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PHOTOCHEMICAL REACTIONS OF 2,3-DIPHENYLBUTADIENE AND 1,2-DIPHENYLCYCLOBUTENE

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The irradiation of 2,3-diphenylbutadiene (I)(1) was undertaken to prepare 1,2-diphenylcyclobutene (II), required as a model compound for studies of a photoisomer of 1,2,4,7-tetraphenylcyclooctatetraene.(2) The work of Crowley(3) and Srinivasan(4) indicated that this was a feasible route. The irradiation of carefully degassed, stirred 0.05 M. solutions of 2,3-diphenylbutadiene in isooctane with light at 2537 Å* for about 24 hours at 40° yielded a mixture from which compounds II, III, IV, and V were isolated.

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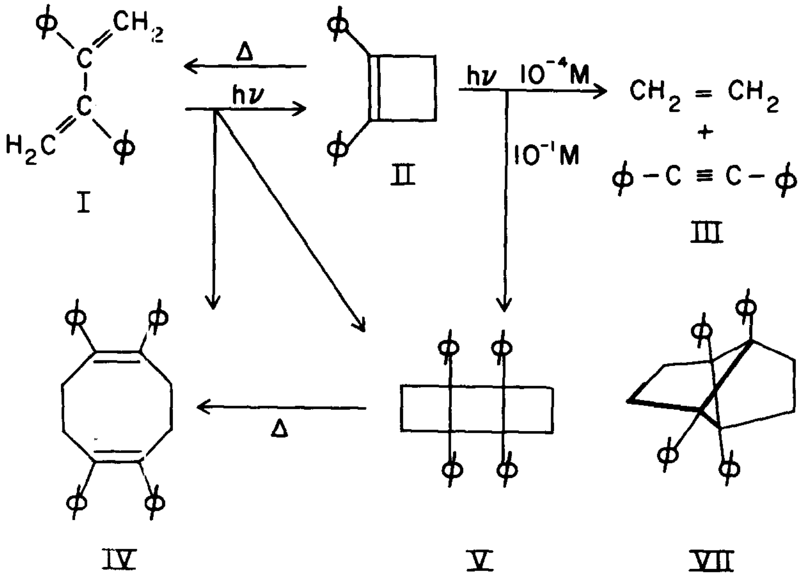
*A Rayonet Photochemical Reactor was used (The Southern N. E. Ultraviolet Company, Middletown, Connecticut).



The mixtures after the irradiations were conveniently separated into fractions boiling below and above 100° at 10^{-2} Torr; these fractions contained monomeric and dimeric species, respectively. The more volatile fraction was treated with maleic anhydride to remove the unreacted butadiene(1), and it was then fractionally recrystallized from hexane at -50° to yield *ca.* 15% of 1,2-diphenylcyclobutene (II), m.p. 54-55°; IR[*]: characteristic bands at 3.44 and 8.26μ; UV: λλ max (log ε): 223 mμ (4.35), 227 (4.38), 297 (4.26); NMR: 7.32τ(singlet) and 2.7-3.2τ(multiplet), peak areas in ratio 2/5. The ultraviolet spectrum is similar to that of 1,2-diphenylcyclobutene-3,4-diol,

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[*] IRs in KBr, UVs in hexane, and NMRs in CCl_4.

as reported by Blomquist(5) (239mμ (4.27) and 249mμ (4.14)), and the NMR band for the allylic protons is close to the position reported for the allylic protons in cyclobutene itself (7.43τ)(6).

