

(42) Reaction of 1,4-dihydronaphthalenedicarboxylic acid-1,2 (XVIIIa) with acetic anhydride. 1,4-Dihydro acid XVIIIa (1 g.) was refluxed with 10 ml. of acetic anhydride for 4 hr. Removal of the solvent gave 0.95 g. of yellow 3,4-dihydronaphthalenedicarboxylic acid-1,2 anhydride (XVI), m.p. 118.5–123.5°. Needles from diisopropyl ether, m.p. 125–126°. Ultraviolet (of crude product): λ_{max} 226 m μ , ϵ 13,750; λ_{max} 287 m μ , ϵ 12,790.

(43) Dehydrogenation of 1,2-dihydronaphthalenedicarboxylic acid-1,2 anhydride (XI) to 1,2-naphthalenedicarboxylic acid anhydride (XIII).⁴ Anhydride XI (5 g.) and 0.8 g. of sulfur were thoroughly mixed in a mortar and placed in a 50 ml. three necked flask, equipped with cold finger and gas inlet. A slow stream of nitrogen was passed through the inlet and the temperature was slowly raised from 140° to 230°. Hydrogen sulfide started evolving at 180°. After 1 hr., only traces of hydrogen sulfide could be shown by lead acetate paper. The product was sublimed at 120°/0.01 Torr. and the yellow 1,2-naphthalenedicarboxylic acid anhydride (XIII) was recrystallized from acetone-diisopropyl ether, m.p. 164–166°; yield, 2.2 g. Ultraviolet: λ_{max} 272 m μ , ϵ 5770;

λ_{max} 284 m μ , ϵ 6980, λ_{max} 294 m μ , ϵ 5600. Titration: $pK_{1(\text{MCS})}^*$ 5.54; $pK_{2(\text{MCS})}^*$ 7.94; ΔpK_{MCS}^* 2.40.

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[CONTRIBUTION NO. 1666 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Some Photochemistry of 1,2,3,4,5-Pentaphenylcyclohexa-1,3-diene¹

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A study of the photosensitized oxidation of 1,2,3,4,5-pentaphenylcyclohexa-1,3-diene revealed the formation of a 1,4-epidioxide, 2,3-dioxa-1,4,5,6,7-pentaphenylbicyclo[2.2.2]oct-5-ene(II), and pentaphenylbenzene(V), along with a small quantity of an isomer, 1,2,3,5,6-pentaphenylbicyclo[3.1.0]hex-2-ene(XIIb). In the absence of oxygen, the exclusive photochemical formation of XIIb was observed. Some information on the mechanism of formation of these products is presented.

As a foundation for further work on the thermal and photochemical rearrangements of 1,4-epidioxides, in which this laboratory has previously shown special biogenetical interests,³ some investigations of the photochemistry of 1,3-homoannular dienes and the formation of 1,4-epidioxides from them were undertaken. Because of the availability and known reactivity to light and oxygen of phenyl substituted 1,3-homoannular dienes,⁴ and also because of the recent interest in the reactivity of *cis*-stilbene derivatives,⁵ the experimental work was centered on 1,2,3,4,5-pentaphenylcyclohexa-1,3-diene (I).

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(2a) National Science Foundation Summer Fellow (1959); Monsanto Fellow (1959–60). (2b) Deceased. (2c) To whom inquiries regarding this paper may be sent.

(3) E. Skau and W. Bergmann, *J. Org. Chem.*, **3**, 166 (1938); W. Bergmann, F. Hirschmann, and E. L. Skau, *J. Org. Chem.*, **4**, 29 (1939); R. J. Conca and W. Bergmann, *J. Org. Chem.*, **18**, 1104 (1953); W. Bergmann, and M. B. Meyers, *Chem. & Ind. (London)*, 655 (1959); *Ann.*, **620**, 46 (1959).

(4a) C. Dufraisse, A. Etienne, and J. J. Basselier, *Compt. rend.*, **244**, 2209 (1957); (b) C. Dufraisse, G. Rio, and J. J. Basselier, *Compt. rend.*, **246**, 1640 (1958); (c) G. Rio and A. Ranjon, *Compt. rend.*, **248**, 111 (1959); (d) J. J. Basselier, *Compt. rend.*, **248**, 700 (1959).

When I, methylene blue, and oxygen were irradiated under photosensitizing conditions,⁶ with light of wave lengths greater than 320 m μ , a 54% yield of a colorless crystalline product, C₃₆H₂₈O₂, was obtained by chromatography of the irradiation mixture on alumina. Since two oxygen atoms had added to the diene I and the infrared spectrum showed no hydroxyl or carbonyl absorption the product may be considered to be either the 1,4-epidioxide (II), or the diepoxide (III).⁷

Although a carbon-carbon double bond stretching vibration was not detected in the infrared, the Raman spectrum of the C₃₆H₂₈O₂ product in chloroform had an emission band at 1625 cm.⁻¹, which was ascribed to the presence of a

(5) Thesis, E. A. Rick, Yale University (1959); W. Bergmann and E. A. Rick, to be published; F. B. Mallory, "Photochemical Synthesis of Phenanthrenes," Delaware Reg. Meet. American Chemical Society, Philadelphia, Pa., Feb. 25, 1960; G. E. Lewis, *Tetrahedron Letters*, **9**, 12 (1960); P. Hugelshofer, J. Kalvoda, and K. Schaffner, *Helv. Chim. Acta*, **43**, 1322 (1960).

(6) G. O. Schenck, H. G. Kinkel, and H. J. Mertens, *Ann.*, **584**, 125 (1953).

(7) Examples of both types of structures are known: (a) G. W. Schenck, W. Muller, and H. Pfennig, *Naturw.*, **374** (1954), (b) C. Dufraisse, A. Etienne, and J. J. Basselier, *Compt. rend.*, **244**, 2209 (1957), (c) C. Dufraisse, *Experientia Suppl. II*, **27** (1955).

TABLE I

Substance	C ₃₆ H ₃₀ O ₂ ^a	Ethylbenzene ^b	<i>cis</i> -Stilbene ^c	Ascaridole ^d	Assigned
Emission bands	998	998			Aromatic C=C
	1030	1030			Aromatic C=C
	1610	1610			Aromatic C=C
	1625		1630	1623	Olefinic C=C
(cm. ⁻¹)			728		O—O

^a We are indebted to Mr. S. Polchlopek of the American Cyanamid Company, Stamford, Conn., for the determination of this spectrum. ^b Ref. 9, spectrum 160. ^c E. Dalligk, B. Susz, and E. Briner, *Helv. Chim. Acta*, **35**, 2145 (1952). ^d Ref. 9.

carbon-carbon double bond in the molecule⁸ (see Table I). Unfortunately, the detection of the Raman emission due to peroxides at 730 cm.⁻¹ ⁹ in the oxidation product was impossible due to the emission band of chloroform, the only useful solvent, in this region.

