

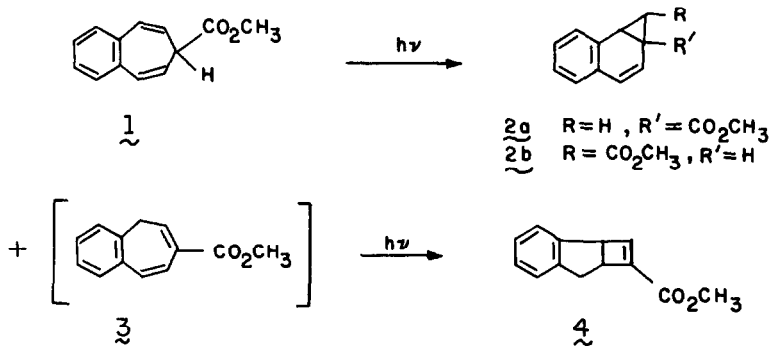
COMPETITION BETWEEN 1,3- AND 1,7-HYDROGEN AND ALKYL MIGRATIONS
IN 3,4-BENZOTROPILIDENE CHEMISTRY

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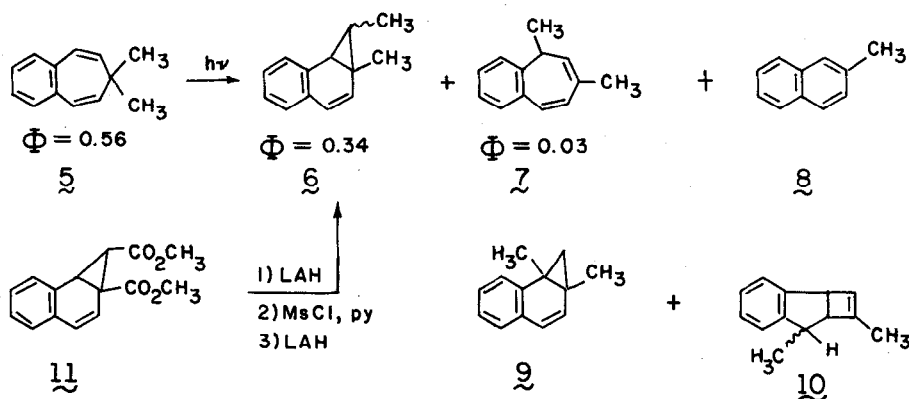
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The photochemistry of 3,4-benzotropilidenes² and the implication of benzotropilidenes in benzonorcaradiene photochemistry^{3a-c} have been of recent interest. While formal 1,7-shifts are well-documented in 1,2-benzotropilidenes, 3,4-benzotropilidenes, and cycloheptatrienes, analogous 1,3-shifts are much rarer. We recently suggested^{2a} that the production of cyclobutene 4 most reasonably arose via secondary photolysis of 3, which was formed by 1,3-hydrogen shift from 1. In the course of migratory aptitude studies of photochemical shifts, we have obtained additional evidence for 1,3-shifts in these systems which we report herein.



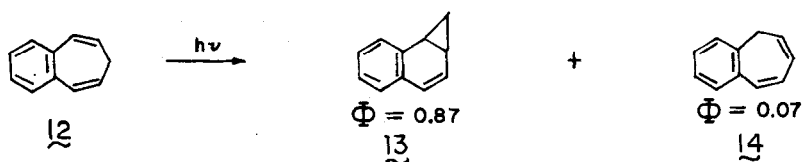
Our first indication of 1,3-shifts in these systems was from the irradiation of the dimethyl derivative 5. Photolysis of 5 at 350 nm⁴ to 8-15% conversion gave 6 and 7 in a ratio of ca 10:1,⁵ and time-dependence studies suggested that both compounds were formed directly from 5. Irradiation until complete disappearance of 5 gave in addition to 6 (38%) and 7 (5%) 8 (3%), 9 (5%) and 10 (6%). No product arising from the di- π -methane process could be detected. The structure of the benzonorcaradiene 6, which exists as a 2:1 mixture of endo and exo 7-methyl isomers, was established by synthesis from 11. The photoisomer 7 showed

spectroscopic properties in agreement with those of 5,7-dimethyl-2,3-benzotropilidene



described by Bertelli.⁶ The structures assigned to 9 and 10 are based on spectroscopic data.⁷

