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PHOTOCHEMISTRY OF 2-METHYLENE-6,7-BENZOBICYCLO[3.2.2]NONA-3,6,8-TRIENE. EFFICIENT TRIPLET DI-π-METHANE REARRANGEMENT OF A "FREE-ROTOR" POLYENE.

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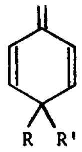
Recent comparisons between the photochemistry of cyclic unsaturated ketones and their exomethylene counterparts have revealed characteristic differences in reactivity between $n-\pi^*$ and $\pi-\pi^*$ excited states of conjugated systems.[1] In contrast to the typical photorearrangement of 2,5-cyclohexadienones originating from their $n-\pi^*$ triplet states, the corresponding hydrocarbons possessing an exocyclic methylene group (e.g. 1) undergo the di-π-methane rearrangement[2] preferentially from the singlet excited state. Although efficient di-π-methane rearrangement of rigid bicyclic polyene hydrocarbons in the triplet state has been observed, the strong preference for singlet rearrangement in 1 and in acyclic polyenes has led Swenton[3a] and Zimmerman[3b] to postulate that, in the latter compounds, free rotation about bonds of low π-order in the excited triplet may provide an energy dissipating mechanism precluding efficient triplet rearrangement.



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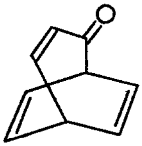

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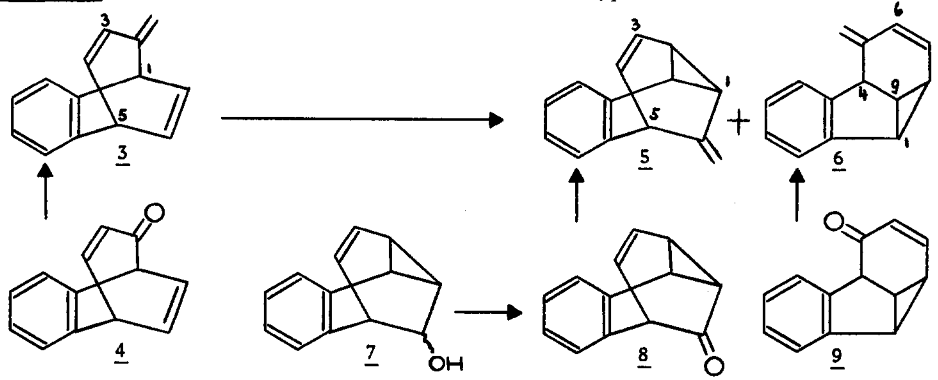
As an extension of earlier studies[4] in the photochemistry of the bicyclo[3.2.2]trienone system 2 we now report the highly regiospecific di-π-methane rearrangement of 2-methylene-6,7-

benzobicyclo[3.2.2]nona-3,6,8-triene (3) *which proceeds preferentially by way of a triplet excited state* in apparent violation of the "free rotor" hypothesis.

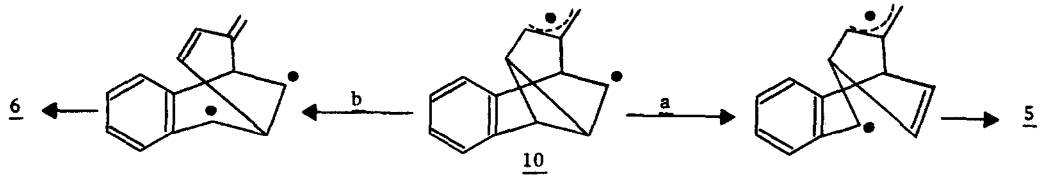


The olefin 3, bp 95° (0.1 mm), mp 43°, was obtained in 70% yield by reaction of methylenetriphenylphosphorane with ketone 4[4a] followed by chromatography over silica gel and distillation.[5] Sensitized photolysis[7] of a 0.3% solution of triene 3 in acetonitrile containing ca. 15% acetone as sensitizer[8] resulted in rapid disappearance of 3 with concomitant formation of two isomeric products in 93% and 4% yields as monitored by glpc[9] using hexadecane as internal standard. The products were separated either by preparative glpc or by preparative tlc over silica gel.

The spectroscopic data indicate structures 5 and 6 for the major and minor photoproducts respectively.[6,10,11] These assignments have been unequivocally confirmed by independent synthesis. Oxidation of the epimeric benzobarbaralols 7[12] with CrO_3-pyridine gave ketone 8[13] which on subsequent reaction with methylenetriphenylphosphorane afforded 5. Similarly, 6 was obtained by the Wittig reaction of ketone 9.[4d]

The direct photolysis of triene 3 also yielded isomers 5 and 6 as the only volatile products. However, direct photorearrangement took place less rapidly than the sensitized reaction and with some loss of monomeric material.[17] Control experiments established that neither direct nor sensitized irradiation of authentic 5 or 6 effect interconversion of these isomers.