Hydrogenation yielded further evidence for structure II. The hydrogenation product C₃₆H₃₀O₂ (84% yield) showed a sharp band at 2.82 μ (3546 cm.⁻¹) attributed to OH groups and an active hydrogen determination (1.8 active hydrogen per mole) supported structure IV for the dihydro product. Refluxing of IV with glacial acetic acid gave pentaphenylbenzene (62% yield). A parallel hydrogenation of the known diepoxide VI showed rapid absorption of two moles of hydrogen in contrast to the behavior of II.

Further support for structure IV was obtained from nuclear magnetic resonance. The spectrum, which was determined in benzene with tetramethylsilane as an internal reference, had thirteen resonance peaks in the nonaromatic region. When the spectrum was observed after heating with deuterium oxide for a short time, the lines at 4.44 τ and 7.95 τ disappeared and are attributed to hydroxylic resonance. The resulting spectrum fitted the calculations for an ABX system¹⁰ with spin-spin coupling constants, J_{AB} 14.0 + 0.4 c/s, J_{AX} 11.3 c/s, and J_{BX} 5.3 c/s, which are reasonable for structure IV.

In apparent conflict with the above conclusions, was the fact that the ultraviolet spectra of the photo-oxidation product II and its dihydro derivative IV showed no maximum in the region above 220 mμ. Since the spectrum of *cis*-stilbene has two maxima¹¹ in this region, while *cis*-stilbene oxide¹²

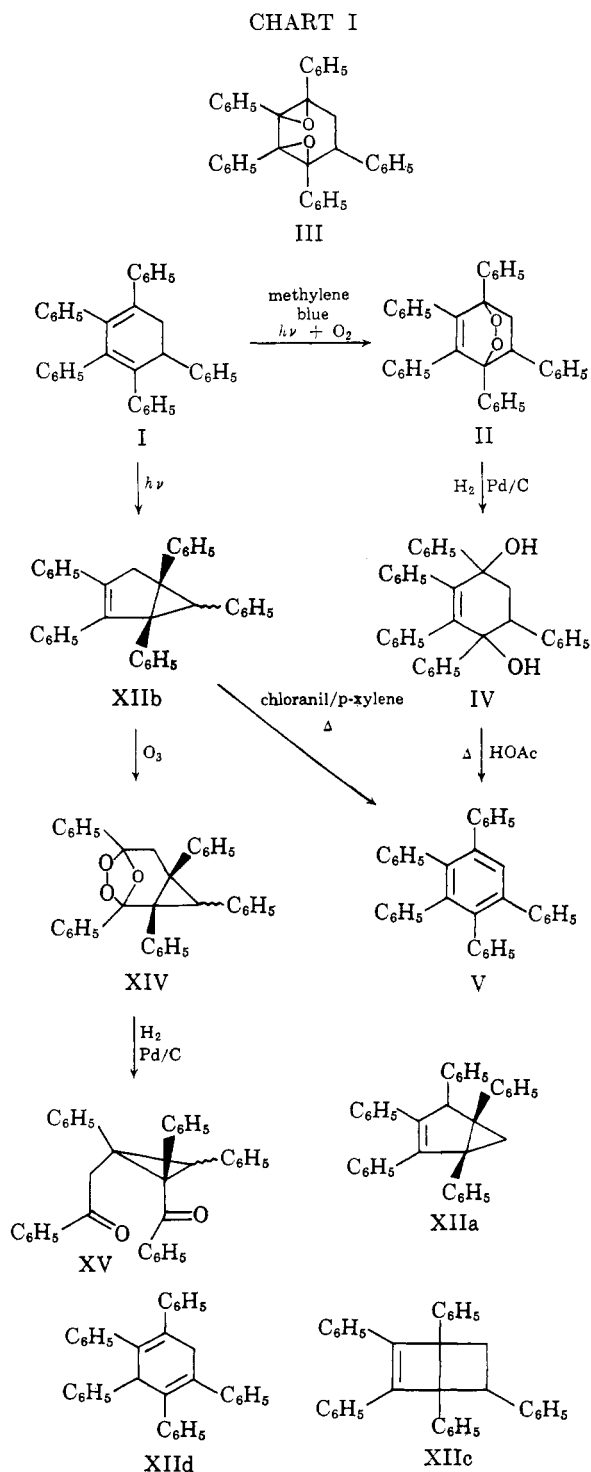
(8) R. F. Stamm, *Anal. Chem.*, **26**, 49 (1954). The intensity of absorption in the infrared of tetrasubstituted ethylene derivatives is low and often not observed; L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd Ed., p. 36.

(9) Raman Spectral Data, American Petroleum Institute Research Project 44, Data on Related Hydrocarbons, Carnegie Institute of Technology, Pittsburgh, 1953, Spectrum 115.

(10) J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance*, McGraw-Hill, New York, (1959), Chap. 6, sec. 6, pp. 130-8.

(11) L. Fieser, *Experiments in Organic Chemistry*, Heath, 1955, p. 180.

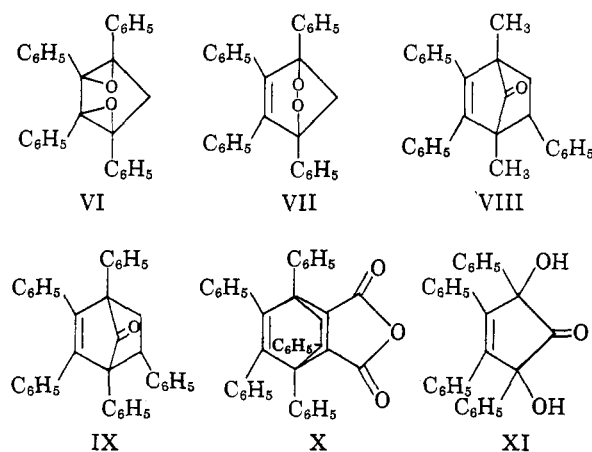
(12) H. E. Knipmeyer, Thesis, *Chem. Abstr.*, **51**, 14635 (1957).



does not, the possibility arose that the photo-oxidation product might in fact be III. Furthermore the spectrum of 1,2,3,4-tetraphenylcyclopentadiene diepoxide (VI),^{4a} did not have a maximum above 220 m μ , and the 1,4-epidioxide of 1,2,3,4-tetraphenylcyclopentadiene (VII)^{4a} showed λ_{\max} 258 m μ , ϵ 1100.

