The Photo-rearrangement of 7-Cyano-2,3-benzobicyclo[4.2.0]octa-2,4-dien-6-yl Hypoiodite to 7-Cyano-2,3-benzobicyclo[5.1.0]octa-2,4-dien-6-one[1]

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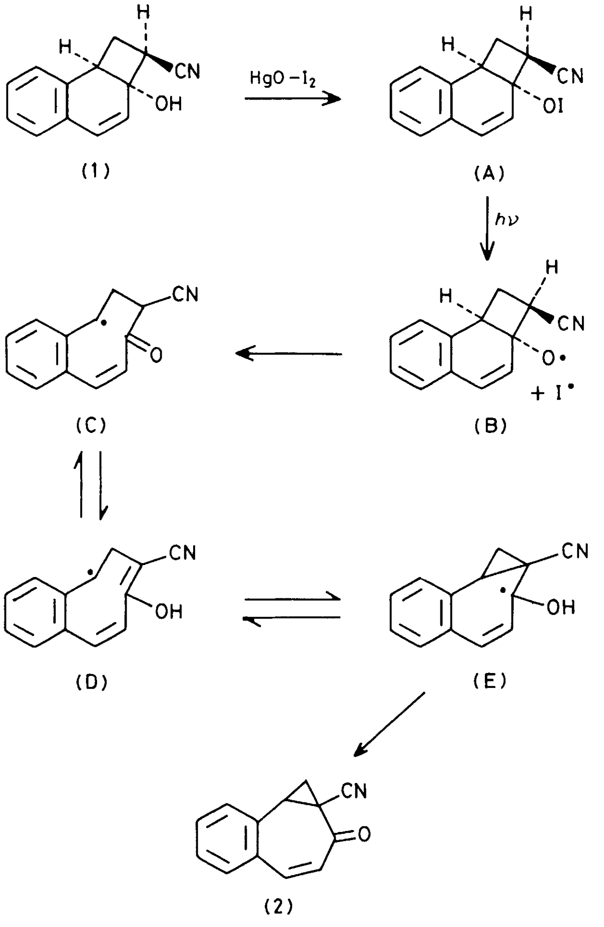
Irradiation of 7-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-dien-6-ol (**1**) in the presence of HgO–I_2 in benzene gives 7-cyano-2,3-benzobicyclo[5.1.0]octa-2,4-dien-6-one (**2**).

Ring expansion is of great importance in organic synthesis. In this paper, we report a novel case in which a 6-membered carbocycle is expanded to a 7-membered ring fused with a cyclopropane ring by photocycloaddition–β-scission.

Thus, irradiation of (**1**)[2] (0.5 g, 2.5 mmol), a photochemical cycloadduct derived from 2-naphthol and acrylonitrile, in benzene (60 ml) containing mercury(II) oxide (0.6 g, 2.75 mmol) and iodine (0.7 g, 2.75 mmol) in a Pyrex vessel with a 100 W high pressure Hg arc for 5 h under a nitrogen atmosphere gave a product (**2**) (m.p. 130—132 °C) in a 40% yield. The molecular formula of (**2**) was determined to be $C_{13}H_9NO$ by elemental analysis and mass spectrometry (M^+,



Scheme 1

m/z 195, 60%) and the structure of (**2**) was confirmed to be 7-cyano-2,3-benzobicyclo[5.1.0]octa-2,4-dien-6-one on the basis of the following spectroscopic evidence.[3]

Compound (**2**): ^{1}H n.m.r. (CDC$_3$–SiMe$_4$, J in Hz) δ 3.28 (1H, dd, J 9.28 and 9.76, 1-H), 6.94 (1H, d, J 13.18, 4-H), 6.06 (1H, d, J 13.18, 5-H), 2.35 (1H, dd, J 9.28 and 5.62, 8-H), 2.47 (1H, dd, J 9.76 and 5.62), and 7.28—7.56 (4H, m, aromatic H); ^{13}C n.m.r. (CDCl$_3$–SiMe$_4$, δ in p.p.m.), 37.9 (d, C-1), 131.1 (s, C-2), 135.4 (s, C-3), 139.7 (d, C-4), 124.5 (d, C-5), 189.6 (s, C-6), 37.9 (s, C-7), 22.1 (t, C-8), 128.3 (d), 130.6 (d), 131.9 (d), and 133.9 (d), (C-9—C-12), and 118.0 (s, C-13); $\nu_{max.}$ (Nujol) 2245 (CN) and 1650 cm^{-1} (C=O); $\lambda_{max.}$ (EtOH) 292 (ε 4 900 dm^3 mol^{-1} cm^{-1}), 233sh, and 209 nm (10 100).

The formation of homotropone (**2**) involves a new rearrangement and obviously starts from an 8-membered carbon-centred radical (C) which is generated by the β-scission of alkoxyl radical (B). There may be several probable paths from the intermediary radical (C) that give the product (**2**). One of the most plausible paths, involving successive intermediates (D) and (E), is depicted in Scheme 1.

This rearrangement constitutes a two-step preparation of homotropone, which is potentially useful for further transformations, from abundantly available starting materials.

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References

1 For the previous paper in this series see: H. Suginome, T. Ōtsuka, K. Orito, C. Jaime, and E. Ōsawa, *J. Chem. Soc., Perkin Trans.* 1, in the press.

2 I. A. Akhtar and J. J. McCullough, *J. Org. Chem.*, 1981, **46**, 1447.

3 For ^{1}H n.m.r. data of 2,3-benzobicyclo[5.1.0]octa-2,4-dien-6-one, see Y. Sugimura, N. Soma, and Y. Kishida, *Tetrahedron Lett.*, 1971, 91; H. A. Corver and R. F. Childs, *J. Am. Chem. Soc.*, 1972, **94**, 6201.