The structure of the cyclobutene was assigned on the basis of the elemental analysis, molecular weight, physical data, the thermal conversion back to 2,3-diphenylbutadiene at 150°, and the formation of one mole of 1,2-dibenzoylethane (VI) on ozonolysis*.

$$\text{II.}\ \xrightarrow[\text{2. } H_2 + Pd]{\text{1. } O_3} \underset{\text{VI}}{C_6H_5COCH_2CH_2COC_6H_5}$$

The mother liquids from the recrystallization of the cyclobutene contained diphenylacetylene (III). This compound was isolated by g.l.c. and identified by m.p., I.R., and by the U.V. spectrum with its characteristic fine structure; yields of about 10-15% were obtained. The diphenylacetylene is a product of the photochemical decomposition of 1,2-diphenylcyclobutene, the other product being ethylene. It is interesting to note that this reaction is temperature sensitive; the irradiation of dilute, degassed solutions of 2,3-diphenylbutadiene at -140° in EPA resulted in the formation of 1,2-diphenylcyclobutene, exclusively. This photochemical cleavage may be of value in the proof of structure of cyclobutenes. Diphenylcyclobutene is quite sensitive to light; a single 500 joule flash from a Xenon discharge tube resulted in the cleavage of about 15-20% of the cyclobutene in a 10^{-4} M. solution in hexane. No 2,3-diphenylbutadiene was formed in the irradiation.

The photochemical cleavage of cyclobutenes has not been reported previously to our knowledge, although the isolation of acetylenes from the irradiations of

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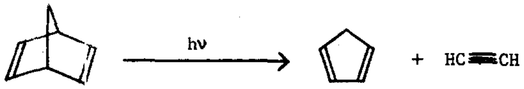
* We have been informed recently by Professor M. S. Newman of the Ohio State University that he has prepared 1,2-diphenylcyclobutene by the reaction of magnesium with 1,2-diphenyl-1,4-dichlorobutene. A sample, kindly provided by Professor Newman, was identical in all respects to our material.

tetraphenylcyclooctatetraene(2) and butadiene(7) may be examples. The formation of acetylene and cyclopentadiene in the irradiation of bicycloheptadiene is a closely related example(8).



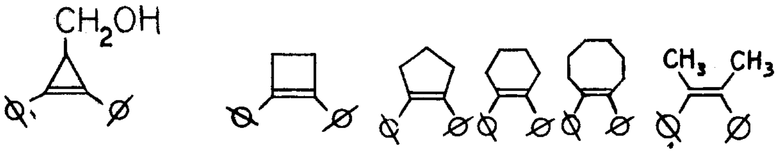
Diphenylacetylene is also a product of the irradiation of 1,2,5,6-tetraphenyl-1,5-cyclooctadiene (IV); this cleavage may be a direct one to give ethylene as the other product, or possibly the reaction sequence IV ⟶ I ⟶ II ⟶ III may be involved.

The less-volatile fraction of the butadiene irradiation products contained two compounds corresponding to dimers of 2,3-diphenylbutadiene. Analogy for the dimerization of butadienes exists in the formation of dimethylcyclooctadiene in the sensitized irradiation of isoprene(9). Fractional crystallization of the mixture contained in the less-volatile fraction permitted the isolation of pure compound IV, but the method was tedious. To simplify the composition of the mixture, it was heated to 170° for 20 minutes to convert the tricyclooctane component (V) into the cyclooctadiene (IV); recrystallization of the product then readily yielded pure 1,2,5,6-tetraphenyl-1,5-cyclooctadiene (IV) with the correct elemental analysis and molecular weight; m.p. 223-224°; <u>I.R.</u>: 3.47, 8.35, and 19.4μ; <u>U.V.</u>: λmax 260mμ (log ε 4.23); <u>N.M.R.</u>: 6.99τ(singlet) and 2.97τ(singlet), areas in ratio 2/5. The structure of the cyclooctadiene was proved by ozonolysis; two moles of 1,2-dibenzoylethane (VI) were formed. The NMR band for the allylic

$$\mathrm{IV} \xrightarrow[2.\ \mathrm{H_2}\ +\ \mathrm{Pd}]{1.\ \mathrm{O_3}} 2\ \mathrm{VI}$$

hydrogens of compound IV is slightly downfield relative to the position for the corresponding band of the parent 1,5-cyclooctadiene (7.63τ). The ultraviolet spectrum is similar to that of 1,2-diphenylcyclooctene (254mμ (log ε 3.91)),(10) but of twice the intensity. Thus, there appears to be little interaction between the two chromophores in compound IV. A similar situation exists in the case of 1,2,5,6-dibenzocyclooctadiene*, which has an ultraviolet spectrum (257mμ (log ε 2.59), 265 (2.70), 268 (2.62), and 272 (2.69)) very similar to that of ortho-xylene and of twice the intensity. We assume that compound IV is the cis, cis isomer since no changes occurred in samples heated to 223°(11).

