

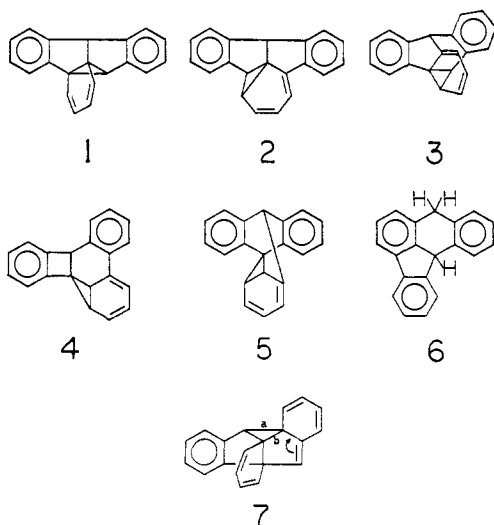
Photochemical Isomerization of Triptycene¹

Sir:

The photochemical behavior of barrelene,² mono-³ and dibenzobarrelene,^{3b,4} and fluorinated derivatives⁵ have been recently reported. Available evidence indicates that substituted cyclooctatetraenes (COT's) result from isomerization of the excited singlet state whereas the triplet produces semibullvalenes.^{3,5}

We have found that triptycene ("tribenzobarrelene") produces a single yellow isomer (λ_{\max} 249, 345 m μ (log ϵ 4.26, 3.89)) upon direct irradiation in dilute ether or acetone solution.⁶ This product is *neither the anticipated semibullvalene (1) nor a COT derivative.*

The nmr spectrum of the product exhibits multiplets at τ 2.56–3.00 (8 H) and 3.87–4.03 (3 H). Three single proton peaks are found at τ 5.57, 7.55, and 8.73, the last two being broad. Hydrogenation (Pd–C) results in the uptake of 1.86 mol. Treatment with tetracyanoethylene in anisole results in immediate decolorization of the solution and precipitation of a Diels–Alder adduct. Maleic anhydride also forms an adduct in benzene at room temperature. Thus, there is a *cis*-1,3-diene containing three hydrogens. The peak at τ 5.57 is assigned to a diphenylmethyl hydrogen, and eight hydrogens are associated with two phenyl rings. This establishes the nature of all but three carbons and two hydrogens. Formula requirements and the high τ values of the two remaining hydrogens establish the presence of a cyclopropane ring containing both of them.



(1) Initial aspects of this investigation were performed at the University of Georgia. The photoisomerization was first reported at the 18th Southeastern Regional Meeting of the American Chemical Society, Lexington, Ky., Oct 1966, p A-54.

(2) (a) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967).

(3) (a) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 4191, 6096 (1968); (b) P. W. Rabideau, J. B. Hamilton, and L. Friedman, *ibid.*, **90**, 4465 (1968).

(4) E. Ciganek, *ibid.*, **88**, 2882 (1966).

(5) (a) J. P. N. Brewer and H. Heaney, *Chem. Commun.*, 811 (1967); (b) R. S. H. Liu, *J. Amer. Chem. Soc.*, **90**, 215 (1968).

(6) Irradiations were conducted for no more than 5 hr using a Hanovia 450-W medium-pressure mercury source in an immersion reactor. Work-up procedures rigorously avoided acids, bases, alumina, and heat since they readily cause isomerization of the product. The isomeric nature of the product was established by microanalysis and by Rast and mass spectral molecular weight determinations.

Only four structures are possible which incorporate the above features (compounds 2–5). The product of thermal isomerization of the photoproduct establishes 2 as the correct choice. Upon melting (mp 135–136°), 8,12b-dihydrobenz[*a*]fluoranthene (6) is produced quantitatively.⁷ Attempted chromatography on neutral alumina as well as treatment with dilute acid also produce this isomer and the dehydrogenated fluoranthene derivative along with other unidentified materials. Dilute alcoholic sodium hydroxide or pyridine affords a mixture containing an unidentified anthracene derivative (uv).

Examination of structures 2–5 shows that only 2 is capable of easily forming the required ring skeleton, requiring only cleavage of the cyclopropane and hydrogen migration to do so.⁹ A mild room-temperature degradation using osmium tetroxide followed by potassium periodate furnished additional evidence favoring 2. Use of excess OsO₄ afforded a keto aldehyde which exhibits carbonyl absorption at 1709 cm⁻¹. This was oxidized by silver oxide to a keto acid whose triethylammonium salt also absorbs at 1709 cm⁻¹. The ketone expected from 3 is a 2-indanone and should absorb at a frequency no lower than 1730 cm⁻¹, especially if one takes into account the geometric restrictions in the rest of the molecule. In contrast, 2 yields a 1-indanone, which is expected to absorb at 1700–1715 cm⁻¹.