Examples of stilbene-type structures are known in which a "steric inhibition of delocalization" has been found to interfere with the observation of the usual ultraviolet absorption bands.¹³⁻¹⁵ Structures VIII, IX, and a maleic anhydride adduct X all exhibit ultraviolet spectra similar to II and IV.

Apparently, steric repulsion, exerted by the bulky substituents on the 3- and 6-positions of the 1,2-diphenylcyclohexene derivatives, prevents, at least to a considerable extent, the planarity of the benzene rings with the ethylenic system. As the bulky substituent is removed from the proximity of the *cis*-stilbene system (such is the case the ring size becomes smaller), this steric inhibition is no longer observed; 2,5-dihydroxy-2,3,4,5-tetraphenylcyclopenta-3-en-1-one (XI) has a maximum at 255 m μ , ϵ 12,700,¹⁶ while the 1,4-epidioxide VII^{4a} has a maximum at 258 m μ . The 1,2-diphenylcyclobutene series,¹⁷ and the 1,2-diphenylcyclopropanes¹⁸ exhibit high intensity maxima above 220 m μ .



In addition to the 1,4-epidioxide II there was obtained an isomer of I from some of the photo-

reactions. This substance, XII, was monomeric, had an analysis corresponding to C₃₆H₂₈ and was the main product (93% yield) of irradiations in the absence of oxygen. XII was not hydrogenated at room temperature and atmospheric pressure; it was dehydrogenated by chloranil in refluxing *p*-xylene to give a 78% yield of pentaphenylbenzene.

On the basis of the photochemical work of Windaus, Dimroth, and Dauben¹⁹ and the photochemical "bond switching" rearrangements reported by Barton,²⁰ it was reasoned that the most probable structures for the diene isomer XII are XIIa, XIIb, and XIIc.

The NMR spectrum of XII in tetrachloroethylene showed a ratio of 25.0 to 21.92 for the aromatic to the aliphatic protons. The aliphatic part of the spectrum consisted of four peaks, which could be interpreted as the spectrum of an AB system with a superimposition of the resonance signal of the N proton with the signal of one of the peaks of the AB system.²¹ That this was in fact the case was verified by changing the anisotropy of the solvent.²² The NMR spectrum in benzene showed five lines. Since after normalization to 3 protons the peak at 6.17 τ had a value of 0.99 protons; it was concluded that the ABN system was present and structure XIIa could be excluded.²³

The spin-spin coupling constant was calculated; J_{AB} 18.4 c/s. Since the geminal angle of a cyclopropane ring is 118°,²⁴ the spin-spin coupling constant of geminal protons should be *ca.* 5 c/s. The observed geminal J_{AB} for styrene oxide was 5.4 \pm 0.1 c/s, (geminal dihedral angle, 116.3°). The dihedral angle for the geminal hydrogens of cyclopentadiene has been reported²⁵ to be 109.5°. Cyclopenten-3,5-dione had a J_{AB} (gem.) of 21.5 \pm 0.3 c/s (HCH dihedral angle of 109.5°²²). From these analogies, the J_{AB} of XII favors the structure in which the five-membered ring has the geminal protons, *i.e.*, XIIb.

The infrared spectrum of XII had a maximum at 9.85 μ (1015 cm.⁻¹) in the region characteristic of

(13) E. A. Braude, *J. Chem. Soc.*, 1902 (1949); E. A. Braude, E. R. H. Jones, H. P. Koch, R. W. Richardson, F. Sondheimer, and J. B. Toogood, *J. Chem. Soc.*, 890 (1949); E. A. Braude, F. Sondheimer, and W. Forbes, *Nature*, **173**, 117 (1954).

(14) K. C. Dewhirst and D. J. Cram, *J. Am. Chem. Soc.*, **80**, 3115 (1958).

(15) C. F. H. Allen and J. A. Van Allan, *J. Am. Chem. Soc.*, **65**, 1384 (1943).

(16) P. Yates and G. H. Stout, *J. Am. Chem. Soc.*, **76**, 5110 (1954).

(17) A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **81**, 667 (1949).

(18) B. Breslow and C. Yuan, *J. Am. Chem. Soc.*, **80**, 5991 (1958).

(19) K. Dimroth, *Ber.*, **70**, 1631 (1937); W. Windaus, K. Dimroth, and W. Breywisch, *Ann.*, **543**, 240 (1940); W. D. Dauben and G. J. Fonken, *J. Am. Chem. Soc.*, **81**, 1460 (1959).

(20) D. H. Barton and A. S. Kende, *J. Chem. Soc.*, 688 (1958).

(21) We are indebted to M. Saunders for his advice in the interpretation of this spectrum.

(22) We are indebted to H. Conroy for this suggestion.

(23) An ABX system has 15 theoretical transitions; however, one is forbidden and two others are weak. Thus in many cases 12 peaks are observed. See also ref. 10.

(24) Reported HCH 118.2 \pm 0.2°; G. W. Wheland, *Resonance in Organic Chemistry*, 1955, Wiley, p. 720.

(25) *Tables of Interatomic Distances and Configuration in Molecules and Ions*, The Chemical Society, London, 1958, p. M180.

the nonsymmetrical ring deformations of cyclopropanes.^{26,27}

A semiquantitative ozonization²⁸ of XII indicated that 114% of one equivalent of ozone per molecule was absorbed at -15° in chloroform. When the ozonization was stopped at 92% of one equivalent of ozone, a 54% yield of a stable crystalline $C_{36}H_{28}O_3$ ozonide was obtained by chromatography. This ozonide had intense absorption at 9.41μ (1063 cm.^{-1}) and 9.48μ (1055 cm.^{-1}), in a region assigned to the carbon oxygen stretching frequencies of ozonides.²⁹ The ozonide had only a weak intensity maximum at $256 \text{ m}\mu$, ϵ 1450, which was attributed to the absorption band of the five isolated phenyl groups.³⁰

The pure ozonide XIV absorbed one mole of hydrogen over 10% palladium-charcoal at atmospheric pressure and room temperature. When the hydrogenation was stopped at 98% completion, an 82% yield of a crystalline $C_{36}H_{28}O_2$ product was obtained after chromatography. The infrared spectrum showed two equally intense carbonyl bands at 5.89μ (1698 cm.^{-1}) and 6.00μ ($16,667 \text{ cm.}^{-1}$) in potassium bromide. The ultraviolet spectrum of the hydrogenated product had a maximum at $327 \text{ m}\mu$, ϵ 540, which can be attributed to the weak intensity R band of conjugated carbonyl compounds,³¹ and a maximum at $243 \text{ m}\mu$, ϵ 32,900 which was attributed to the phenylbenzocyclopropane chromophore in the diketone XV. 1-Phenyl-2-benzoylcyclopropane has a reported³² maximum at $242 \text{ m}\mu$, ϵ 18,000.

