Dissertation, The Johns Hopkins University, 1967.

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PART III

PYROLYSIS OF 2-METHYLENE-3,4,5,6-DIBENZO-3',4'-(9,10-PHENANTHRO)SPIROBICYCLOHEXANE

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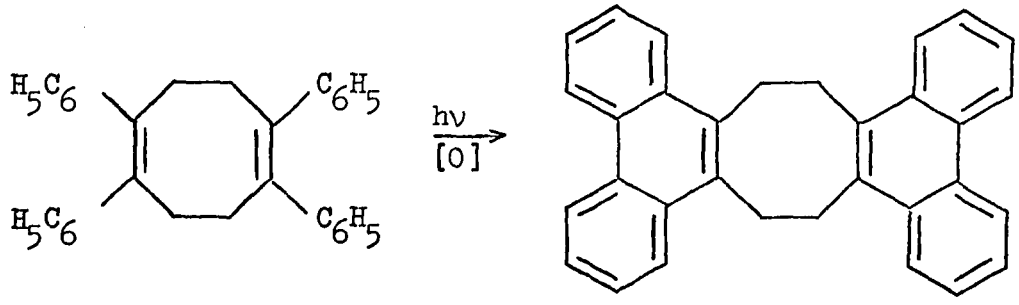
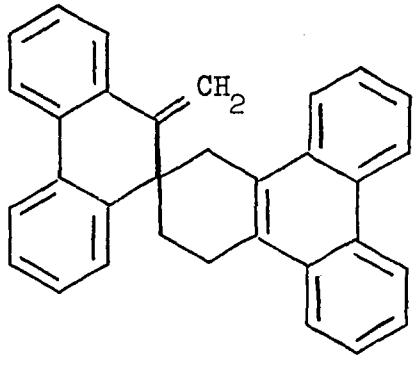
In a previous communication we reported the synthesis of 1,2,5,6-tetraphenylcycloocta(1,5)diene (1)[1]. We noted that irradiation of 1 in the presence of oxygen led to the apparent formation of 1,2,5,6-bis (9,10-phenanthro)cycloocta(1,5)diene (2) with an ultraviolet spectrum consistent with the presence



1 2

of two isolated phenanthrene chromophores. Likewise, 1,2,5,6-dibenzocycloocta(1,5)diene[2] (7) gave an ultraviolet spectrum similar to that of o-xylene and of twice the molar extinction. The bis(9,10-phenanthro)cyclooctadiene (2) had been previously reported from the pyrolysis of 2-methylene-3,4,5,6-dibenzo-3',4'-(9,10-phenanthro)spirobicyclohexane (3)[3,4]. The material obtained by Stille and Foster, however, showed a large



3

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bathochromic shift compared to 9,10-dimethylphenanthrene. These factors suggested that an alternative structure must exist for the product obtained from pyrolysis of 3.

A generous sample of this pyrolysis product was kindly provided by Professor Stille for our study. Recrystallization of this material from N,N-dimethylformamide followed by sublimation gave a very lightly colored product which gave infrared, ultraviolet, and mass spectra identical to that of the material received. Analysis of the purified material showed it to be a $C_{30}H_{18}$ hydrocarbon. The mass spectrum showed a very intense molecular ion at m/e 378. Prominent m/e values of 152, 234, and 408 reported in the literature[3] for the pyrolysis product were not evident either before or after purification. In fact, the mass spectrum is remarkable in its simplicity and in the abundance of doubly charged ions. The analysis and mass spectrum suggested a nonsubstituted, annellated aromatic hydrocarbon. Comparison of the ultraviolet spectrum ($\lambda_{max}^{CHCl_3}$ 294 mμ, log ε 4.98) with other compounds of this type, such as dibenz(a,c)anthracene (λ_{max}^{EtOH} 286 mμ, log ε 5.11)[5] and dibenz(a,h)-anthracene ($\lambda_{max}^{C_6H_6}$ 300 mμ, log ε 5.1)[6], suggested an aromatic system of five rings. The empirical formula suggested a system of seven rings; and thus, a cross-conjugated system such as tetrabenz(a,c,h,j)anthracene (4) was considered.

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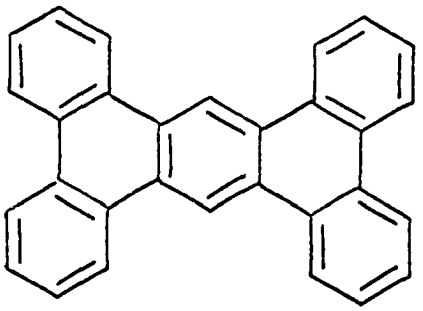
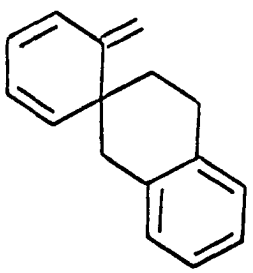


4

This compound had been prepared in an unambiguous manner by Lambert and Martin[7], and the structure had been confirmed by X-ray analysis[8]. On comparison, the pyrolysis product of 3 was identical in every respect to authentic 4.

Discussion

With the structure of the pyrolysis product from 3 elucidated, we next turned to the mechanism for its formation. In an apparently analogous reaction, the pyrolysis of o-xylene to give anthracene, which presumably could proceed through formation of o-xylylene and spiro(5,5)-2,3-benz-6-methyleneundeca-7,9-diene (5), proceeds instead through the intermediary 1,2-di-o-tolylethane (6)[9].



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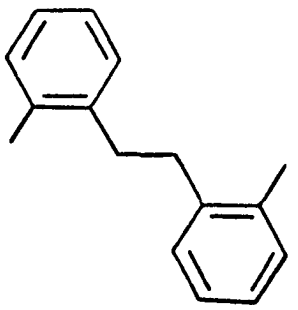

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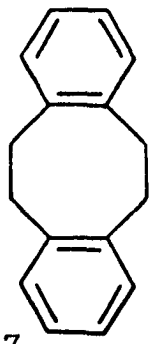

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The formation of o-xylylene under pyrolytic conditions in the absence of a hydrogen source leads to benzocyclobutene, 5, and 1,2,5,6-dibenzocycloocta(1,5)diene (7). At room temperature 5 converts rapidly to a polymer[10]. Similarly, the formation of benzene in the pyrolysis of 4-vinylcyclohexene has been explained by a mechanism which involves loss of a vinyl radical[11]. Such a mechanism would not be expected to produce 4 in the pyrolysis of 3. The transformation of 3 to 4, therefore, appears to be without good precedent.

The mass spectrum of 3 showed the facile loss of C_2H_4 (M^+-28) and retro-Diels-Alder cleavage to give an abundant ion at m/e 204 ($C_{16}H_{12}^+$). Pyrolysis of 3 in degassed solutions of naphthalene at 235° and 285° led to the formation of tetrabenzanthracene (4) and gaseous products. The gaseous products consisted primarily of ethane and ethylene in amount about equal to the amount of 4 formed. Ethane predominated in the mixture with a ratio of 3:1 for the pyrolysis at 235° and 6:1 for the pyrolysis at 285°. A trace of methane as well as small amounts of propane, butane, and propene were formed at the higher temperature. These C_3 and C_4 hydrocarbons formed in larger proportion at the higher temperature may arise from catalytic cracking of 3 on active sites present in Pyrex glass[12].

Among the several plausible mechanisms which one can propose for the formation of 4 in the pyrolysis of 3, we would like to

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consider two for which we find some experimental support. We will further limit this discussion of mechanism principally to the formation of ethylene in the pyrolysis. The formation of ethane appears to involve many steps and therefore many branching points and ramifications on which we prefer not to speculate.

Two-Step Mechanism. The formation of bicyclo[2,2,2]octene-2 from 4-vinylcyclohexene on acidic catalyst at 250° has been demonstrated[13]. This is formally an intramolecular ene reaction (Figure 1), although in the case cited, this mechanism was not proposed[14]. In the pyrolysis of 3, a similar first step

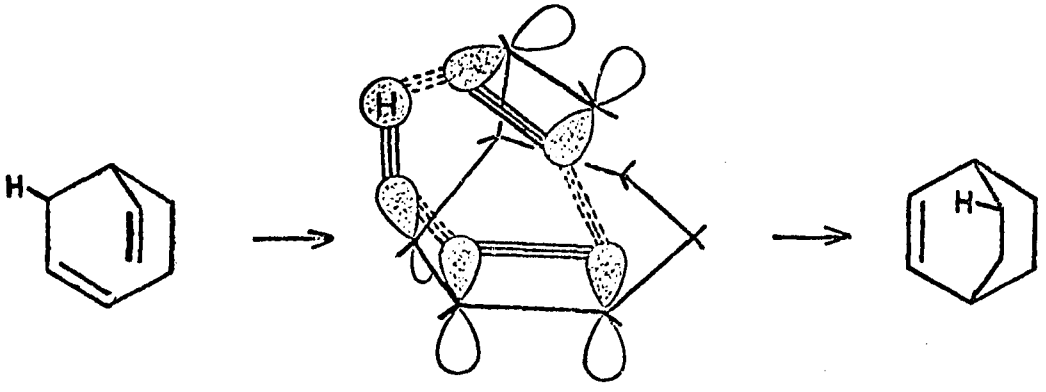

Figure 1.

can be drawn (Figure 2) to give 4a, 8a-ethano-10,10a-dihydrotetrabenz(a,c,h,j)anthracene (8). Loss of the ethano bridge from 8 would lead to 10,10a-dihydrotetrabenzanthracene (9).