There is no reason to postulate a pathway for triptycene photoisomerization which is radically different from that proposed for barrelene.^{2b} Since 2 is related to 1 through a Cope rearrangement, the latter could well be the initial photoproduct which rearranges to the more stable 2. Molecular models clearly indicate that 2 is the most strain-free of all the possibilities, with the major source of strain for 1 and 3 being the ring which is absent in the other barrelene derivatives which have been investigated. If 1 is indeed produced, its formation most likely does not involve either path I or IIB in the Zimmerman scheme^{2b} since these paths require the disruption of an additional aromatic system prior to the final ring closure, producing 7. Path IIA, in contrast, produces 1 directly.

Also noteworthy is the absence of a detectable COT derivative even though such compounds are the usual result of direct irradiation. The quadricyclene-type mechanism proposed by Brewer and Heaney^{5a} for COT production requires at least one nonbenzenoid double bond in the initial barrelene; triptycene does not fit into this category. Alternatively, the path originally proposed by Zimmerman^{2a} would produce a COT derivative from triptycene in which at least one of the benzene rings would be forced into an *o*-quinoid structure. The only tribenzocyclooctatetraene possible

(7) The product was identified by its melting point and conversion to benz[*a*]fluoranthene, which agreed in all respects with material reported by Campbell and Marks.⁸ (The isomerization also occurs in the inlet of the mass spectrometer.)

(8) N. Campbell and A. Marks, *J. Chem. Soc.*, 2941 (1951).

(9) It must be pointed out that 2 and 3 are related, through 1, as Cope rearrangement isomers. Any chemical structure proof must carry with it the realization that it is conceivable that interconversions among 1, 2, and 3 can occur to allow further reaction of any of them. The homogeneous nature of the product indicates that such a process is not occurring to an appreciable extent at room temperature, however, and is highly unlikely under the mild conditions in which rearrangement has been observed.

is the 1,3,5-tribenzo derivative. Its formation requires extensive rearrangement, but it can be envisioned as arising from **7** by a rearrangement involving bond a, followed by a further bond rearrangement. Cleavage of bond b, however, produces **1**. Since the formation of **7** itself is unlikely, **1** being able to be formed instead without disruption of an aromatic system, the absence of a COT derivative is readily rationalized.

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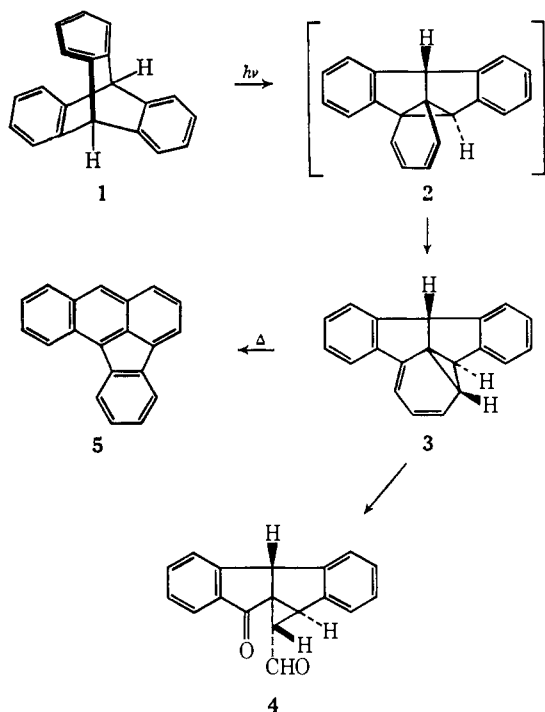
Photochemistry of Triptycene¹

Sir:

Interest in an extension of previous work on the photochemistry² and the intriguing possibilities of excitation migration³ of benzobarrelenes prompted us to report our investigation of the photochemistry of some triptycenes.