The NMR spectrum of the diketone XV had five peaks, which could be treated as an ABN system with the middle peak as the uncoupled N proton. Unfortunately, due to the absence of adequate models, this NMR spectrum (and that the diene isomer XIIb) cannot be fully evaluated at this time.

It has also been possible to obtain evidence indicating that the diene isomer XIIb and the diene I are not in a photodynamic equilibrium. Since the photosensitized oxidation reaction of I gives high yields of the 1,4-epidioxide II, oxygen should serve as a trapping agent for any of the diene I,

formed from a photo-equilibrium of XIIb and I. When XIIb was irradiated under the normal photosensitized conditions for formation of II from I, no evidence for the 1,4-epidioxide II (nor evidence for the normally observed photochemical decomposition products) was found.

In addition to the 1,4-epidioxide II, 54%, and XIIb, 3%, an 18% yield of pentaphenylbenzene was isolated, when I was irradiated with oxygen in the presence of Methylene Blue. When II, or XIIb, was irradiated under the same conditions, only a trace of pentaphenylbenzene, 2% and 4% respectively, was produced. It was also observed that in the absence of either Methylene Blue or oxygen, the amount of pentaphenylbenzene formed from I or XIIb was negligible. The irradiation of I with oxygen in the presence of Methylene Blue gave XIIb as the main product, and only 1% of pentaphenylbenzene was found. Quite surprisingly, however, since the photodehydrogenation of dihydrospecies like I by dyes or sensitizers has been proposed as a significant side reaction in photosensitized oxidation,³³ the irradiation of Methylene Blue and I in the absence of oxygen did not yield any pentaphenylbenzene.

Since a photochemical attack by oxygen or Methylene Blue on I or XIIb, cannot account for the yield of pentaphenylbenzene,³⁴ there must be a photosensitized species, either a complex of Methylene Blue and oxygen, or oxygen in an excited state³⁵ (which receives its energy from photoactivated Methylene Blue), that is responsible for the formation of pentaphenylbenzene by reaction with I.

EXPERIMENTAL³⁶

The photosensitized oxidation of 1,2,3,4,5-pentaphenylcyclohexa-1,3-diene (I). A solution of 6.56 g. (14.2 moles) of I, which was prepared by the method of Abramov and Mitropoltanskaya,³⁷ m.p. $158.5-159.1^{\circ}$ (reported, m.p. $157-158^{\circ}$), and 157 mg. (0.42 mole) of Methylene Blue³⁸ in 850 ml. of

(33) G. O. Schenck, *Naturw.*, **40**, 205 (1953); in his discussions on the mechanism of photosensitized oxidations, proposed that the sensitizer was excited to a diradical state, and this species is the active reagent in the dehydrogenation. In Schenck's proposal, the sensitizer eosin, has a quinoid structure, which is not present in Methylene Blue, a isophenanthiazine derivative. Chloranil, a *p*-quinone, does photochemically dehydrogenate the diene I readily.

(34) Control experiments have excluded the possible thermal dehydrogenation by Methylene Blue, alone or in the presence of oxygen, under the reaction conditions. Similarly, the possibility of a photochemical or thermal attack of Methylene Blue and/or oxygen on the 1,4-epidioxide III was shown to be insignificant, since only 2% V was found.

(35) H. Kautsky, *Ber.*, **64**, 2677 (1931).

(36) Melting points are corrected. Analyses by Schwarzkopf Microanalytical Laboratories.

(37) V. S. Abramov and Ts. L. Mitropolitanskaya, *Khim. Referat. Zhur.*, **4**, No. 3, 31 (1941); *Chem. Abstr.*, **37**, 4369 (1943); *J. Gen. U.S.S.R.*, **10**, 207 (1940); *Chem. Abstr.*, **34**, 7284 (1940).

(38) N. F. crystals, Matheson, Coleman and Bell, East Rutherford, N. J.

(26) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, 1958, p. 29.

(27) H. E. Knipmeyer, thesis, University of Illinois; University Microfilm Inc., Publ. No. 20869; *Chem. Abstr.*, **51**, 14635 (1957).

(28) *Basic Manual of Applications and Laboratory Ozonization Techniques*, First Rev., The Welsbach Corp., The Ozone Div., Philadelphia, Pa., p. 19.

(29) R. Criegee, A. Kerckow, and H. Zinke, *Ber.*, **88**, 1878 (1955).

(30) Since benzene has a maximum at $225 \text{ m}\mu$ and a molar extinction coefficient of 244, five benzene rings should give an extinction value of 1100.

(31) Braude and Nachod, *Determination of Organic Structures by Physical Methods*, Academic Press, 1955, Chap. 4.

(32) R. J. Mohrbacher and N. H. Cromwell, *J. Am. Chem. Soc.*, **79**, 401 (1957).

distilled benzene and 250 ml. of 95% ethanol, was irradiated for 110 min. in a 1 l. three-necked cylindrical flask housing Hanovia quartz water cooled immersion well, 450 watt high pressure, mercury vapor lamp,³⁹ equipped with a Pyrex filter,⁴⁰ while a stream of oxygen was passed through the solution (further agitation was obtained by stirring the solution). After irradiation, the solvent was removed at reduced pressure at a water bath temperature 40–50°. The resultant blue solid was chromatographed on an alumina column (3.3 cm. × 57 cm.), which was composed of 570 g. of Merck alumina with hexane solvent. The column was eluted with solvents of gradually increasing polarity from hexane-benzene, and collected on a fraction collector. The eluant was analyzed as follows: (a) by determining the % transmission on a Bausch and Lomb Spectrophotometer in order to detect the diene isomer XIIb; b) by infrared spectroscopy of the residual solids to check the fractions as they emerged from the column. The solvent was removed at reduced pressure and at 40–50° water bath temperature, and the residue was weighed. A tabulation of eluant and solids is recorded below.

Volume Eluant (l.)	Solvent Ratio Hexane: Benzene	Solids (mg.)	Fraction
0–1.6	5:1	182	A
1.6–1.8	3:1	3	A
1.8–2.9	3:1	86	A + B
2.9–10.5	3:1	1,027	B
10.5–11.8	2:1	38	B
11.8–13.5	1:1	117	B
13.5–14.0	1:1	15	B + C
14.0–15.6	1:1	345	C
15.6–17.2	1:1	86	C + D
17.2–19.4	1:1	1,792	D
19.4–23.0	1:3	1,110	D

The entire column was then extracted with chloroform and upon evaporation of the solvent, 1.1 g. of a yellow solid, Fraction E, was obtained. The total solids, 6.79 g., amounted to 105% recovery.