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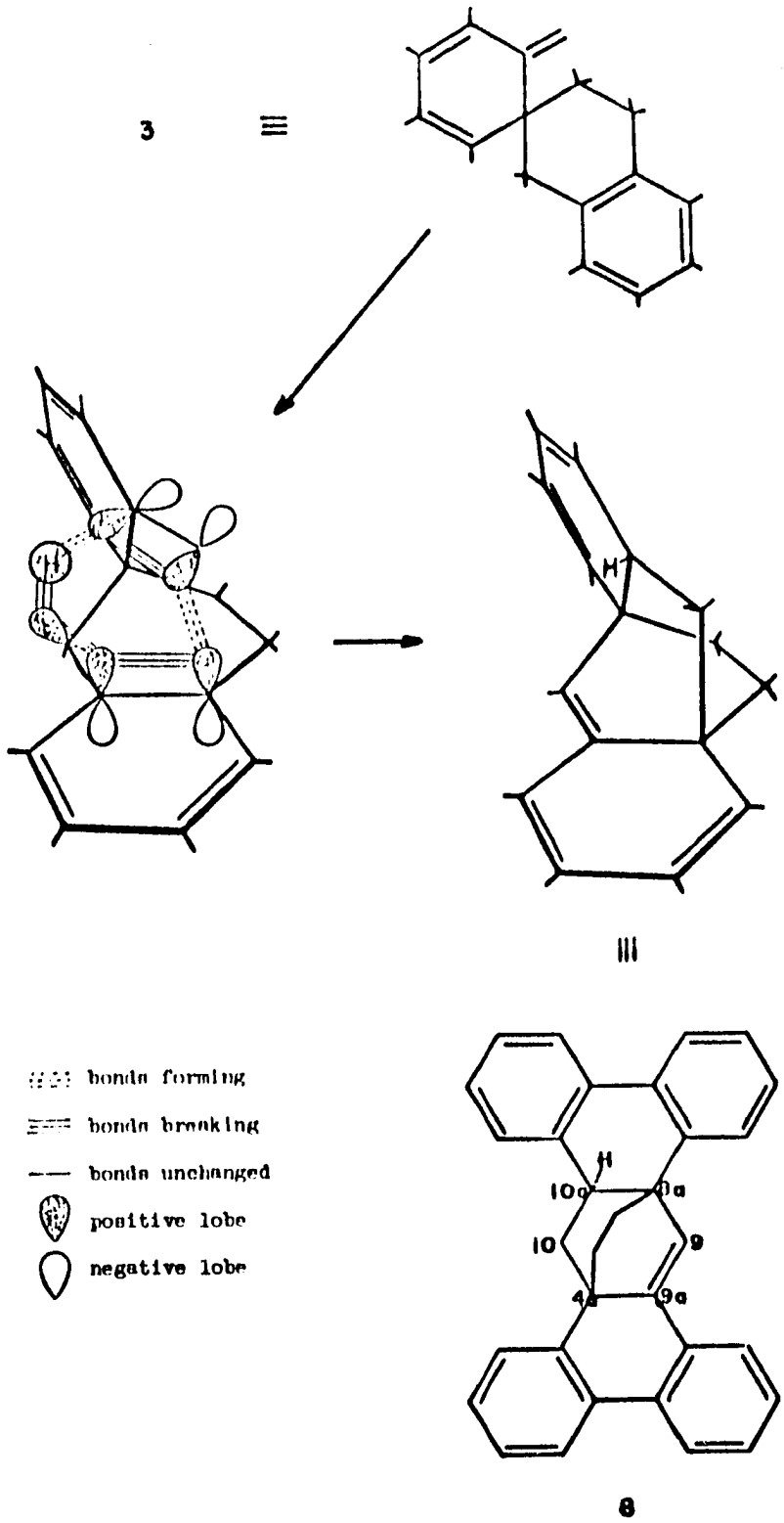

Figure 2.

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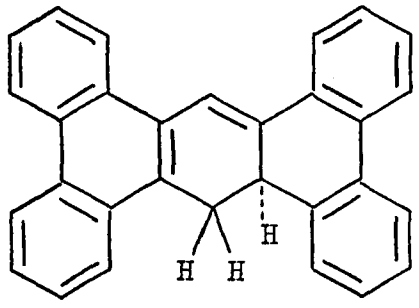
This compound would be expected to be colored by analogy to 9-phenyl-9,9a-dihydroanthracene[15] and 9,9,10-triphenyl-9,8a-dihydroanthracene[16] and could account for a portion of the transient yellow color observed in the pyrolysis of 3. Compound 9 would



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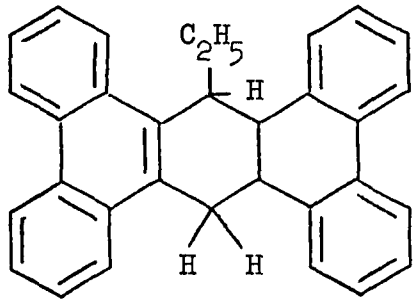

10

also be expected to convert readily to the fully aromatic 4[17].

There are a variety of reasonable mechanisms by which 8 can give ethane. One reasonable intermediate is 9-ethyl-9,10-dihydrotetrabenzanthracene (10). This, for example, could arise from homolytic cleavage of the ethano bridge followed by abstraction of a hydrogen from C_{10} to give 8a-ethyl-8a,10a-dihydrotetrabenzanthracene. Subsequent [1,5] suprafacial migration of the ethyl group to C_{10} would give 10-ethyl-10,10a-dihydrotetrabenzanthracene, which would be expected to convert to 10[17]. The subsequent loss of ethane from 10 has precedent in the reported formation of methane and toluene in the pyrolysis of trans-3,6-dimethylcyclohexa-1,4-diene[20]. The pyrolysis of cis-3,6-

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dimethylcyclohexa-1,4-diene, in contrast, leads to preferential loss of hydrogen to give only p-xylene[20]. In 10, however, loss of hydrogen to give 9-ethyltetrabenzanthracene would be inhibited by steric interaction of the ethyl group with the peri hydrogens.

In addition to 4, two other products have been recovered by chromatography from the pyrolysis of 3 at 285°. One compound, isolated in 2% yield, gave an ultraviolet spectrum consistent with the presence of a phenanthrene chromophore[21]. The mass spectrum showed the facile loss of the elements of C_2H_5 and C_2H_6 with the formation of stable ions at m/e 379 and 378. The remainder of the spectrum showed a fragmentation pattern similar to that of tetrabenzanthracene. Pyrolysis of this material for 2 hr at 360° in an evacuated tube without solvent gave pure tetrabenzanthracene from the ultraviolet spectrum. This unknown material was possibly 10, unfortunately, too little was available for a rigorous structure determination. A second crystalline product was isolated in 1% yield. This material gave an ultraviolet spectrum lacking the finely resolved structure of a nonconjugated phenanthrene chromophore. The mass spectrum showed prominent, successive losses of methyl radical and an intense peak at m/e 231. The lack of a prominent ion at m/e 204 ($C_{16}H_{12}^+$) suggests that this compound is not 2, and the data does not warrant the proposal of other structures.

Concerted Formation of Ethylene. The photochemical di-π-methane rearrangement of 1,4-pentadienes can be described as a

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trans addition of a σ bond to a π bond[22]. This point of view describes a [$_{\sigma}2a + _{\pi}2a$] cycloaddition, and is accordingly allowed in the excited state[23]. The present transformation can be viewed as a thermally allowed [$_{\pi}2s + _{\sigma}2s + _{\sigma}2s$] cycloaddition (Figure 3) to give dihydrotetrabenzanthracene (11) followed by loss of hydrogen to give 4. The addition of dienophiles to quadricyclane (12) is similar[24], and only the nonparticipating carbon skeletons differ (equation 1). In the quadricyclane case both termini of

12 — nonparticipating carbon skeleton

---- reacting bonds

each of the reacting σ bonds are joined together and the superstructure of the molecule prevents the elimination of an ethylene molecule; whereas, in the rearrangement of 3, one terminus of each of the reacting σ bonds is joined together directly, and the other terminus is joined together by a two carbon bridge. Thus a six membered ring is formed, and the loss of ethylene is not constrained by the presence of additional structure.

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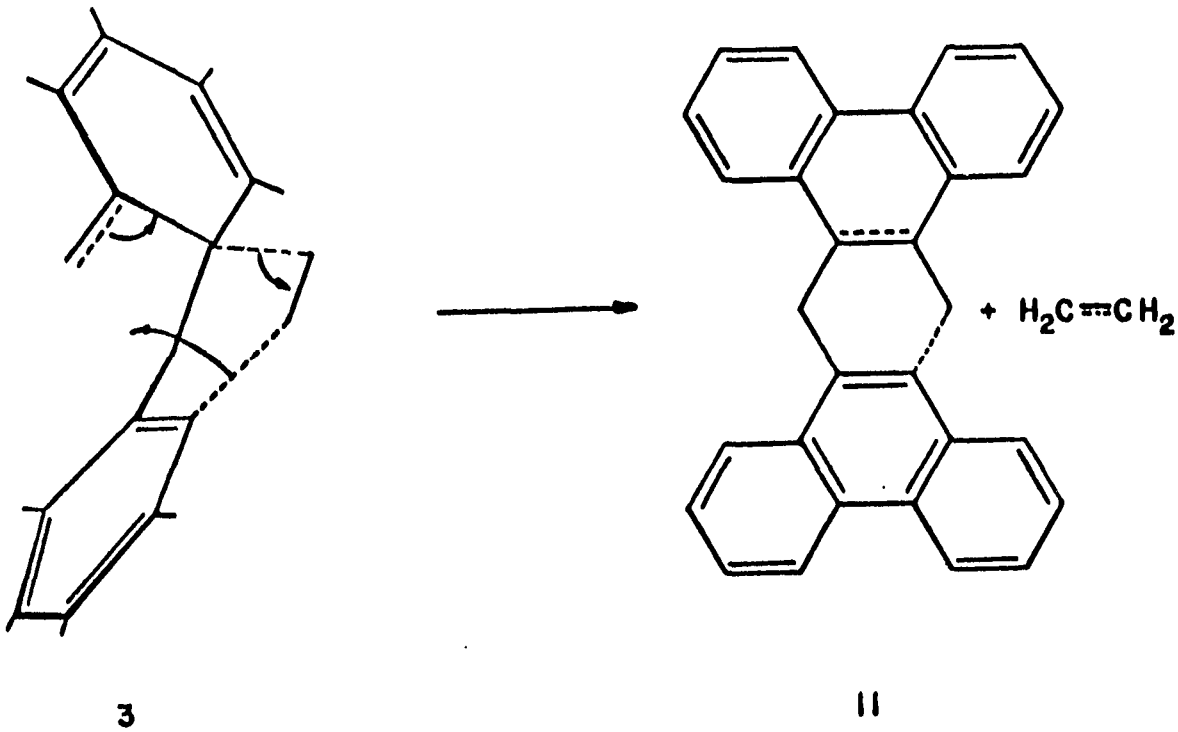

Figure 3.

