Photochemical Behaviour of the Bicyclo[5,1,0]octadienyl Anion

By H. KLOOSTERZIEL* and MRS. G. M. GORTER-LA ROY
(Gorlaeus Laboratoria, Postbox 75, The University, Leiden, The Netherlands)

Summary Irradiation of solutions of the bicyclo[5,1,0]-octadienyl anion yields the cyclo-octatetraene dianion.

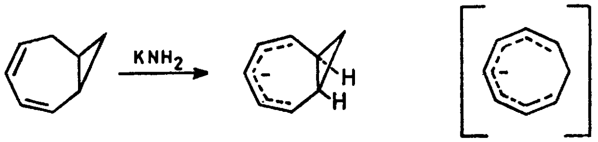
THE electrocyclic interconversion of the two $C_8H_9^-$ species bicyclo[5,1,0]octadienyl anion (**1**) and (all *cis*) cyclo-octatrienyl anion (**2**) is—as a disrotatory process—thermally forbidden by the Woodward–Hoffmann rules.[1] The thermal isomerisation of (**1**) takes a different course.[2] The allowed photochemical interconversion of (**1**) and (**2**) cannot be studied starting from (**2**). Attempts to prepare (**2**) are thwarted by its instability to disproportionation into cyclo-octatriene and the cyclo-octatetraene dianion,[2] see reaction (1). We have studied the behaviour of solutions

$$(\mathbf{2}) + (\mathbf{2}) \rightarrow C_8H_{10} + C_8H_8^{2-} \qquad (1)$$

of (**1**) in liquid ammonia obtained by reaction (2), upon

$$(\mathbf{3}) + KNH_2 \rightarrow (\mathbf{1}) \qquad (2)$$

irradiation with a Philips HP500 mercury arc at $-70°$. ^1H N.m.r. spectra (100 MHz) of the solutions revealed a rapid and complete disappearance of the signals of (**1**). The features that appear depend upon the molar ratio KNH_2:(**3**) used in the preparation of solutions of (**1**). (i) With a ratio of 1:1 the signals of (**3**) as well as a strong singlet at δ 5·64 are observed. (ii) With a ratio of 2:1 the singlet is the only new signal. The ratio dependence and the value[2] of δ prove that the cyclo-octatetraene dianion is formed.†



(**3**) (**1**) (**2**)

This observation agrees with an initial photochemical isomerisation of (**1**) to (**2**), followed by one or more proton transfers such as: (**1**) + (**2**) → (**3**) + $C_8H_8^{2-}$, reactions (1) and (2), and KNH_2 + (**2**) → $C_8H_8^{2-}$.

Though other pathways can be envisaged for the initial reaction (**1**) → (**2**), we consider the photochemically allowed disrotatory electrocyclic ring opening of (**1**) as the most likely.

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† Addition (case ii) of NH_4Cl and work-up (evaporation of NH_3; addition of CCl_4) gave (g.l.c.) cyclo-octa-1,3,5- and -1,3,6-triene (mass: 106 = C_8H_{10}; n.m.r.: correct shifts and intensities), which confirms the conclusion.

[1] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim, 1970.

[2] H. Kloosterziel and E. Zwanenburg, *Rec. Trav. chim.*, 1969, **88**, 1373.