Fraction A was recrystallized three times from benzene-hexane to give colorless prisms; m.p. 163.9–164.7°. From the ultraviolet and infrared spectra, it was identified as XIIb, 3% yield, which is also the main product of the photorearrangement of I in the absence of oxygen.

Fraction B, upon recrystallization from benzene–95% ethanol, gave colorless prisms, m.p. 250.0–250.6°; an admixture with an authentic sample of pentaphenylbenzene⁴¹ melted, m.p. 250.1–250.4°, while the synthetic sample melted, m.p. 250.5–250.7°; reported 246–247°. The infrared spectrum of Fraction B and the synthetic pentaphenylbenzene in potassium bromide were identical.

Fraction C, which was obtained in 5% yield, is believed to be a polymeric peroxide. Attempts to crystallize this material from benzene-hexane, benzene–95% ethanol, tetrahydrofuran, ethyl acetate, or ethyl ether-benzene led only to a white flocculent precipitate.

Fraction D, for which the 1,4-epidioxide structure II is proposed, 2,3-dioxo-1,4,5,6,7-pentaphenylbicyclo[2.2.2]octa-5-ene, was obtained in 54% yield. On recrystallization from benzene-hexane, colorless prisms, m.p. 195.8–196.5°, were obtained.

Anal. Calcd. for C₃₆H₂₆O₂: C, 87.77; H, 5.73. Found: C, 88.06; H, 5.78.

The NMR spectrum of II was determined in benzene with tetramethylsilane as an internal reference. The spectrum was

(39) Englehardt Industries, Inc., Newark, N. J.

(40) The Pyrex filter is a 2-mm. thick cylindrical tube, which removes wave lengths lower than 320 m μ .

(41) W. Dilthey, W. Schommer, and O. Troshen, *Ber.*, 66B, 1627 (1933).

a typical ABX pattern,¹⁰ having 12 peaks, $\nu_0 \delta_{AB}$ 25.3 \pm 0.6 c/s, J_{AB} 13.2 \pm 0.6 c/s, J_{AX} 9.7 c/s, and J_{BX} 4.5 c/s.

Fraction E exhibited intense carbonyl absorption in its infrared spectrum, and further analysis through chromatography led to two isomeric carbonyl derivatives, which are typical photorearrangement products of II, and which shall not be discussed further in this paper.

The hydrogenation of II. In a laboratory hydrogenation apparatus, 679 mg. of 10% palladium charcoal was hydrogenated during stirring in 10 cc. of reagent ethyl acetate. By means of a glass boat, 285 mg. (0.579 mmoles) of II were added and the amount of hydrogen consumed was plotted vs. time. The consumption of hydrogen calculated to 0° and 760 mm. pressure was 13.5 ml. (0.603 mmoles); 104% of theory. The solvent was carefully removed at reduced pressure and a water bath temperature that did not exceed 40°. In this manner 288 mg. of a colorless solid was obtained, which was chromatographed on a silicic acid column (2.1 cm. × 35 cm.), composed of 30 g. of silicic acid and 30 g. of Celite, and hexane-benzene (3:1). The column was eluted with a mixture of hexane-benzene-chloroform. In the benzene-chloroform mixture (99:1) 234 mg. of a colorless oil was obtained. Trituration with hexane and recrystallization from hexane-benzene gave colorless prisms; m.p. 216.5–217.4°; 82% yield of 3,6-dihydroxy-1,2,3,4,6-pentaphenylcyclohexene (IV); $\lambda_{\text{max}}^{\text{CHCl}_3}$ 2.83 μ (3546 cm.⁻¹).

Anal. Calcd. for C₃₆H₃₀O₂: C, 87.42; H, 6.11. Found: C, 86.78; H, 6.20.

The NMR spectrum of IV was determined in benzene with tetramethylsilane as an internal reference. The following is a tabulation of the resonance peaks in shifts from tetramethylsilane in p.p.m., which are reproducible within \pm 0.006 τ .

Line	τ in P.P.M.
1	5.482
2	5.524
3	5.724
4	5.759
5	6.723
6	6.955
7	7.187
8	7.439
9	7.865
10	7.903
11	7.947
12	8.100
13	8.137

When two drops of deuterium oxide were added to an 11% solution of IV (24 mg.) in dry distilled benzene, and the tube sealed and heated for 10 sec., on a steam bath, the resonance peaks of the hydroxylic protons were easily determined due to their absence in the spectrum of this solution. The remaining 11 peaks were analyzed as an ABX system $\nu_0 \delta_{AB}$ 61.5 c/s, J_{AB} 14.0 \pm 0.4 c/s, J_{AX} 11.3 c/s, and J_{BX} 5.3 c/s.

Active hydrogen determination of IV. The apparatus and procedure for active hydrogenation determinations has been described by Linstead *et al.*⁴² using methylmagnesium iodide as the base and anisole as the solvent. In three determinations, the number of active hydrogens per molecule were: 1.76, 2.00, and 1.92.

Acid catalyzed dehydration of IV. When 53.7 mg. (0.109 mmole) of IV was refluxed for one hour in glacial acetic acid, and the acetic acid removed at reduced pressure, a solid was obtained, which, upon recrystallization twice from benzene-hexane, gave 30 mg. (60% yield) of colorless

(42) Linstead, Elvidge, and Whalley, *A Course in Modern Techniques of Organic Chemistry*, Academic Press Inc., New York, 1955, p. 138.

prisms; m.p. 250.0–250.3°. A mixed melting point with a synthetic sample of pentaphenylbenzene⁴¹ was not depressed; m.p. 250.0–250.3°.

The maleic anhydride adduct of I (X). A mixture of 1.03 g. (2.22 mmoles) of I and 2.07 g. (20.5 mmoles) of maleic anhydride was heated to 180° for 5 hours. The cooled melt was dissolved in chloroform, and treated with cold saturated sodium bicarbonate solution. The chloroform layer was dried and evaporated to give 921 mg. of a yellow solid. This material was chromatographed on a silicic acid column, which was composed of 50 g. of silicic acid and 50 g. of Celite in hexane-benzene (3:1). When the polarity of the solvent was increased to benzene-chloroform (25:1), 120 mg. of a yellow solid was obtained; recrystallized twice from tetrahydrofuran-hexane, a 17% yield based on C₄₀H₃₀O₂ of prisms, m.p. 283–284°C. was obtained; $\lambda_{\text{max}}^{\text{KBr}}$ 5.35 μ (1861 cm.⁻¹), 5.61 μ (1783 cm.⁻¹).