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The homologous series of ground state cycloadditions beginning with the allowed [2a + 2s] and including the [2s + 2s + 2s] cycloaddition reaction has been thoroughly discussed by Woodward and Hoffman[23]. The rearrangement of 3 to 11 represents a member of this series.

In the Woodward and Hoffman classification of cycloaddition reactions, only one π bond in the di-π-methane rearrangement is explicitly considered. Zimmerman has presented an alternative point of view in which both π bonds are considered to be involved in a cyclic transition state[22]. Likewise, the 9-10 π bond of the phenanthrene chromophore in 3 may be considered to participate without important alteration in the stereochemical process. A transition stage in this representation is shown in Figure 4. This representation illustrates an 8 π electron cycle with a single inversion (or odd number of inversions) and is therefore a Möbius species, which is favored in the ground state when involving 4n electrons[26].

One functional difference between the concerted and two step mechanism is that in the two step mechanism, a group or a hydrogen must migrate from the methylene bridge in 3 to form an isodihydrotetrabenzanthracene; whereas, in the concerted process, a dihydrotetrabenzanthracene is formed. Substitution of these hydrogens by groups less prone to migrate, or better, replacement of the methylene bridge with a group without substituents may

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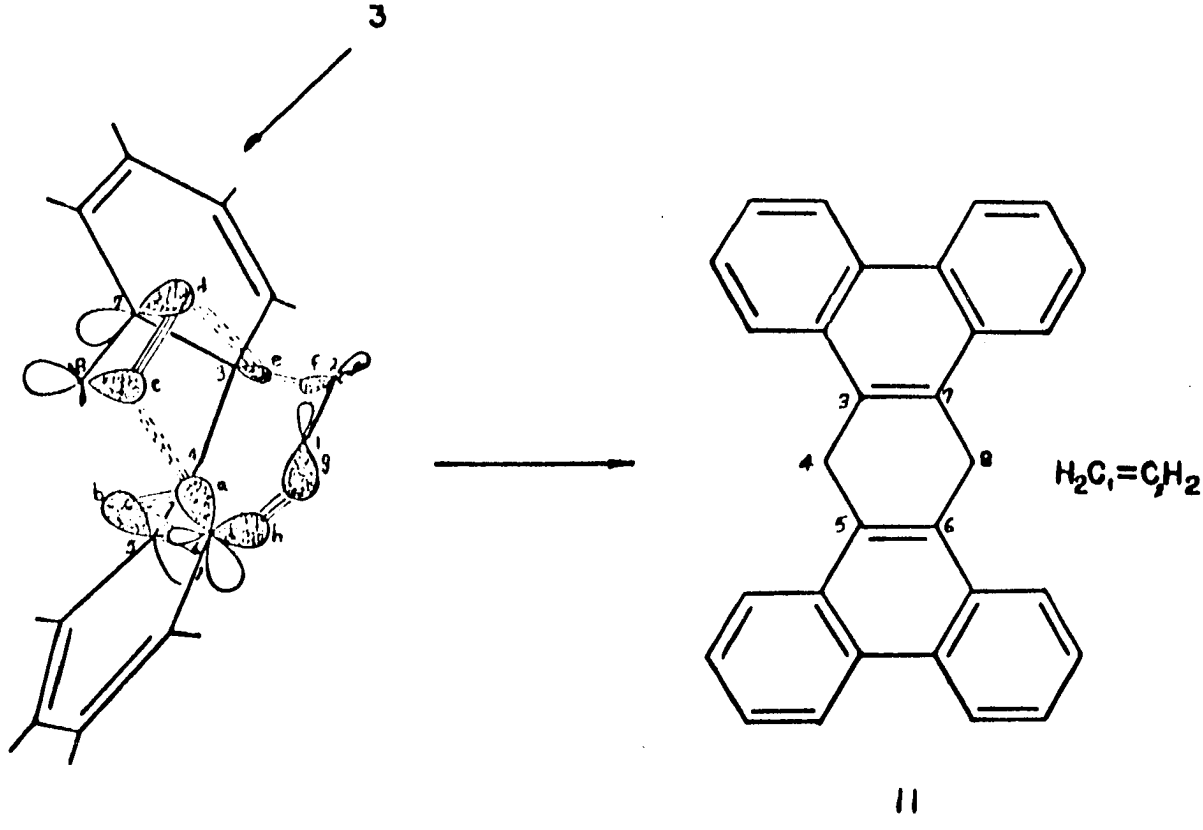

Figure 4.

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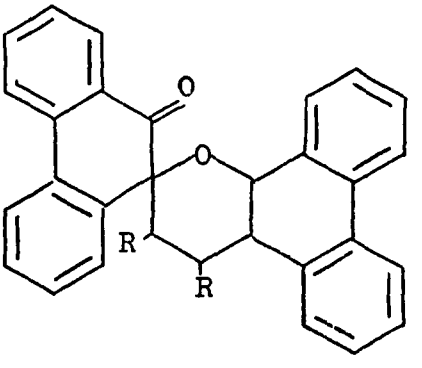
serve to differentiate the two mechanisms. The exocyclic methylene would also require similar treatment since it can be made equivalent to the methylene bridge by a Cope rearrangement. A compound with the latter characteristics has been prepared by Sullivan, Ullman, and Shechter[27]; however, to our knowledge compound 13 has not been pyrolysed.



R = C_6H_5

13

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Experimental Section

Melting points, except where noted, were taken with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by either Mr. Joseph Walters in this department or by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Infrared spectra were determined on Perkin-Elmer Model 337 or 521 infrared spectrometers, and were calibrated against known absorption bands of polystyrene. Ultraviolet spectra were determined on a Cary Model 14 spectrometer. Proton magnetic resonance spectra (nmr) were determined on Varian Associates A-60 or HA-100 spectrometers using tetramethylsilane as an internal standard for nonaqueous solutions and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) for aqueous solutions. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-6 mass spectrometer.

Thin-layer chromatography (tlc) was performed on Eastman Chromatogram sheets containing a fluorescent indicator. Visualization was with 2537 Å light.

9-Bromomethyl-10-chloromethylphenanthrene. With only slight modification, the method of Stille and Foster[3] was followed. 9-Chloromethyl-10-methylphenanthrene[28] (1.00 g, 4.16 mmoles) was dissolved in carbon tetrachloride (40 ml). N-bromosuccinimide (0.824 g, 4.57 mmoles) and dibenzoylperoxide (20 mg) were then

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added and the mixture was heated to reflux for 3 hr. After standing overnight, the mixture was diluted with carbon tetrachloride (200 ml) and extracted with two 100 ml portions of water followed by 100 ml of saturated aqueous sodium chloride. The carbon tetrachloride layer was separated, filtered through sodium sulfate, and evaporated on a rotary evaporator to give a solid which was recrystallized from carbon tetrachloride to give 0.926 g (2.9 mmoles, 70%) of 9-bromomethyl-10-chloromethylphenanthrene as very fine needles: mp 216-217.5° dec (lit.[28] 219.5-220.5°); ir (KBr) 1251, 1201, and 761 cm^{-1}. The mother liquor from this crystallization was evaporated to dryness and the residue was recrystallized from ethanol-water to give an additional 0.201 g (0.63 mmoles, 15%) of product, mp 201-212° dec.

2-Methylene-3,4,5,6-dibenzo-3',4'-(9,10-phenanthro)spirobicyclohexane (3). The title compound was prepared in 72% yield (mp 237-243°) from 9-chloromethyl-10-bromomethylphenanthrene (300 mg, 0.937 mmole) and sodium iodide (600 mg) in refluxing acetone according to the method of Stille and Foster[3]. Recrystallization twice from benzene-ethanol solution gave 99.8 mg (0.245 mmole, 52.3%) of colorless fine plates: mp (Kofler) 252-253° (lit.[3] 250-251°); ir (KBr) 894, 771, 749, and 720 cm^{-1}; uv (EtOH) 215 (log ε 4.72), 225 (4.71), 247 (4.81), 256 (4.81), 268 (4.46), 272 (4.45), 278 (4.39), 287 (4.32), 300 (4.19), 336 (2.83), 342 (2.63), and 351 mμ (2.85); nmr ($CDCl_3$) δ 9.23 (m, 2.1 H), 8.32 (m, 1.2 H), 7.50 (m, 14 H), 5.27 (s, 1.0 H), 5.07 (s, 0.93 H), 3.87 (s, 2.1 H), and an A_2B_2

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multiplet appearing as two triplets with centers at δ 2.89 (2.0 H) and 1.98 (2.1 H); mass spectrum (70 eV) m/e (rel intensity) 408 (54), 393 (22), 380 (39), 204 (100), 203 (61), and 202 (30).

Anal. Calcd for $C_{32}H_{24}$: C, 94.08; H, 5.92. Found: C, 93.81; H, 5.94.