The exceptional regiospecificity of the rearrangement of 3 demands a strong preference for a bond-breaking sequence at C-5 rather than at C-1 and may be summarized by the valence bond representation 10 which, by subsequent rebonding as shown, can lead to both the major and minor photoproducts, 5 and 6; the preference of path a over path b is consistent with retention of maximum electron delocalization during rearrangement.[14] This path however differs markedly from the di-π-methane rearrangement of the related enone 4 where only path b is utilized (to give 9) via a triplet excited state.[4d]



Alternatively, a benzo-vinyl di-π-methane rearrangement at C-5 may account for formation of 5. Such a route has been recently invoked in the photoisomerization of other exocyclic methylene systems[1a,b,f] and cannot be excluded at present.[15]

Finally, we note that, in sharp contrast to previous observations,[1] the triplet of 3 is highly reactive. Quantum yields for the direct and the acetone-sensitized rearrangement of 3 (Table 1) indicate at least[16] a five-fold advantage to the triplet rearrangement pathway for 3.

Table I. Quantum Yields for Photolysis of Triene 3

Quantum Yield For:	Direct[17]	Sensitized[18]
Disappearance of 3	0.15	0.44
Formation of 5	0.05	0.28
Formation of 6	0.008	0.013

We conclude from our quantitative data, and from other qualitative observations in the recent literature,[19] that significant structural limitations may exist on the "free rotor" hypothesis.[20]

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5. Olefin 3: m/e 180; ν_{max}^{neat} 1620, 1475, 890 cm^{-1}; λ_{max}^{EtOH} 230 nm (ε 11,600), 225 sh (7000); nmr ($CDCl_3$):[6] δ3.84 (H_5, broad t, J = 8.0, 6.5, 1.5, 1.0 Hz), 4.14 (H_1, d, t, 6.5, 1.5, 1.5), 4.63 (1H methylene, d,d, 1.5,~1.0), 5.12 (1H methylene, t, 1.5, 1.5), 5.50 (H_3,

broad d, 10, 1.5,~1.0), 6.15 (H_4, broad t, 10, 8.0, 1.5, ~1.0), 6.40 (H_8, sept, 8.0, 6.5, 1.5), 6.68 (H_9, sept, 8.0, 6.5, 1.5), 7.1 (4H aromatic, m). Satisfactory elemental analysis.

6. Nmr spectra were taken on a Varian HA-100D apparatus. Positional assignments were verified by spin decoupling measurements.

7. Hanau Q81 high pressure burner immersion lamp, under N_2, Pyrex filter.

8. Similar results were obtained using benzophenone as sensitizer.

9. Glpc analyses were conducted using 10% SE-30 on Chromosorb W, at 140°.

10. Comp. 5: m/e 180; ν_{max}^{neat} 1650, 1470, 880 cm^{-1}; λ_{max}^{EtOH} 225 sh nm (ε 9000), 267 (500); nmr ($CDCl_3$) δ2.35 (H_2, deca, J = 7.5, 7.5, 6.0, 1.5 Hz), 2.75 (H_1, H_8, m), 3.72 (H_5, d, d, 6.5, 1.5), 4.81, 4.95 (2H methylene, d each, 1.5), 5.45 (H_3, q, 8.5, 5.5) 5.89 (H_4, sept, 8.5, 6.5, 1.5), 7.1 (4H aromatic, m).

11. Comp. 6: m/e 180; ν_{max}^{neat} 1630, 1480, 880 cm^{-1}; λ_{max}^{EtOH} 252 nm (ε 6400), 275 sh (3000); nmr ($CDCl_3$) δ1.78 (H_8, sext, 8.0, 8.0, 4.0), 2.38 (H_9, q, 8.0, 7.5, 6.0), 2.76 (H_1, q, 8.0, 6.0), 4.00 (H_4, d, 7.5), 4.80, 5.06 (2H methylene, broad s each), 5.64 (H_7, q, 9.0, 4.0), 6.12 (H_6, d, 9.0), 7.14 (4H aromatic, m).

12. Benzobarbaralols 7, first prepared by Drs. P.T. Izzo and R. Montaigne (unpublished results from this laboratory) were fully characterized by nmr, ms and analyses.

13. Ketone 8, first prepared by Dr. P.T. Izzo (unpublished results) gave satisfactory ms, analytical and 100 MHz nmr data.

14. H.E. Zimmerman and A.C. Pratt, *J. Amer. Chem. Soc.*, **92**, 1409 (1970).

15. Cf. H.E. Zimmerman, R.S. Givens and R.M. Pagni, *ibid.*, 90, 6096 (1968); L.A. Paquette, J.R. Malpass and G.R. Krow, *ibid.*, **92**, 1980 (1970).

16. Products 5 and 6 in the direct photolyses may in part arise via intersystem crossing of excited 3 and thus need not wholly represent singlet rearrangement.

17. Direct photolyses were carried out in quartz vessels using a Rayonet photochemical reactor equipped with low pressure "2537 Å" lamps emitting ca. 20% at 3130Å. Quantum yields were determined using neat cyclopentanone as actinometer [P. Dunion and C. Trumbore, *J. Amer. Chem. Soc.*, **87**, 4211 (1965)]. Analyses were carried out by glpc.

18. Quantum yields of the sensitized reaction were determined on the above apparatus using Pyrex vessels, cyclopentanone in Pyrex was employed as actinometer.

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20. The authors gratefully acknowledge stimulating discussions with Professor J.C. Dalton during the course of this investigation.