Anal. Calcd. for C₄₀H₃₀O₂: C, 85.99; H, 5.41. Found: C, 85.68; H, 5.68.

Irradiation of 1,2,3,4,5-pentaphenylcyclohexa-1,3-diene (I). Preparation of 1,2,3,5,6-pentaphenylbicyclo[3.1.0]hex-2-ene (XIIb). A solution of 4.25 g. (9.23 mmoles) of I in 1.1 l. of distilled benzene was purged with prepurified nitrogen for 24 hours. The solution was irradiated in the previously described Hanovia immersion apparatus equipped with a Vycor filter (a 2-mm. thick, cylindrical tube, to remove wave lengths below 240 m μ), for 65 min. under a prepurified nitrogen atmosphere. The course of the reaction was followed by ultraviolet spectroscopy; 1-ml. aliquots of the solution were diluted to 50 ml., and the spectrum observed in the region 280 m μ , to 400 m μ every 10 min. After 30 min. the band at 319 m μ of the diene I had disappeared, and the 295 m μ band of the diene isomer XIIb was present. Further irradiation did not increase the intensity of the band.

After removal of the solvent, the yellow solid was chromatographed on an alumina column (2.5 cm. \times 49 cm.), which was composed of 250 g. of alumina in hexane. The column was eluted with hexane-benzene (9:1), and the eluant was analyzed spectroscopically. In this manner 3.97 g. (93% yield of XIIb) of a slightly yellow solid was obtained. Upon recrystallization from benzene-hexane, colorless prisms were obtained; m.p. 163.1–163.6°.

Anal. Calcd. for C₃₈H₂₈: C, 93.87; H, 6.13. Found: C, 93.99; H, 6.17.

The ultraviolet spectrum of XIIb in acetonitrile had a maximum at 295 m μ ϵ 8,400. The NMR spectrum of XIIb was determined in dry benzene and in tetrachloroethylene with tetramethylsilane as an internal reference. The values

NMR SPECTRUM VALUES OF XIIb IN BENZENE

Line	τ	Energy		Intensity	
		Calcd. c/s	Found	Calcd.	Found
1	6.094	234.4	234.1	1.00	0.881
2	6.168				
3	6.400	216.0	216.0	2.25	2.60
4	6.901	186.0	186.0	2.25	2.27
5	7.207	167.6	167.6	1.00	1.00

NMR SPECTRUM VALUES OF XIIb IN TETRACHLOROETHYLENE

Line	τ in P.P.M.
1	2.568
2	2.949
3	3.105
4	6.207
5	6.483
6	7.007
7	7.307

of the resonance bands are reproducible within $\pm 0.005 \tau$. The ratio of aromatic to aliphatic protons was determined in tetrachloroethylene and found to be 25.0:2.92.

The molecular weight of XIIb was determined in benzene at room temperature by the Signer-Barge method⁴³ (isothermal distillation).

Anal. Calcd. for C₃₈H₂₈: Mol. wt., 460. Found: Mol. wt., 469.

Dehydrogenation of XIIb. A solution of 104 mg. (0.226 mmole) of XIIb and 355 mg. (1.48 mmoles) of chloranil in 6 ml. of freshly distilled *p*-xylene was refluxed for 17.5 hours. After removal of solvent the orange solid was chromatographed on an alumina column (1.1 cm. \times 33 cm.), which was composed of 32 g. of alumina in hexane. The column was eluted with mixtures of hexane-benzene, and the eluant was analyzed by chromatography. In this manner 81 mg. (78% yield of V) of a white solid was obtained. Recrystallization from benzene-hexane gave colorless prisms; m.p. 250.0–250.3°. A mixed melting point determination with a synthetic sample of pentaphenylbenzene⁴¹ showed no depression; m.p. 250.2–250.6°. The infrared spectra of the colorless prisms and pentaphenylbenzene in potassium bromide were identical.

The ozonization of XIIb. A semiquantitative ozonization procedure, suggested by the Welsbach Corporation²⁸ was used to determine the number of nonaromatic double bonds in XIIb. A solution of 389.8 mg. (0.854 mmole) of XIIb in 80 ml. of reagent chloroform in a gas washing bottle, was cooled to ca. -15° by an ice-ethanol cooling bath in a Dewar flask. A fine stream of ozone (1.93 mg./min.) was passed through the solution, and the ozone that had not reacted, was decomposed in a 2% potassium iodide solution. The latter solution was analyzed for iodine after acidification, by titration with 0.1N sodium thiosulfate to a starch end point. Such data were obtained every 10 min. After 24 min. of ozonization and complete consumption of ozone during this time, the yellow color of potassium triiodide was noticed in the potassium iodide trap. At this point, 46.3 mg. (0.965 mmole) of ozone had been consumed by XIIb, which represented a consumption of 114% $\pm 10\%$ of one equivalent. A continuation of the ozonization revealed that after falling to a low level, ozone consumption steadily increased until it reached a level of 1.51 mg./min., which is indicative of further oxidation, although slow, of the aromatic rings and of the ozonide. The ozonide was not isolated in this experiment.

Large scale ozonization of VIIb. A solution of 2.538 g. (5.51 mmoles) of VIIb in 80 ml. of reagent chloroform was ozonized by a stream of ozone (2.13 mg./min.) and analyzed in the same manner as described in the semiquantitative procedure. The ozonization was stopped after 243 mg. of ozone had been consumed, or after 92% of the calculated amount of one equivalent of ozone/olefinic double bond (there was no yellow color of potassium triiodide in the potassium iodide trap during the ozonization period, nor was there any iodine detected on titration with 0.1N sodium thiosulfate solution). The ozonized solution was purged with nitrogen for 10 min., and then agitated along with a 2% potassium iodide solution for 12 hours. After this period, 10 ml. of 1N hydrochloric acid was added and the solution was neutralized with 0.1N sodium thiosulfate to a starch end point. The chloroform layer was separated from the aqueous layer, and extracted with a 10% sodium bicarbonate solution, separated, and dried.

The sodium bicarbonate layer was acidified and extracted with benzene. The benzene layer was separated, dried, and evaporated to give 9 mg. of a colorless solid, which did not have an infrared spectrum like that of a carboxylic acid.

The chloroform layer was evaporated to dryness and 3.58 g. of a yellow solid was obtained. This solid was chromatographed on a silicic acid column (3.5 cm. \times 40 cm.), which was composed of 60 g. of silicic acid and 60 g. of Celite in

(43) E. P. Clark, *Anal. Chem.*, **13**, 820 (1941).

hexane. The column was eluted with hexane-benzene (9:1) and the eluant was analyzed spectroscopically.

The first fraction was 357 mg. (14%) of the starting material, as determined by its infrared and ultraviolet spectra.