Structure Reassignment for 1,2,5,6-Bis (9,10-phenanthro)cyclooctadiene (2). The product obtained in 33% yield from the pyrolysis of 3 in diethyl phthalate by Stille and Foster[3], was recrystallized twice from N,N-dimethylformamide and sublimed at 300° and 5 x 10^{-3} torr. The infrared (KBr), ultraviolet ($CHCl_3$), and mass spectra were unchanged after this purification. The purified material was identified as tetrabenz (a,c,h,j) anthracene (4) by comparison to authentic material[7]: mp (heated block) 426-428° (lit[7] 428-429°); ir (KBr) 1425, 1238, 870, 851, 749, and 712 cm^{-1}; uv ($CHCl_3$) 259 (log ε 4.63), 269 (4.70), 294 (4.98), 304 sh (4.85), 333 (4.58), 362 (3.39), 371 (2.87), and 382 mμ (3.33); mass spectrum (70 eV) m/e (rel intensity) 378 (100), 377 (8.5), 376 (13), 375 (5.7), 374 (8.6), 189 (23), 188.5 (4.4), 188 (9.7), 187.5 (6.5), 187 (12), 186.5 (2.9), and 186 (5.6).

Anal. Calcd for $C_{30}H_{18}$: C, 95.21; H, 4.79. Found: C, 95.22; H, 4.86. Literature anal.[3] C, 94.16, H, 5.85.

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Pyrolysis of 2-Methylene-3,4,5,6-dibenzo-3',4'-(9,10-phenanthro)spiro bicyclohexane (3). The pyrolysis apparatus was constructed from a Pyrex 10 mm O.D. break-seal. One end was sealed and then expanded to form a bulb of 5 ml capacity. To the same end of the break-seal, a side arm was attached near the breakable portion for addition of reactants and degassing. To the other end of the break-seal, a side arm of 25 cm x 8 mm was attached. This side arm was bent downward toward the reaction vessel at a right angle and parallel to the longitudinal axis of the break-seal. The distal end of this side arm was drawn to a fine point bent over on itself and could be easily cracked under water. The end of the break-seal to which this side arm was attached was connected to a vacuum system with a Veeco quick coupling[29]. In a run, this end was sealed off after degassing.

1. Naphthalene Blank (285°). Naphthalene (2.5 g) was placed in the reaction vessel. The vessel was attached to the vacuum system and evacuated to 5×10^{-3} torr. The naphthalene was then cooled in liquid nitrogen and pumped on for 30 min. The liquid nitrogen was removed, and the naphthalene pumped on for an additional 10 min at room temperature. The tube connecting the vessel to the vacuum system was cooled with Dry Ice. The vessel was then submersed in boiling water to melt the naphthalene. After this has occurred the water bath was removed and the naphthalene allowed to solidify. Any naphthalene condensed in the tubing

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by the Dry Ice was sublimed back into the reaction vessel. The vessel was then evacuated to 5×10^{-3} torr and sealed off. The reaction vessel was then heated for 10 hr at 285°. After cooling to room temperature, the reaction vessel was cooled in liquid nitrogen and then allowed to warm back to room temperature. The neck of the side arm was cooled with Dry Ice, and the stem was immersed in liquid nitrogen. The break-seal was opened, and any gases present were allowed to transfer to the liquid nitrogen cooled portion for 2 min. The side arm was then sealed off below the area cooled by Dry Ice. After warming to room temperature, the side arm was opened by cracking the finely drawn point under water which had been degassed by boiling followed by cooling without being disturbed. The same length of 8 mm tubing evacuated, sealed, and opened under water trapped approximately 10 µl of air. GLC of the trapped gas from the naphthalene blank (10 µl) showed only a trace of methane (Table 1).

2. Pyrolysis of 3 at 285°. Compound 3 (5.100, 12.49 µmole) and naphthalene (2.5 g) were placed in the reaction vessel and degassed in the same manner as the blank. During the first 8 hr at 285° the reaction solution turned yellow. On placing in a dark oven at 110° for 20 hr the color did not change; however, on remaining in the laboratory (exposed to room lighting) for 20 hr, the color faded completely. The reaction vessel was replaced in the oven at 285°. Almost immediately (5 min) the solution turned yellow;

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Table 1. GLC of Gas Mixtures from Pyrolysis of II[a]

Run	% Composition[b] (μmoles) Methane	Ethane	Ethylene	Propane	Butane	Propene	Total μmoles/of gas
1 (blank)[d]	trace	0.0	0.0	0.0	0.0	0.0	0.0
2 [d]	1.1 (0.10)	83.0 (4.0)	13.0 (0.69)	2.4 (0.079)	0.18 (0.0045)	0.40 (0.014)	4.9
3 (blank)[c]	trace	0.0	0.0	0.0	0.0	0.0	0.0
4 [c]	trace	77.0 (0.34)	23.0 (0.11)	0.8 (0.0024)	e	e	0.45

[a] GLC performed on a 6 ft x 0.25 in column packed with 5% squalene on 60/200 mesh silica gel at 80-85° and 60 ml/min. He flow measured at room temperature.

[b] Gases are listed in order of elution, methane eluting first. The composition is by weight and is based on relative area only. No adjustment has been made for relative response of the various components, nor for the differing solubilities in water. Adjustment is made for the amount of air present (10 μl). [c] 235°. [d] 285°. [e] Not observed.

however, this time the color was less intense. The reaction was heated an additional 20 hr at 285°, and then allowed to cool at room temperature in ambient light until the very light yellow color faded. The mixture of gases formed were trapped as described above. The composition of this mixture as found by glc is given in Table 1. The ethane (4.0 μmoles) and ethylene (0.69 μmole) represent yields of 32% and 5.5% respectively. The naphthalene was removed from the reaction mixture by sublimation. The residue was triturated with benzene (three 0.5 ml portions) to give 2.06 mg of benzene soluble material. TLC of this material on alumina (carbon tetrachloride) showed only two spots of Rf 0.30 and 0.42. No spot corresponding to 3 (Rf 0.50) was present. Preparative scale tlc of the benzene soluble material on alumina (carbon tetrachloride) gave two bands corresponding to the above spots. These were separated and extracted with chloroform. Five other minor bands of material were resolved by this chromatography; the material in these bands was not studied further. From the band of lower Rf, 0.10 mg (0.25 μmole, 2% of crystalline material was obtained: uv max (cyclohexane) 248 (rel intensity 0.98), 254 (1.00), 270 sh (0.35), 279 (0.26), 288 (0.17), 300 (0.14), 333 (0.01), and 349 mμ (0.01); ir (KBr) 748 and 717 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) 408 (9.4), 379 (100), 378 (22), 377 (14), 376 (18), 363 (11), and 189 (13). A sample of this material was heated in an

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evacuated tube for 2 hr at 360°. On cooling, a nicely crystalline residue was present which gave uv max ($CHCl_3$) 257, 269, 294, 304 sh, 333, 362, and 382 mμ identical in relative intensity and position to tetrabenzanthracene (4).

From the band of higher Rf, 0.05 mg (0.1 μmole, 1%) of crystalline material was obtained: uv max (cyclohexane) 250 sh (rel intensity 0.99), 254 (1.00), 270 sh (0.49), 290 sh (0.23), 302 (0.23), 340 sh (0.04), and 355 mμ (0.02); ir (KBr) 746 and 716 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) 408 (76), 393 (50), 379 (41), 378 (48), 231 (100), 216 (56), 215 (56), 205 (59), and 189 (52).

The benzene insoluble material (3.04 mg, 8.0 μmoles, 64%) melted at 426-428°. Under precisely the same conditions, the purified material from Stille[3] melted at 426-428°. Authentic tetrabenzanthracene (4) from Martin[7] melted at 425-427°. The infrared and ultraviolet spectra of the benzene insoluble material were identical to tetrabenzanthracene (4).

3. Naphthalene Blank (240°). Naphthalene (2 g) was sublimed directly into the reaction vessel at 5 x 10^{-3} torr. The vessel was then sealed and heated for 20 hr at 240°. After cooling to room temperature, the gases formed were trapped as described above. GLC (Table 1) showed only a trace of methane present.

4. Pyrolysis of 3 at 235° in naphthalene. The procedure used with the blank was repeated with 3 (3.8 mg, 9.3 μmoles) added

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to the reaction vessel before addition of naphthalene (4 g). On warming to 100°, the naphthalene melted and dissolved 3. The reaction was heated for 16 hr at 235°, during which time the solution became yellow. This color faded on standing overnight in the laboratory. The composition of the gases trapped (20 µl) is given in Table 1. Based on the loss of one mole of C_2 hydrocarbon for each mole of 3, the yield of ethane (0.34 µmole) is 3.7% and the yield of ethylene (0.11 µmole) is 1.2%. The naphthalene was removed from the reaction mixture by sublimation. TLC on alumina (carbon tetrachloride) of the residue showed mainly 3 (Rf 0.39); however, light spots at Rf 0.46 and 0.23 and the origin were present. The residue was triturated with hexane. The ultraviolet spectrum of the hexane soluble material showed the same maxima as 3; however, these maxima were less well resolved. No tetrabenzanthracene 4 was evident in this fraction. From the intensity of the maxima at 300 mµ, the amount of 3 was estimated at 3.7 mg (7.8 µmoles, 84%). The hexane insoluble material was triturated with benzene and then chloroform. The ultraviolet spectrum of the chloroform solution had maxima characteristic of tetrabenzanthracene (4) at 382, 362, 333, 304 sh, and 294 mµ; however, the presence of other maxima indicated a mixture.

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could possibly convert either directly, or via a [1,5] suprafacial hydrogen shift to cis or trans-4a,9a-dihydrotetrabenzanthracene followed by the loss of two hydrogens to give 4.

