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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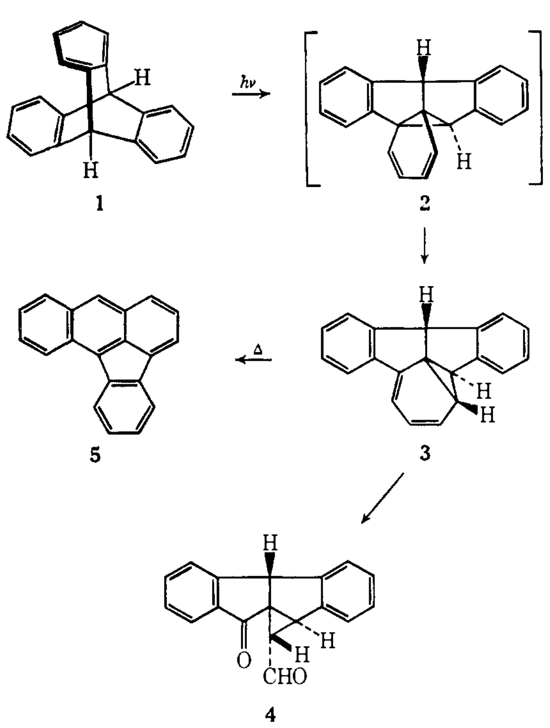
Photochemistry of Triptycene[1]

Sir:

Interest in an extension of previous work on the photochemistry[2] and the intriguing possibilities of excitation migration[3] of benzobarrelenes prompted us to report our investigation of the photochemistry of some triptycenes.

Irradiation[4] of triptycene (**1**) results in the smooth formation ($\Phi = 0.3$) of one product, **3**: mp 135.5–136.0°; nmr (CS_2, 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-benzfluoanthene (**5**).[5] Ozonolysis of **3** yields the keto aldehyde **4**: nmr (CS_2, 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 (CCl_4) 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 rearrangement[6] 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 constants[7] 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 T_1.

Compound **3** represents one of the few examples of a (nonbenzo) norcaradiene which is not the minor component in equilibrium with corresponding tropylidene[8] at room temperature.

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