Increasing the polarity of the solvent to 1:1 hexane-benzene, gave 1.508 g. (54% yield based on XIV, $C_{36}H_{28}O_3$) of a colorless solid. Upon recrystallization from benzene-hexane, fine needles were obtained; m.p. 200.4–201.0°, without evolution of gas.

Anal. Calcd. for $C_{36}H_{28}O_3$: C, 85.01; H, 5.55. Found: C, 85.36; H, 5.51.

The infrared spectrum was determined in potassium bromide: λ_{max}^{KBr} 6.36 μ (1572 cm^{-1}), 8.10 μ (1235 cm^{-1}), 8.51 μ (1175 cm^{-1}), 8.64 μ (1157 cm^{-1}), 9.41 μ (1063 cm^{-1}), and 9.48 μ (1055 cm^{-1}). The ultraviolet spectrum of the ozonide had only a low intensity band at 256 $m\mu$, ϵ 1450.

On increasing the polarity of the solvent gradually to 1:4 hexane-benzene, the third fraction (627 mg.) was a mixture of oxidation and decomposition products of the ozonide, as exhibited by the many and the intense bands in the carbonyl region of its infrared spectrum. This fraction was not investigated further.

Hydrogenation of the ozonide XIV. In a laboratory hydrogenation apparatus, 19 mg. of 10% palladium-charcoal in 5 ml. of reagent ethyl acetate was hydrogenated during stirring. By means of a glass boat, 100.52 mg. (0.198 mmole) of the ozonide XIV was added to the ethyl acetate slurry, and the hydrogen consumption was measured. After 25 min., 4.78 cc. of hydrogen was consumed at 26.0° and 760 mm., or 4.36 cc. at STP. The hydrogenation was stopped after 98% of one equivalent was absorbed, and the solution was filtered. After the solvent was removed at reduced pressure, the resultant white solid was chromatographed on a silicic acid column (2.1 cm. \times 29 cm.), which was prepared from 20 g. of silicic acid and 20 g. of Celite in hexane. The column was eluted with hexane-benzene (65:35), and the eluant was analyzed spectroscopically. In this manner a fraction was obtained, which had a maximum at 243 $m\mu$ (81 mg.). Further elution gave residues which gradually shifted the ultraviolet absorption maximum from 243 $m\mu$ to 247 $m\mu$. These latter solids, 10 mg., were not investigated further. Upon continuing the elution, a fraction was obtained (12 mg.), which had a maximum at 247 $m\mu$, but was not identified and is still under investigation.

The first fraction from the column, which had the maximum at 243 $m\mu$, was recrystallized from benzene-95% ethanol to give micro-crystalline needles; m.p. 159.8–160.2°C.

Anal. Calcd. for $C_{36}H_{28}O_2$: C, 87.77; H, 5.73. Found: C, 87.73; H, 5.73.

The infrared spectrum had the following significant maxima: λ_{max}^{KBr} 5.89 μ (1698 cm^{-1}), 6.00 μ (1667 cm^{-1}); $\lambda_{max}^{CHCl_3}$ 5.88 μ (1701 cm^{-1}), 5.98 μ (1672 cm^{-1}). The ultraviolet spectrum of XV in acetonitrile had maxima at 243 $m\mu$, ϵ 32,900, and 327 $m\mu$, ϵ 540. This was an 82% yield of the diketone XV.

The NMR spectrum of the diketone XV was determined in benzene with tetramethylsilane as an internal reference. The spectrum was calculated for an ABN system²¹; J_{AB} 18.6 \pm 0.4 c/s, $\nu_0 \delta_{AB}$ 38.5 c/s. The observed values are reproducible within \pm 0.006 τ .

Line	τ in P.P.M.	Intensity Found
1	5.145	0.28
2	5.454	0.85
3	5.669	0.97
4	5.857	0.68
5	6.167	0.22

The photo-oxidation of I in the absence of Methylene Blue. A solution of 4.01 g. (8.70 mmoles) of I in 1.1 l. of distilled

benzene was irradiated by the Hanovia mercury vapor lamp equipped with a Vycor filter, for 130 min., while the solution was saturated with oxygen. After the removal of the solvent, the orange solid was chromatographed on an alumina column (2.1 cm. \times 47 cm.), which was composed of 200 g. of alumina in hexane. The column was eluted with hexane-benzene (9:1), and the eluant was analyzed spectroscopically.

The first fraction was a yellow solid, 1.29 g., which was recrystallized from benzene-95% ethanol to give colorless prisms; m.p. 163.6–163.8°. The infrared spectrum in potassium bromide and the ultraviolet spectrum in acetonitrile were identical with the spectrum of the diene isomer XIIb. The yield of XIIb was 32%.

The next homogeneous fraction was 244 mg. of a yellow oil, which was triturated with 95% ethanol to give colorless rods; m.p. 172.4–173.4°. The yield based on $C_{36}H_{28}$ was 9%.

Anal. Calcd. for $C_{36}H_{28}$: C, 93.87; H, 6.13. Found: C, 94.19, 94.02; H, 6.23, 6.17.

The ultraviolet spectrum of this material had many maxima: 251 $m\mu$, ϵ 47,900; 258 $m\mu$, ϵ 51,400; 274 $m\mu$, ϵ 20,400; 299 $m\mu$, ϵ 10,500; 311 $m\mu$, ϵ 10,500; 30 $m\mu$, ϵ 800; and 357 $m\mu$, ϵ 900. This spectrum had maxima which were indeed similar to phenanthrene:⁴⁴ 252 $m\mu$, ϵ 50,000; 295 $m\mu$, ϵ 12,500; 330 $m\mu$, ϵ 250. All attempts to form a picrate of this material were unsuccessful. Since this material was isolated in other irradiations (photosensitized oxidation of XIIb and photosensitized irradiation of I), it shall be referred to as compound A. This material is not being investigated further.

The next fraction from the column was a yellow solid, 48 mg., which was identified by its melting point and by comparison of its spectra with a synthetic sample of pentaphenylbenzene. The yield of pentaphenylbenzene is 1%.

The column was eluted further with more polar solvents; however, the fractions that were obtained, contained oxygen, as deduced from the carbonyl absorption bands in their infrared spectra. Since the infrared spectra of the latter were not similar to the carbonyl compounds isolated from the photosensitized oxidation of I, they were not investigated further.