While the results from 5 indicated 1,3-methyl migration was occurring competitively with the 1,7 process, the complexity of the system on extended irradiation warranted confirmation of this result in a second system. Thus, the photochemistry of the 3,4-benzotropilidene 12 was reinvestigated. The photolysis of 12 (>99.9% pure) at 350 nm through Pyrex showed at 10-15% conversion the formation of 13 and 14 in a ratio of ca. 10:1. The identity of the 1,2-



benzotropilidene was established by its glc retention time and its characteristic doublet in the nmr at 7.02 τ .⁸ That 14 was not arising from secondary photolysis of 13 is evident by the absence of naphthalene and 1,2-benzobicyclo-[3.2.0]-5,6-heptene, 15, even in preparative irradiations of 12. It has previously been shown that the rates of rearrangement of 13 to 14 and of 13 to naphthalene and 15 are comparable.⁹ The maximum amount of 14 (4%) occurred at 40% conversion of 12 and completely disappeared on extended irradiation. The failure to detect this process in earlier studies was apparently due to the use of 12 which contained $\pm 3\%$ of 14 as impurity.^{2b}

The results reported here establish two important facets of 3,4-benzotropilidene

chemistry First photochemical 1,3-migrations may compete to the extent of ~10% with the more common 1,7-shifts in these systems While 1,3-shifts have not been detected in the photochemistry of simple cycloheptatrienes and there is no agreement as to the allowed or forbidden character of this process,¹⁰ the closer competition between 1,3- vs 1,7-shifts in the benzo-systems may result from the 1,3-shift process not involving disruption of the aromatic system Second, the high quantum yields noted in these systems indicate that group migration serves as a major pathway for excited state decay even in the case of alkyl shifts. Thus, either the rate constants for migration, while varying markedly with the migrating group, are much faster than the rates of nonreactive processes or the rates of methyl and hydrogen migration are very similar in these systems¹¹

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- 3 a M Kato, M. Kawamura, Y Okamoto, and T Miwa, Tetrahedron Letters, 1171 (1972) b. H Durr and H Kober, ibid., 1255 (1972). c. D M Madigan and J S Swenton, J Amer Chem. Soc, 93, 6316 (1971)
4. All preparative photolyses were performed with RPR-3500 Å light available from New England Ultraviolet Co, Middletown, Connecticut All quantum yields were measured at 330 nm with light from a Bausch and Lomb monochromator as previously described.^{2a} The estimated errors in the quantum yields are ±10% All new compounds gave acceptable combustion analyses.
5. Analyses were performed on a 25' x 1/8" column -- 15% Apiezon M - on 60/80 Chrm W--180°
- 6 D J Bertelli and W J Rossiter, Tetrahedron, 24, 609 (1968) The material isolated by vpc showed contamination of 7 by its 1,5-hydrogen shift isomer The absorptions due to 3,5-dimethyl-1,2-benzotropolidene were not detected in the nmr spectrum of the crude photolysis mixture
7. 9 nmr (CCl₄) 2.38-2.98 (m, 4H), 3.92 (center of AB quartet, J=9 Hz), 8.42 (s, 3H), 8.59 (s, 3H), 8.94 (d, J=4 Hz), and 9.92 (d, J=4 Hz)τ 10 nmr (CCl₄) 2.96 (s, 4H), 4.06 (m, 1H), 5.98 (br m, 1H), 6.75-7.15 (m, 2H), 8.33 (br s, 3H), and 8.83 (d, J=7 Hz, 3H)τ.
- 8 A 25' x 1/8"-5% SE-30 on 60/80 Chrm. G at 130° allowed baseline separation of 12 from 14 at low conversion. However, only ca 80% separation of 13 from 12 could be achieved. The quantum yields in this system could be in error by as much as ±20%

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11. Irradiation of the 7-methyl-3,4-benzotropolidene, 1, gives only the hydrogen migrated product, 11, in high yield (>90%) and with high efficiency ($\Phi=0.93$). Whether the high hydrogen to methyl migratory aptitude (>1000) is due to different rates of migration or conformational factors present in the tropilidene remains to be established

