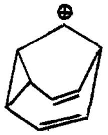
Tetrahedron Letters No. 37, pp 3621 - 3622, 1973. Pergamon Press. Printed in Great Britain.

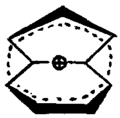
PHOTOCHEMICAL TRANSFORMATIONS OF 2-METHYLENE-BICYCLO[3.2.2]NONA-3,6,8-TRIENE. (METHYLENEHOMOBARRELENE).

Zeev Goldschmidt* and A. Worchel
Department of Chemistry, University of Bar-Ilan, Ramat-Gan, Israel.

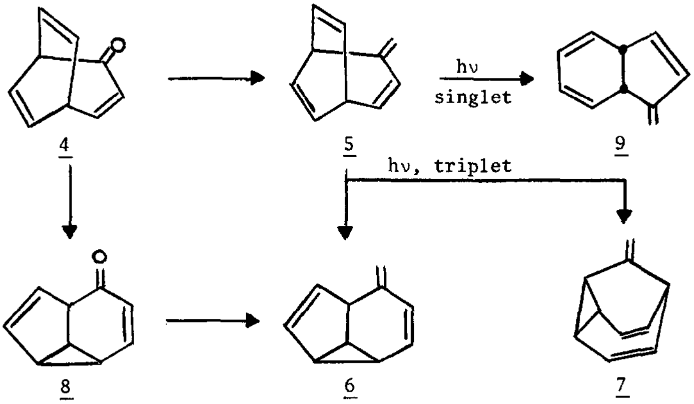
(Received in UK 5 July 1973; accepted for publication 3 August 1973)

Current theoretical developments concerning the topological aspects of aromaticity in polycyclic hydrocarbons[1] prompts us to report a facile and synthetically useful preparation of two representatives of these systems, the barbaralyl (1) and bishomotropylium (2) cations[2,3], by a photochemical synthesis of their hydrocarbon precursors.


1


2

Thus, the acetone-sensitized photolysis[4] *of* 2-methylene-bicyclo[3.2.2]nona-3,6,8-triene (5),[5] readily prepared in 80% yield by the Wittig reaction of ketone 4[6] with methylenetriphenylphosphorane, resulted in the rapid disappearance of 5 with concomitant formation of ca. 1:1 mixture of two isomeric products 6 and 7 in practically quantitative yield. Separation was best effected by preparative glpc.[7]



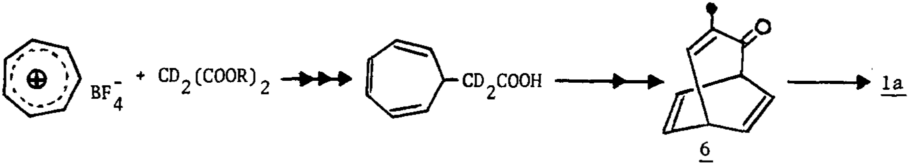
Methylenehomosemibullvalene (6) was characterized by concordant nmr and mass spectra,[8] as well as by independent synthesis by the Wittig reaction of ketone 8, obtained by the sensitized irradiation of 4.[9] The physical properties of methylenebarbaralane (7) and its temperature-dependent nmr spectrum were identical to those recently reported by Lambert *et al.*[10]

Interestingly, the direct irradiation of 5 using 2537Å light takes another course, affording a photoequilibrium of 5 with its isomeric methylendihydroindene 9, also a potentially bishomotropylium (2) species.[2] The nmr spectrum of 9 was indistinguishable from that of the independently synthesized one by Radlick *et al.*[11]

Although Mechanism A bears a formal analogy to the [1,3] and [3,3] photoismerizations of the corresponding ketone,[3] it seemed less favorable than Mechanism B since it involves a vinyl cleavage. On the other hand, Mechanism B strongly resembles the photochemical transformation of barralene to cyclooctatetraene.[4]

In order to determine which one of the above mechanism operates, methylenehomobarralene-3-d (1a) was prepared by condensation of tropylium fluoroborate with dideuterated malonate[5,6] followed by hydrolysis and decarboxylation to form dideuterated cycloheptatrienyl acetic acid[6] which was converted to ketone 6[7] and finally by Wittig reaction [8] to 1a. (Scheme III).

Scheme III.



6

Irradiation of 1a in pentane solution with 2537Å light afforded dihydroindene exclusively labeled at C-2 as shown in 2a, clearly supporting the a priori less favorable Mechanism A.

We gratefully acknowledge stimulating discussions with Professors A.S. Kende and M. Sprecher This work was supported in part by the Bar-Ilan Research Committee under Grant No. 161-84-15-8.

REFERENCES

1) Dihydroindene 2: nmr ($CDCl_3$) δ 3.70 (2H, broad s), 4.77 (1H, broad s), 5.01 (1H, broad s), 5.64 (4H, broad s), 6.01 (1H,d,J=6Hz), 6.30 (1H,d,J=6Hz), Cf. P. Radlick, W. Fenicel and G. Alford, ibid., 2707 (1970).

2) Cf. K. Hafner and H. Tappe, Angew. Chem. internat. Edit., 8, 593 (1969).

3) A.S. Kende, Z. Goldschmidt and P.I. Izzo, J. Amer. Chem. Soc., 91, 6858 (1969).

4) H.E. Zimmerman et al., ibid., 90, 6096 (1968).

5) M. Pomerantz and G.W. Gruber, ibid., 93, 6615 (1971).

6) K. Conrow, ibid., 81, 5461 (1959).

7) M.J. Goldstein and B.G. Odell, ibid., 89, 6356 (1967). J. Grutzner and S. Winstein, ibid., 94 2200 (1972).

8) See preceding communication.