Despite the possession of superficially similar chromophores, compounds II and IV show ultraviolet absorptions at widely different wave lengths. The presence of the chromophores is reasonably well established, and it seems worthwhile to relate the wavelength shifts to some property of the molecules. That the shift is a function of ring size is shown by the data of Fig. 1. The hypsochromic shifts relative to trans-stilbene (295 mμ) are presumably the effect of non-coplanarity of the phenyl and ethylene groups (16); electronic factors are probably involved as well, however, in determining the absorptions of the smaller ring compounds.



λmax	308sh	317	333sh	297	307sh	272	253	254sh	252
log ε	4.41	4.47	4.32	4.26	4.23	4.01	4.02	3.91	3.95
Solv.		Ether		C_6H_{14}		C_6H_{12}	CH_2Cl_2	C_6H_{12}	C_7H_{16}
Ref.		12		-		13	14	10	15

Fig. 1

Effect of Ring Size on the Ultraviolet Absorption Maxima for Various Diphenylethylenes

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*We thank Professor M. P. Cava, Wayne State University, for a sample of this compound.

The isomeric dimer formed in the irradiation of 2,3-diphenylbutadiene can be obtained pure by fractional crystallization, but a simpler method based on the relative unreactivity of this dimer (compound V) was developed. Reaction mixtures from which most of the cyclooctadiene IV had been separated by crystallization were ozonized and the products were chromatographed on silica gel. The carbonyl compounds formed from the olefinic constituents were retained on the silica gel permitting the facile elution of the dimeric hydrocarbon, which proved to be 1,2,5,6-tetraphenyl-$[4,2,0,0^{2,5}]$ tricyclooctane (V), m.p. 222.5-223°; IR: 8.49, 8.98, 16.9 and 17.5μ; UV: λmax (log ε): 228mμ (4.46), 255 (3.15), 262 (3.13), 268 (2.93), 272 (2.86); NMR: 7.38τ (singlet), 2.56τ (broad multiplet), areas in ratio 2/5. The structure of this compound was arrived at on the basis of the correct elemental analysis and molecular weight, the stability to ozone, the quantitative conversion of this compound at 150° into 1,2,5,6-tetraphenylcyclooctadiene (IV), the synthesis from compound II, and the physical data. The compound has a weak absorption in the ultraviolet with fine structure in the band. These are features characteristic of alkylbenzenes; in fact, the spectrum is very similar but slightly shifted from that of *tert*-butylbenzene in isooctane (λλmax, 248, 252, 258, 264, and 267mμ, log ε, 2.02, 2.17, 2.26, 2.13 and 2.01)(17) and of approximately four times the intensity. A better model is 1,2,3,4-tetraphenylcyclobutane (m.p. 153°, all *trans*) with absorption in the UV at 250mμ(log ε 2.92), 256 (3.00), 261 (3.07), 263 (3.05), and 271 (2.92). The NMR spectrum in carbon tetrachloride consists of a multiplet for the phenyl protons and a sharp singlet for the other hydrogens. This pattern suggested that the dimer was 1,2,5,6-tetraphenyl-$[3,3,0,0^{2,6}]$-tricyclooctane (VII), a compound with only one type of alkyl hydrogen. Similar evidence was cited by Srinivasan(18) to establish the structure of the only known compound of this type, the parent $[3,3,0,0^{2,6}]$-tricyclooctane.