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PART IV

THE DECOMPOSITION OF N-NITROSOKETIMINES

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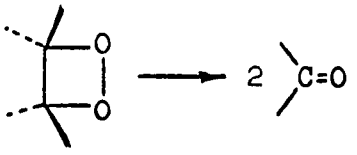
The synchronous cleavage of a dioxetane (1) into two carbonyl functions has been proposed[1], and in some cases reasonably well established[2], as leading initially to an electronically excited state of one of the fragments.



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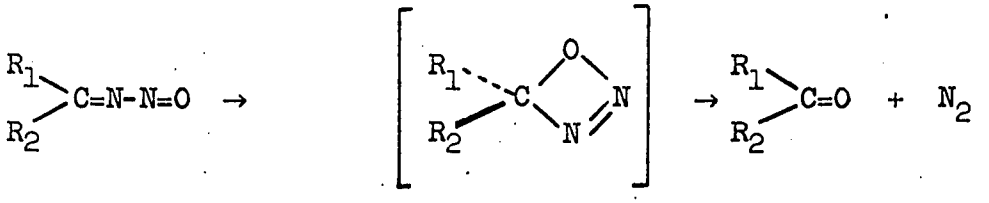
In some cases, these excited states have been detected by their emission of light or by transfer of their energy to an acceptor molecule which then may emit light or undergo a reaction from the excited state. In the same vein, we considered the decomposition of N-nitrosoketimines. This decomposition conceivably proceeds through a four-membered intermediate, which then loses nitrogen to give a ketone (equation 1)[3]. This first step is related to the thermal



2

(1)

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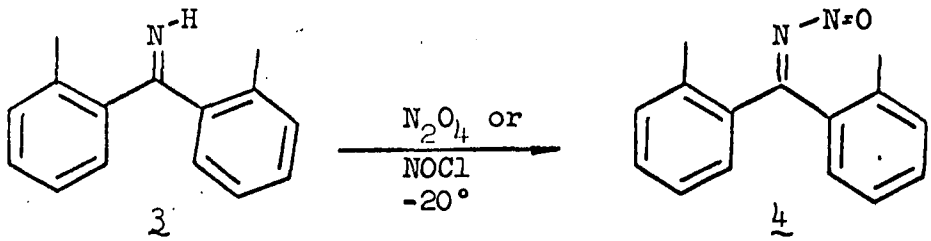
closure of a butadiene to a cyclobutene[4]. The concerted decomposition of this intermediate (2) is symmetry-forbidden[5,6]. Since the reaction (1) should be highly exothermic and the decomposition is known to occur with ease, we felt that the ketone might be formed in an electronically excited state.

N-Nitrosoketimines were prepared in an impure state in these laboratories several years ago[7]. The pure N-nitrosoketimines were later obtained by Thoman and Hunsberger[3] by nitrosation of the appropriate imine. These authors found that the stability of the nitrosoketimine was enhanced by the presence of bulky substituents. This stability paralleled the reactivity of the parent ketimine toward hydrolysis. We attempted the synthesis of N-nitroso-2,2'-dimethylbenzophenonimine (4) by nitrosation of 2,2'-dimethylbenzophenonimine (3) with dinitrogen tetroxide or nitrosylchloride. Unfortunately, complete nitrosation did not occur and mixtures of 3 and 4 were isolated. We were, however, able to obtain N-nitroso-



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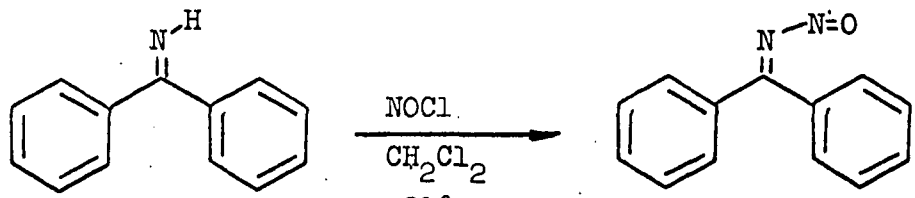
benzophenonimine (6) in an analytically pure form by nitrosation of benzophenonimine (5) with nitrosyl chloride at -20°, followed by careful recrystallization under anhydrous conditions at low temperature. This compound was prepared in an impure state by Thoman and Hunsberger[3].



5 6

It has been well established that the lowest (n,π^*) triplet of benzophenone is involved in the photoreduction of benzophenone to benzopinacol in secondary alcohols[8]. The low reactivity of the (π,π^*) triplet of 2-acetonaphthone towards photoreduction in secondary alcohols[9] supports the assumption that the (n,π^*) triplet of benzophenone is the only state which is reactive toward reduction in secondary alcohols. Furthermore, the observed independence of quantum yield for formation of acetone in the photolysis of benzophenone in 2-propanol upon wavelength of exciting light (2537 Å ~ 3660 Å) suggests that the (π,π^*) singlet of benzophenone decays

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almost exclusively through the (n,π^*) triplet[10]. Unfortunately the formation of benzopinacol was measured at only 3130 Å and 3660 Å; however, at each wavelength the formation of benzopinacol was equal to the formation of acetone. Therefore, the possible formation of an excited state of benzophenone in the decomposition of 6 eventually would give the lowest (n,π^*) triplet state.

The benzophenone sensitized isomerization of trans to cis-stilbene[11], the reduction of benzophenone to benzopinacol in 2-propanol[10], and the phosphorescence of tetraethylammonium tetrakis(1,3-diphenyl-1,3-propanedionato)europate-(III) by energy transfer from benzophenone triplet[12] were used in attempts to detect the triplet of benzophenone in the decomposition of 6. In none of these attempts was this triplet detected.

The possibility that the decomposition of 6 may involve water in a chain reaction (equation 2) was not completely

$$H_2O + \begin{matrix} R \\ R \end{matrix}\!\!>\!C{=}N{-}N{=}O \rightarrow HO{-}\overset{\overset{R}{|}}{C}{-}N{=}N{-}OH \rightarrow \begin{matrix} R \\ R \end{matrix}\!\!>\!C{=}O + N_2 + H_2O \qquad (2)$$

excluded by Thoman and Hunsberger[3]. These authors presented rough kinetic study of the decomposition of N-nitroso-2,4'-dimethylbenzophenonimine in the presence of water vapor. The data from this study best fit for a first order decomposition.

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The decomposition of 6, however, could be more sensitive to hydrolysis by analogy to the parent ketimines. We found that the rate of decomposition of 6 in carbon tetrachloride was independent of the presence of water. We also found, in accord with Thoman and Hunsberger[3], that the major organic product is benzophenone. Other minor products were detected by tlc and glc.

Baumgarten[7] has reported that the decomposition of N-nitroso-2-camphanimine (7) at 30° gives 20% N-nitro-2-camphanimine (8) and 35% camphor (9), as well as lesser amounts of camphor azine (10) and α-camphenonitrile (11). The formation of these products cannot easily be explained in terms of the intermediate 2, and the reasons for the divergence of the reaction pathways of the aromatic and aliphatic nitrosoimines is not known at the present time. The present data tends to support the intermediacy of 2 for at least a portion of the reaction of 6 leading to benzophenone.

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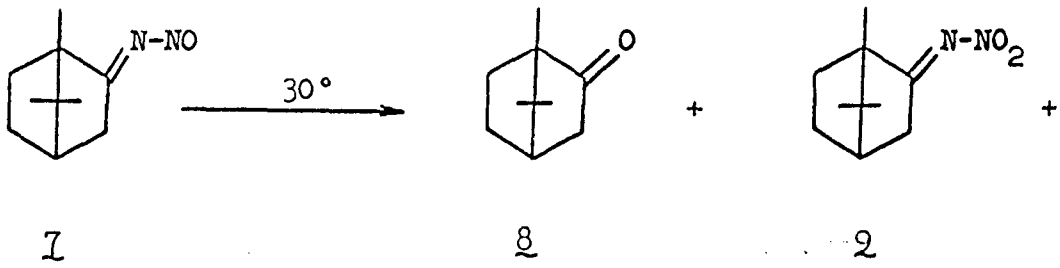

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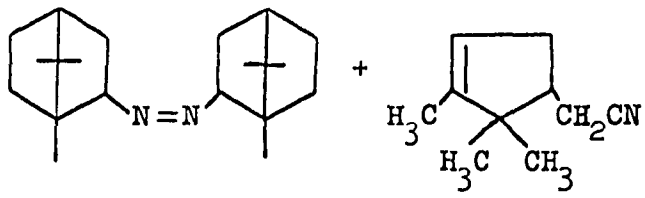

10 11

Although the concerted decomposition of cyclobutane to two molecules of ethylene is symmetry-forbidden in the ground state, the formation of an excited state product is not a requisite for the reaction. In such a symmetry-forbidden process, a molecular orbital of the ground state reactant correlates with an excited state molecular orbital of the products. As the process proceeds upon the reaction coordinate, the energy of this ground state orbital increases due to the antibonding character it possesses in the products. At some point during the reaction, this orbital will become iso-energetic with an unoccupied molecular orbital of the reactant which correlates with a ground state orbital of the products. At some point

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near this crossing, an electron in the occupied orbital may cross over into the unoccupied molecular orbital of different symmetry which is, necessarily, decreasing in energy as the reaction proceeds. When both electrons of the reactant molecular orbital cross over, a ground state product is formed. There is a finite probability that an electron will not cross over to this ground state orbital. In this case, an excited state product would be formed. Such a process would require a highly exothermic reaction in order to be probable. In the decomposition of 2, none but trivial symmetry elements exist, and a meaningful correlation diagram cannot be constructed. Nevertheless, a large barrier to concerted decomposition will exist by analogy to the decomposition of cyclobutane[5]. The barrier to formation of excited states in the decomposition of 6 may be sufficiently high to prevent formation of electronically excited benzophenone, yet still allow decomposition to occur readily at room temperature given that the reaction is exothermic.

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Experimental Section

Melting points were taken with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Mr. Joseph Walters in this department.