Irradiation⁴ of triptycene (**1**) results in the smooth formation ($\Phi = 0.3$) of one product, **3**: mp 135.5–136.0°; nmr (CS₂, TMS internal reference) δ 1.25 (1 H, m), 2.40 (1 H, m), 4.46 (1 H, m), 6.10 (3 H, m), and 7.2–7.9 (8 H, m). Upon heating **3** is converted to 2,3-benzfluoranthene (**5**).⁵ Ozonolysis of **3** yields the keto aldehyde **4**: nmr (CS₂, TMS) δ 2.08 (1 H, d of d, $J = 6, 4$ cps), 3.28 (1 H, d of d, $J = 4, 1.5$ cps), 4.25 (1 H, d, $J = 1.5$ cps), 7.1–7.9 (8 H, m), 9.84 (1 H, d, $J = 6$ cps); mass spectra, m/e 260 (m^+ , 35%); ir max (CCl₄) 1709 and 1716 cm⁻¹. Compound **4** was converted to a diol by lithium aluminum hydride. Nmr spectra of this diol analysis demonstrated the presence of a tertiary benzylic (δ 5.6) and primary (δ 4.0) alcohol, thereby corroborating the structural assignment of **4**.

These results contrast with previous results on the photochemistry of barrelene and its benzo derivatives which yield a mixture of semibullvalenes and cyclooctatetraenes when irradiated.² Formation of **3** can be interpreted in terms of formation of the semibullvalene **2** which then undergoes a sigmatropic rear-



angement⁶ to **3**. Models indicate that the rearrangement of **1** to **2** can plausibly lead only to the stereoisomer shown which likewise by sigmatropic rearrangement is most likely to yield stereoisomer **3**. The structural assignment is consistent with the low coupling constants⁷ between the cyclopropyl hydrogens of **3** ($J \sim 3$ cps) and **4** ($J = 4$ cps). The formation of **3** cannot be quenched by 1,3-pentadiene, but conversion of **1** to **3** also occurs smoothly in photosensitizing solvents such as benzene and acetone. Thus, the conversion of **1** to **3** may be a very fast triplet rearrangement, in analogy to those found for other barrelene derivatives. However, since formation of **3** is also observed in photolyses at 77°K (under conditions such that the phosphorescence ($\tau_p = 3$ sec) of **1** is observable), unless the rate of this rearrangement possesses a remarkably large temperature coefficient, it appears unlikely that the reaction occurs from T₁.

Compound **3** represents one of the few examples of a (nonbenzo) norcaradiene which is not the minor component in equilibrium with corresponding tropyliene⁸ at room temperature.

(1) (a) Molecular Photochemistry. XII. The authors at Columbia gratefully acknowledge the generous support of this work by the Air Force Office of Scientific Research (Grant AFOSR-68-1381). The authors at Case Western Reserve acknowledge the support from the National Cancer Institute (Public Health Service Research Grant No. CA-07909-03). (b) Presented in part at 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstracts No. PHYS-167.

(2) (a) P. W. Rabideau, J. B. Hamilton, and L. Friedman, *J. Am. Chem. Soc.*, **90**, 4465 (1968); (b) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 4191 (1968); (c) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); (d) J. P. N. Brewer and H. Heaney, *Chem. Commun.*, 811 (1967); (e) R. S. H. Liu, *J. Am. Chem. Soc.*, **90**, 215 (1968); (f) E. Ciganek, *ibid.*, **88**, 2882 (1966).

(3) M. S. deGroot and J. H. van der Waals, *Mol. Phys.*, **6**, 545 (1963).

(4) Nearly quantitative conversions of **1** to **3** were obtained by irradiation of ~0.1% solutions of **1** in a variety of solvents. Compound **3** appears to be identical with that obtained by T. D. Walsh, *J. Am. Chem. Soc.*, **91**, 515 (1969). The authors wish to thank Professor Walsh for providing us with a manuscript of his results prior to publication.

(5) N. Campbell and A. Marks, *J. Chem. Soc.*, 2941 (1951)

(6) J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, *J. Am. Chem. Soc.*, **89**, 4076 (1967); J. A. Berson and M. R. Willcott, *ibid.*, **87**, 2751, 2752 (1965); **88**, 2494 (1966); *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **27**, 139 (1966).

(7) A. A. Bothner-By, *Advan. Magnetic Resonance*, **1**, 195 (1965).

(8) (a) E. Ciganek, *J. Am. Chem. Soc.*, **87**, 652, 1149 (1965); (b) T. Mukai, H. Kubota, and T. Toda, *Tetrahedron Letters* 3581 (1967), and references therein; (c) W. von E. Doering and M. R. Willcott, *ibid.*, 663 (1962).

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