The photosensitized oxidation of XIIb. A solution of 993 mg. (2.16 mmoles) of XIIb and 16 mg. (0.042 mmole) of Methylene Blue in 850 ml. of benzene and 250 ml. of 95% ethanol was irradiated by the Hanovia mercury vapor lamp, which was equipped with a Pyrex filter. During the irradiation period of 130 min., the solution was saturated with oxygen. After removal of solvent, the blue solid was chromatographed on an alumina column (2.1 cm. \times 49 cm.), which was prepared from 200 g. of alumina in hexane. The column was eluted with hexane-benzene (9/1), and the eluant was analyzed spectroscopically. In this manner 344 mg. (35%) of XIIb was recovered. The next fraction from the column was 37 mg. of a yellow oil, which upon trituration with hexane, and recrystallization from hexane-benzene, gave colorless prisms. These prisms were identified by their melting point, infrared and ultraviolet spectra, and found to be a 4% yield of pentaphenylbenzene. The third fraction from the column was 54 mg. of a yellow oil. Trituration with hexane, and recrystallization from hexane-benzene, gave colorless rods, that were identified as Compound A (see photo-oxidation of I in the absence of Methylene Blue) by its melting point, infrared, and ultraviolet spectra. This was a 5.4% yield of Compound A. Increasing the polarity of the eluant did not lead to any other hydrocarbon, or known oxygenated products. Finally, a fraction was obtained, 131 mg., that exhibited a carbonyl absorption band in the infrared region. This compound was not similar to any of the carbonyl containing products isolated from the photosensitized oxidation of I.

(44) W. V. Mayneord and E. M. F. Roe, *Proc. Roy. Soc., (London)*, **A152**, 299 (1935).

The photosensitized irradiation of I. A 3:1 mixture of benzene-95% ethanol was distilled twice in a vacuum system in order to remove dissolved oxygen. A third distillation was used to convey the solvents into the reaction vessel, which was then sealed under vacuum. The reaction vessel contained 101 mg. (0.219 mmole) of the diene I and 84 mg. (0.22 mmole) of Methylene Blue. The Pyrex tube was water-cooled and rotated during irradiation by a General Electric 275 watt, 110-125 v., 50-60 cycle AC sunlamp, which was ca. 6 in. from the vessel. After removal of the solvent the blue solid was chromatographed on an alumina column (2.1 cm. \times 40 cm.), which was composed of 160 g. of alumina in hexane. The column was eluted with hexane-benzene (9:1) and the eluant was analyzed spectroscopically. In this manner, 63 mg. (62% yield) of a white solid was obtained, that gave colorless prisms, m.p. 163.0-163.4°, on recrystallization from benzene-95% ethanol. A mixed melting point depression was not observed from an admixture of this product with XIIb; m.p. 163.1-163.6°. The infrared spectra were also identical.

Further elution gave 3 mg. of a yellow solid that was not pentaphenylbenzene. Pentaphenylbenzene was not isolated from the chromatogram. No hydrocarbon other than the diene isomer XIIb was obtained and identified from the reaction mixture. The reason for the low yield of the diene isomer XIIb in this reaction was probably due to the room temperature extraction procedure of the initial blue solid by benzene.

The above reaction with an irradiation period of 243 hours was repeated. Of the four substances that were isolated from the alumina chromatogram, no pentaphenylbenzene, no diene I, nor diene isomer XIIb was found. Only 17 mg. of Compound A (see photo-oxidation of I in the absence of Methylene Blue) was identified by the four distinct fractions. Compound A was identified by melting point and infrared and ultraviolet spectra; the yield of Compound A was 17%.

The photodehydrogenation of I by chloranil. A solution of 2.03 g. (4.41 mmoles) of I and 6.12 g. (25.5 mmoles) of chloranil in 1.l.l. of distilled benzene, which was purged with nitrogen for 6 hours, was irradiated by the Hanovia mercury vapor lamp equipped with a Vycor filter, under a nitrogen atmosphere for 140 min. After removal of the solvent, the red solid was chromatographed on an alumina

column (2.1 cm. \times 52 cm.), which was composed of 200 g. of alumina in hexane-benzene (20/1). The column was eluted with this solvent ratio and the eluant was analyzed spectroscopically. In this manner, 2.01 g. of a colorless solid were obtained along with 15 mg. of a yellow solid as the only hydrocarbon fractions from the column.

The white solid, pentaphenylbenzene, was recrystallized from benzene-hexane; colorless prisms, m.p. 250.3-250.6°; a mixed melting point was determined with a synthetic sample of pentaphenyl melting point was determined with a synthetic sample of pentaphenylbenzene,⁴⁸ m.p. 250.3-250.8°C. The infrared spectra of the two samples were identical.

The yellow solid that was obtained from the column exhibited all the spectral properties of pentaphenylbenzene, and was assumed to be impure pentaphenylbenzene.

The yield of pentaphenylbenzene is 99%.

The photosensitized oxidation of II. A solution of 1.008 g. (2.05 moles) of II and 18 mg. (0.047 moles) of Methylene Blue in 850 ml. of benzene and 250 ml. of 95% ethanol was irradiated by the Hanovia mercury vapor lamp, which was equipped with a Pyrex filter, for 130 min., while the solution was saturated with oxygen. After removal of the solvent, the blue solid was chromatographed on an alumina column (2.1 cm. \times 50 cm.), which was composed of 200 g. of alumina in hexane. The column was eluted with hexane-benzene (7:5) and the eluant was analyzed spectroscopically. In this manner 17 mg. of a colorless solid was obtained. This was recrystallized from benzene-hexane and identified by its melting point and infrared spectrum as pentaphenylbenzene, 2% yield.

The next fraction was obtained from the hexane-benzene (1:4) eluants, from which 590 mg. of a yellow solid was obtained. This material upon recrystallization from benzene-hexane gave colorless prisms, which were identified as starting material II by the infrared spectrum; 59% recovery of II.

Further elution gave 216 mg. (22% by weight) of a mixture of II and a carbonyl derivative, which had been previously isolated from the photosensitized oxidation of I, and which arises from the photorearrangement of II.

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[JOINT CONTRIBUTION FROM THE NATURAL PRODUCTS RESEARCH DEPARTMENT, SCHERING CORPORATION, AND THE RESEARCH INSTITUTE FOR MEDICINE AND CHEMISTRY]

The Photolysis of Organic Nitrites. VII. Fragmentation of the Steroidal Side Chain

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Certain steroidal nitrite esters substituted vicinally by several oxygen-bearing moieties undergo oxidative carbon-carbon fission upon irradiation.

Various ramifications of the photochemical reactions of nitrile esters have recently been made the subject of a number of investigations.^{1d} It would appear that structural features very much

determine the outcome of such reactions. In general, it has been convenient to treat nitrite photolysis as proceeding by way of alkoxide radicals; the various pathways by which such radicals react further to give rise to more stable structures have been reviewed.² They include internal hydrogen abstraction, rearrangement, disproportiona-

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(2) P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959).