Infrared spectra were determined on a Perkin-Elmer Model 337 infrared spectrometer, and were calibrated against known absorption bands of polystryene. Ultraviolet spectra were determined on a Cary Model 14 spectrometer. Proton magnetic resonance spectra (nmr) were determined on a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard.

Thin layer chromatography (tlc) was performed on Eastman Chromatogram sheets containing a fluorescent indicator. Visualization was with 2537 Å light.

2,2'-Dimethylbenzophenonimine Hydrochloride[13]. The general method used by Pickard and Tolbert[14] for ketimine synthesis was followed. A Grignard reagent was prepared by the addition (over a 30 min period) of o-bromotoluene (34.2 g, 0.20 mole) in 100 ml of ether to magnesium turnings (5.1 g, 0.21 mole) in 25 ml of ether. After addition was completed and the reaction had subsided, the etheral solution was refluxed for 1 hr. Dry toluene (100 ml) was added and the mixture was distilled until the distillate reached a temperature of 96°. A heavy precipitate was present at this time. The mixture was allowed to cool

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and o-tolunitrile (23.4 g, 0.20 mole) dissolved in 30 ml of toluene was slowly added. Initially the precipitate disappeared; however, after about one quarter of the nitrile had been added a new precipitate began to form. The mixture was refluxed for 28 hr. At the end of the reflux period, the mixture was cooled and 50 ml of absolute methanol were slowly added. The mixture was stirred for 1 hr and filtered. The solid was washed with several portions of methanol (a total of 175 ml). Toluene (100 ml) was added and the methanol was removed by azeotropic distillation (250 ml of distillate). Addition of ether caused a precipitate. This precipitate was collected and washed with ether. The ether layers were combined, extracted with water, dried with sodium sulfate, and filtered. The imine hydrochloride was then precipitated by addition of hydrogen chloride. This precipitate was then dried and dissolved in 600 ml of warm chloroform. The addition of 600 ml of ether caused the hydrochloride to precipitate, giving 34.6 g (0.141 mole, 71%) of 2,2'-dimethylbenzophenonimine hydrochloride, mp 273-274.5° dec (lit.[13] 273°). The hydrochloride could also be crystallized from a mixture of ethanol and ethyl acetate to give nicely shaped crystals.

2,2'-Dimethylbenzophenonimine (3)[13]. 2,2'Dimethylbenzophenonimine hydrochloride (12.28 g, 0.05 mole) was added with 100 ml of methylene chloride to a separatory funnel. The

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mixture was extracted with 100 ml of 0.5 N sodium hydroxide. The methylene chloride solution was next washed with water and then filtered through sodium sulfate. It was then evaporated to an oil on a rotary evaporator. The resulting oil was vacuum distilled at 111.0-112.2° and 4 x 10^{-1} torr to give 4.85 g (0.023 mole, 47%) of product. TLC of this product on silica gel (benzene-hexane 1:3) gave a major spot at the origin which quenched the fluorescent background of the tlc sheet and an extremely light spot at Rf 0.30 which also quenched the fluorescence. Since the distillate had yellowed, it was redistilled at 10^{-2} torr and 78.5-81°; nmr (CCl_4) δ 7.11 (s, 8.0 H), 2.24 (s, 6.0 H), and 9.77 (broad); ir (CCl_4) 3240 (N-H), 1602 (C=N), and 1365 cm^{-1} (C=NH bending[3]).

Attempted Nitrosation of 2,2'-Dimethylbenzophenonimine (3). Several attempts were made to nitrosate 3 as well as the imine hydrochloride at -20° in methylene chloride using dinitrogen tetroxide or nitrosyl chloride as described for the nitrosation of benzophenonimine (5). The infrared spectra of the resulting blue oils indicated a mixture of N-nitroso-2,2'-dimethylbenzophenonimine (4) and unreacted 3. After 30 min at room temperature, the infrared spectrum of this mixture showed a weak band at 1670 cm^{-1} which was probably carbonyl absorption of the ketone.

In one run, the product from the dinitrogen tetroxide nitrosation of the imine hydrochloride (1.23 g, 5.0 mmoles)

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was mixed with trans-stilbene (18.0 mg, 0.1 mmole) in benzene (10 ml) and degassed by five freeze-pump-thaw cycles at 3×10^{-3} torr. Decomposition of the nitrosoketimine (4) was complete in 8 hr, as was evident by a change in color from blue to brown. GLC analysis of the reaction mixture on 10% SE-30 at 190° and 5% QF-1 at 150° showed no enhancement of the cis-stilbene concentration over the trace quantities present in the starting material.

Benzophenonimine (5). The method of Pickard and Tolbert[14] was followed. A Grignard reagent was prepared by the reaction of bromobenzene (31.4 g, 0.20 mole) in ether (100 ml) with magnesium turnings (4.98 g, 0.205 mole) in ether (20 ml). The etheral solution was heated to reflux for 1.5 hr after the initial reaction had subsided. After cooling, benzonitrile (19.60 g, 0.19 mole) in ether (50 ml) was slowly added. A precipitate formed immediately. The reaction mixture was stirred under reflux for 14 hr. After cooling, the magnesium complex was decomposed by the slow addition of 50 ml of absolute methanol (about 6 molar equivalents)[15]. The subsequent work-up was exactly as described by Pickard and Tolbert[14] to give, after vacuum distillation, 18.28 g (0.101 mole, 53%) of benzophenonimine. The infrared spectrum (CCl_4) showed no absorption characteristic of benzophenone. Distinctive bands were at 3250 (N-H), 1602 (C=N), and 1370 cm^{-1} (C=NH bending).

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The literature[16] reports corresponding bands at (CCl_4) 3236 (N-H) and 1603 (C=N) cm^{-1}.

N-Nitrosobenzophenonimine (6). Compound 6 was prepared by nitrosation of benzophenonimine (5) with slight modification of the method of Thoman and Hunsberger[3]. Benzophenonimine (3.48 g, 19.2 mmoles) was added over a 5 min period to a stirred solution of nitrosyl chloride (1.9 g, 29 mmoles) in methylene chloride kept at -20° (internal temperature). Also stirred with the methylene chloride was potassium acetate (8.3 g, 84 mmoles). After stirring for 45 min, the mixture was rapidly extracted with cold 10% potassium bicarbonate (100 ml) followed by water (100 ml). Magnesium sulfate was added to the methylene chloride solution which was then filtered. Evaporation of the methylene chloride at -50° under vacuum gave a blue crystalline product. This product was dissolved in ether (60 ml), filtered, and cooled to give 6. Due to its instability at room temperature, the product was not weighed; however, the yield appeared to be quite good.

Anal. Calcd for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.79. Found: C, 74.06; H, 4.83. Literature Anal.[3] C, 79.08; H, 5.26.

Decomposition of N-Nitrosobenzophenonimine (6) in the Presence of trans-Stilbene. The decomposition of N-nitroso-benzophenonimine (6) in the presence of trans-stilbene was carried out at two different concentrations in benzene (10 ml).

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In each case, the concentration of trans-stilbene was about 0.04 molar (60 ~ 80 mg). The concentration of N-nitroso-benzophenonimine in one was about 0.04 molar (80 ~ 100 mg) and in another case about 0.7 molar (1 ~ 2 g). The samples were degassed by four freeze-pump-thaw cycles at 1×10^{-3} torr and sealed off. After decomposition, as was evident by the loss of the initial blue color, in the dark at room temperature (12 hr), the solutions were concentrated and chromatographed on silica gel using hexane as the eluent. All of the stilbene present was collected in one fraction. GLC of the stilbene fraction from each run on a 5% QF-1 column at 130° showed 0.5% cis-stilbene. The trans-stilbene used in these reactions contained 0.6% cis-stilbene. GLC of the crude reaction mixtures on 5% QF-1 at 140° showed mainly trans-stilbene and benzophenone. In addition to cis-stilbene, only two other peaks (< 1%) which were not identified were present. The presence of mostly benzophenone was confirmed by the infrared spectrum of the neat reaction mixture.

Decomposition of N-Nitrosobenzophenonimine (6) in Isopropanol. N-Nitrosobenzophenonimine (about 100 mg) was dissolved in 3 ml of isopropanol containing one drop of acetic acid per 75 ml. The solution was degassed by four freeze-pump-thaw cycles at 1×10^{-3} torr and sealed off. After decomposition, as was evident by the loss of the initially blue color, tlc on silica

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gel (benzene) gave four spots of Rf 0.00, 0.10, 0.32, and 0.48. The spot of Rf 0.48 corresponded to benzophenone. No benzopinacol (Rf 0.56) was observed. In addition, the insolubility of benzopinacol in isopropanol would indicate that if any appreciable amount of benzopinacol was formed in the decomposition, it would precipitate. No such precipitate was observed.

Decomposition of N-Nitrosobenzophenonimine (6) in the Presence of Tetraethylammonium tetrakis(1,3-diphenyl-1,3-propanedionato)europate-(III). Approximately 20 mg of N-nitrosobenzophenonimine and 10 mg of tetraethylammonium tetrakis(1,3-diphenyl-1,3-propanedionato)europate-(III) were mixed in benzene (1 ml). Nitrogen was bubbled through the solution while it was heated to reflux in a dark room. No light was observed (eyes dark adapted) during the decomposition of 6.

The Effect of Water in the Decomposition of N-Nitrosobenzophenonimine (6). N-Nitrosobenzophenonimine (26 mg, 0.12 mmole) was added to each of two flasks. Both flasks were then attached to a vacuum system and evacuated to 5×10^{-3} torr for 15 min at room temperature (23°), and then 20 min additionally after being placed in an ice-bath. The flasks were then cooled in liquid nitrogen. Carbon tetrachloride (10 ml) which had been degassed and dried over phosphorus pentoxide was transferred into each flask through the vacuum system. Water (40 mg, 2.2 mmoles) was degassed and then similarly transferred into

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only one of the flasks. Both flasks were then isolated from the vacuum system and placed in ice-baths with stirring. After 1 hr, both solutions had changed from a dark blue to a brown-purple. After 9 hr additional both solutions were brown. Infrared spectra and tlc on silica gel (benzene) of each sample confirmed the predominant presence of benzophenone.