The alternative structure for the saturated dimer (V) contains two types of alkyl hydrogens (in both the syn and anti forms) and it was expected that the NMR spectrum would be complex, similar to that reported for [2,2,0]-bicyclohexane(19a) and implied for the parent [4,2,0,$0^{2,5}$]-tricyclooctanes.(19b) Despite the simplicity of the NMR spectrum, this dimer appears to be 1,2,5,6-tetraphenyl-[4,2,0,$0^{2,5}$]-tricyclooctane (V). The NMR spectrum of a benzene solution shows a broadened peak for the alkyl hydrogens with some hint of fine structure. Furthermore, high yields of the dimer were obtained in the irradiation of 1,2-diphenylcyclobutene (II), whereas the dimer was not formed in the irradiation of well-degassed 10^{-4} M solutions of the cyclooctadiene (IV) in isooctane at 2537 Å. This irradiation actually yielded some diphenylacetylene along with a compound that gave an elementary analysis approximately correct for the starting compound plus one molecule of isooctane. We conclude that the difference in chemical shifts for the alkyl hydrogens in compound V is quite small, possibly as a result of shielding by the phenyl groups.

The irradiation of the cyclooctadiene (IV) in a well-degassed solution led to the formation of a yellow-orange solution which presumably contained the corresponding dihydrophenanthrene.(20,21b) Allowed to stand in darkness, the color faded as the reversal of the photochemical reaction occurred. The irradiation of incompletely degassed solutions of the cyclooctadiene and also of 1,2-diphenylcyclobutene, on the other hand, led to the development of ultraviolet spectra almost identical to that of cyclopentanophenanthrene(22) and of the correct intensity. This photochemical conversion of "cis-stilbenes" into phenanthrenes is apparently a very general reaction.(21)

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REFERENCES

(1) K. Alder and J. Haydn, Ann. Chem., 570, 201 (1950).

(2) E. H. White and R. L. Stern, Tetrahedron Letters, No. 4, 193 (1964).

(3) K. J. Crowley, Proc. Chem. Soc., 334 (1962).

(4) R. Srinivasan, J. Am. Chem. Soc., 85, 4045 (1963).

(5) A. T. Blomquist, Abstracts of the Sixteenth National Organic Chemistry Symposium, Seattle, Washington, 1959, p. 11.

(6) S. Borčić and J. D. Roberts, J. Am. Chem. Soc., 87, 1056 (1965).

(7) R. Srinivasan, ibid., 82, 5063 (1960).

(8) B. C. Roquitte, ibid., 85, 3700 (1963).

(9) G. S. Hammond and R. S. H. Liu, ibid., 85, 477 (1963) (In both cases, cis-divinylcyclobutanes may be intermediates).

(10) A. C. Cope and D. S. Smith, ibid., 74, 5136 (1952).

(11) L. E. Craig, Chem. Rev., 49, 103 (1951).

(12) We wish to thank Dr. Rolf Graeve for this measurement.

(13) Kindly provided by Professor Frank Mallory, Bryn Mawr University.

(14) P. Tomboulian, J. Org. Chem., 26, 2652 (1961).

(15) H. Suzuki, Bull. Chem. Soc. Japan, 33, 396 (1960).

(16) G. R. Evanega, W. Bergmann, and J. English, Jr., J. Org. Chem., 27, 13 (1962); Theory and Applications of Ultraviolet Spectroscopy, H. H. Jaffé and M. Orchin, John Wiley and Sons, Inc., New York, 1962, Chapt. 15.

(17) Organic Electronic Spectral Data, Vol. 1, M. J. Kamlet, Ed., Interscience Publishers, New York, 1960, p. 345.

(18) R. Srinivasan, J. Am. Chem. Soc., 85, 819 (1963).

(19) (a) S. Cremer and R. Srinivasan, Tetrahedron Letters, No. 21, 24 (1960)

(b) R. Srinivasan, J. Am. Chem. Soc., 86, 3318 (1964).

(20) A. A. Lamola, G. S. Hammond, and F. B. Mallory, Photochem. and Photobiol., 4, 259 (1965).

(21) (a) F. B. Mallory et al, J. Am. Chem. Soc., 84, 4361 (1962); ibid., 85, 828 (1963). (b) W. M. Moore, D. D. Morgan, and F. R. Stermitz, ibid., 85, 829 (1963).

(22) A. Butenandt, H. Dannenberg, and A. Rahman, Chem. Ber., 88, 1395 (1955).