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Part V

Appendix

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Sample Calculations for Part I.

A. GLC Analysis of Photolysis Mixtures.

Let: A_i = area of ith component

A_s = area of standard (phenanthrene)

V_2 = volume of aliquot taken

V_1 = volume of reaction solution

W_s = weight of standard (phenanthrene) added to V_2

m_i = molecular weight of ith component

M_i = moles of ith component in photolysis mixture

M_o = moles of cyclobutene initially present

Then:

$$\frac{A_i}{A_s}(W_s)(V_1/V_2) = W_i$$

$$\frac{W_i}{m_i} = M_i$$

$$\frac{M_i}{M_o} = \text{percent of } i^{th} \text{ component formed}$$

B. Quantum Yields.

Let: M_i = moles of ith component formed

V_2 = volume of aliquot

V_1 = volume of diluted aliquot

C = concentration of cyclobutene in reaction solution calculated from glc analysis

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ϵ^{λ} = extinction coefficient of cyclobutene at the wavelength of photolysis (21,500 at 230 mμ; 8,100 at 270 mμ)

OD_1 = calculated optical density of cyclobutene in diluted aliquot at the wavelength of photolysis

OD_2 = observed optical density of diluted aliquot at the wavelength of photolysis

M_i = moles of ith component formed

I_o = total incident light absorbed by reaction mixture (einsteins)

I = total light absorbed by cyclobutene (einsteins)

φ_i = quantum yield for formation of ith component

f = fraction of light absorbed by cyclobutene at end of photolysis

F = average fraction light absorbed by cyclobutene during photolysis

Then:

$$\frac{V_2}{V_1}(C)(\epsilon^{\lambda}) = OD_1$$

$$\frac{OD_1}{OD_2} = f$$

$$(f + 1)/2 = F$$

$$F(I_o) = I$$

$$\frac{M_i}{I} = \varphi_i$$

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Infrared and NMR Spectra.

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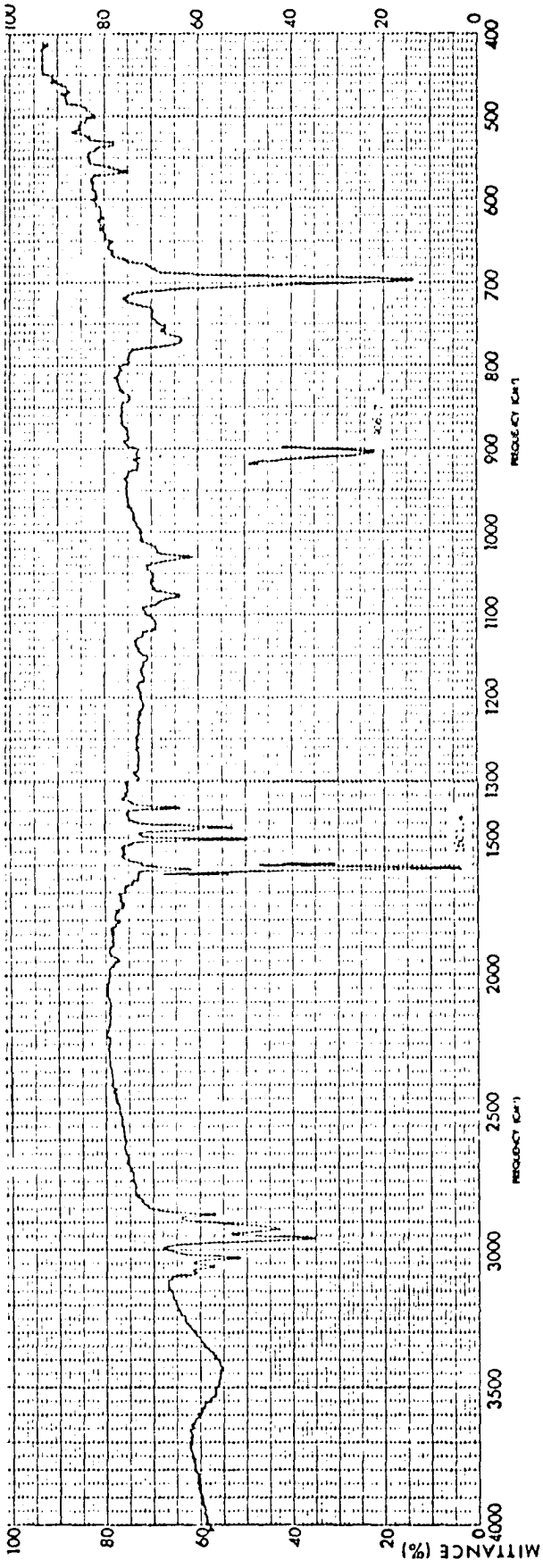

Figure 1. 1,2-Diphenyl-3,4-dimethylcyclobutane (KBr).

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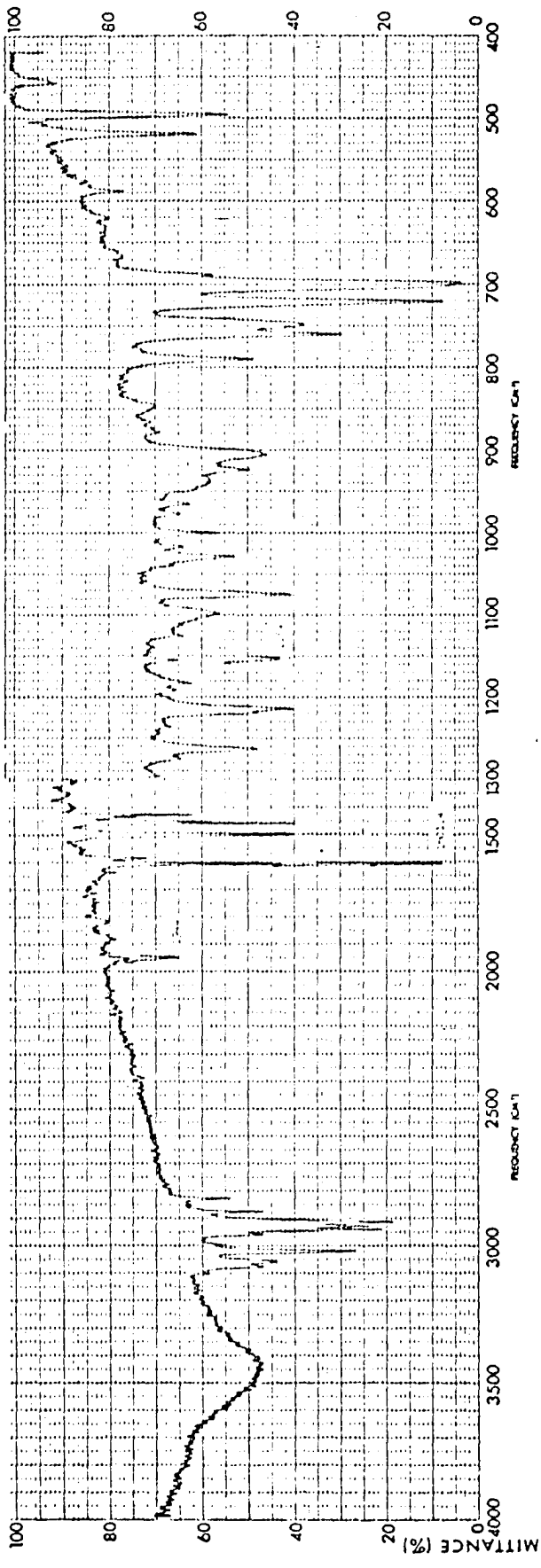

Figure 2. 6,7-Diphenyl-3-thiabicyclo[3.2.0]heptane (KBr).

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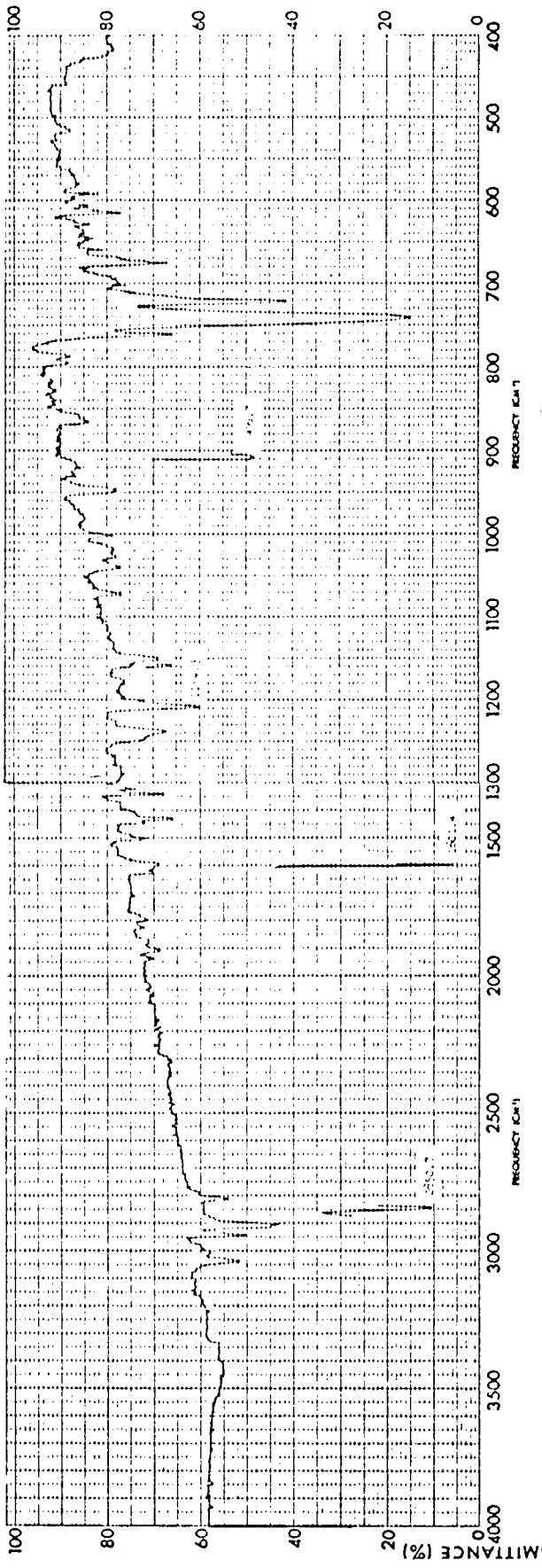

Figure 3. 9,10-Cyclobutenophenanthrene (KBr).

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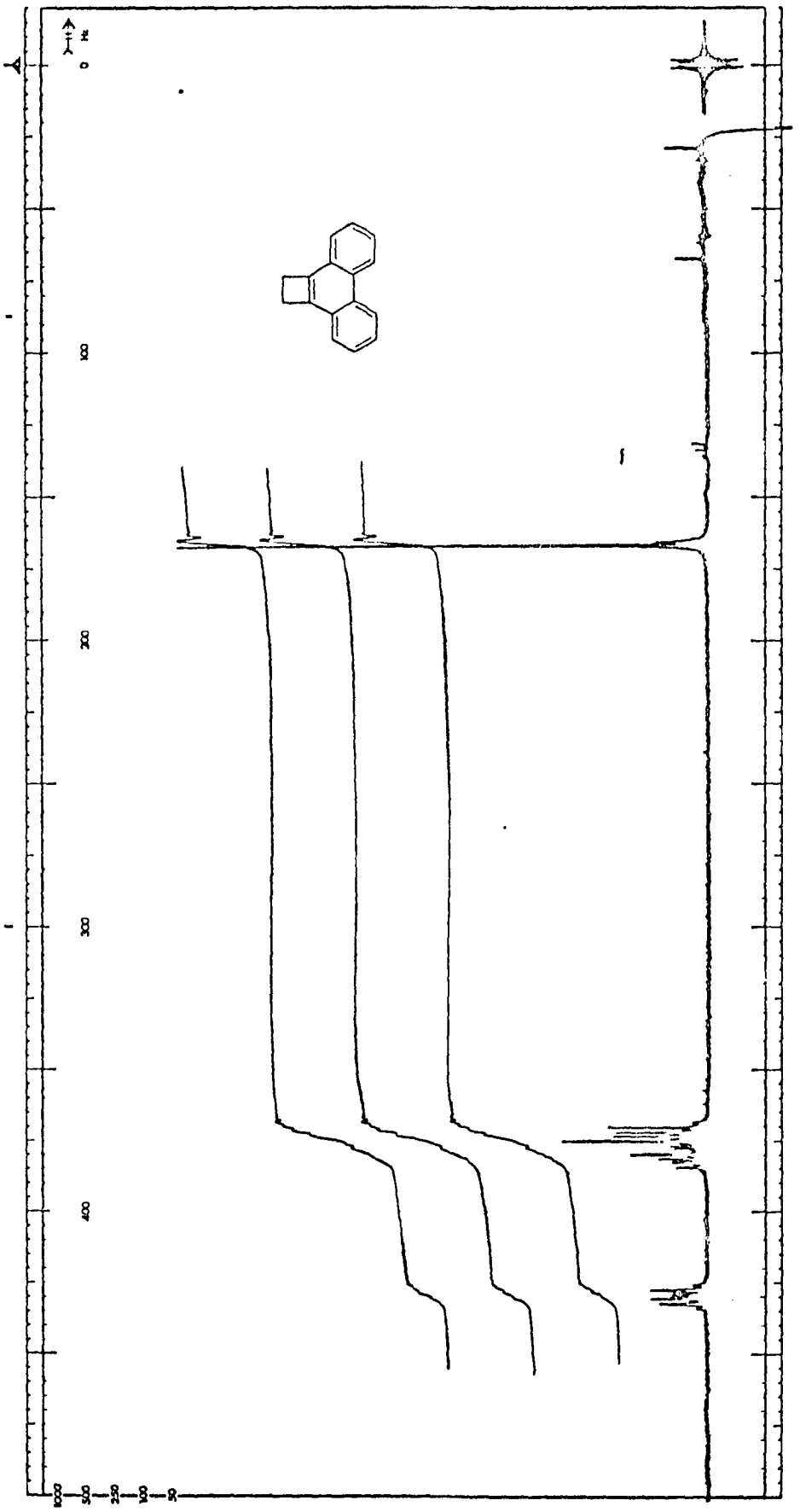

Figure 4. 9,10-Cyclobutenophenanthrene (100 mHz).

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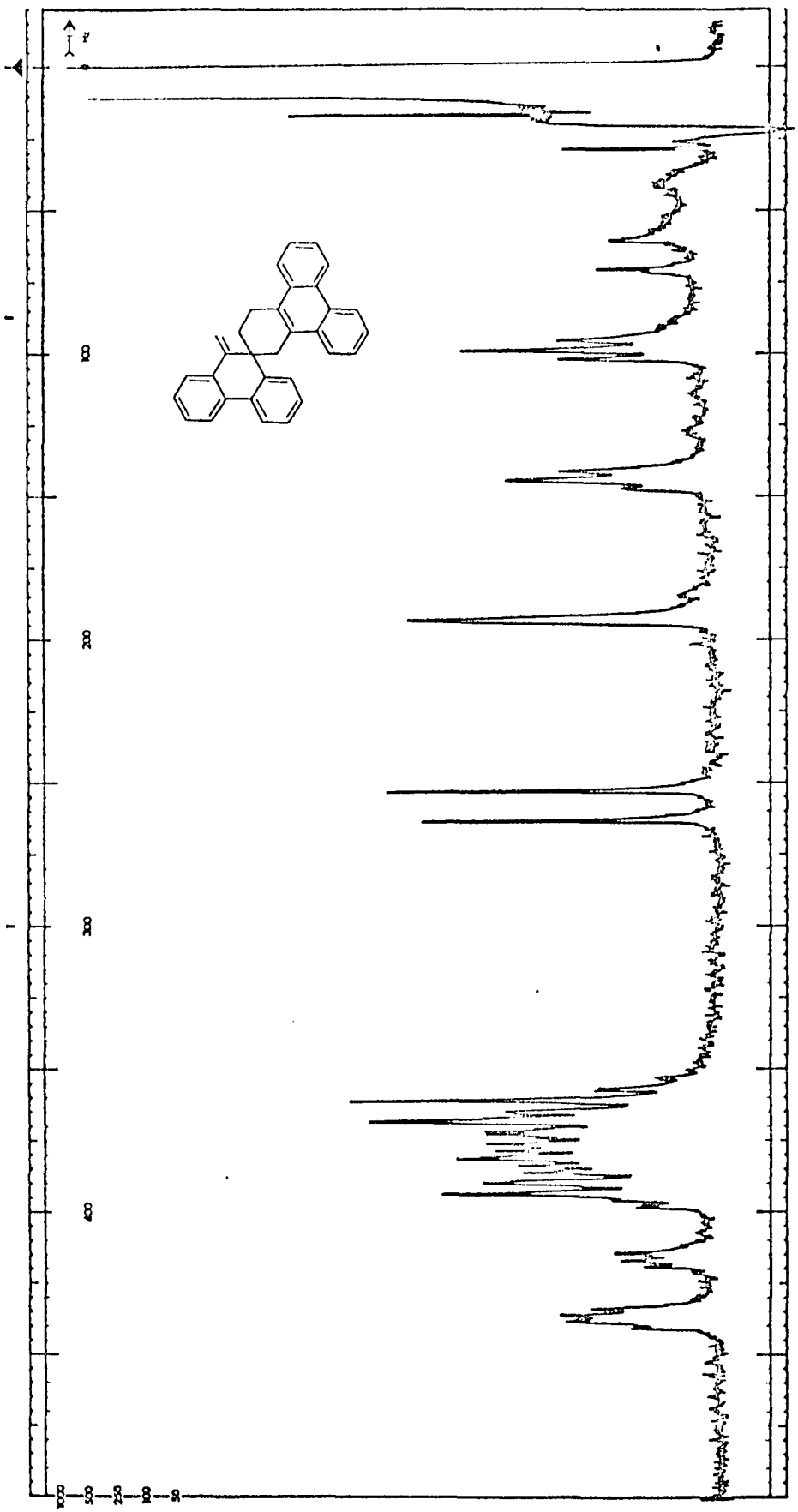

Figure 5. 2-Methylene-3,4,5,6-dibenzo-3',4'-(9,10-phenanthro)spirobicyclohexane (100 mHz).

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Vita

John Paul Anhalt was born in Boise, Idaho on September 9, 1943. He was graduated from Mark Keppel High School in June, 1961. The following September, he attended Occidental College in Los Angeles, California. He then transferred to the sophomore class of The Johns Hopkins University and received his B.A. in February, 1965. Until the following fall, he was a research assistant to Dr. Emil H. White, The Johns Hopkins University. In September, he attended the School of Medicine, Washington University, St. Louis, Missouri, where he studied for one year. He then matriculated in the graduate school of the department of chemistry, The Johns Hopkins University, September, 1965.

He was a supervisor of introductory organic chemistry in the Evening College for one year (1966-67), junior instructor for organic qualitative analysis for one semester (1967-68) and a supervisor for the introductory chemistry in the Evening College for one semester (1968).

In the graduate school, he held a Gilman Fellowship (1966-1970) and a departmental teaching fellowship 1966-68. He is a member of Phi Lambda Upsilon and the American Chemical Society.

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