Mechanism of Photoformation of 1-Cyanobenzosemibullvalene

By Christopher O. Bender* and Elaine H. King-Brown

(*Department of Chemistry, University of Lethbridge, Lethbridge, Alberta, Canada* T1K 3M4)

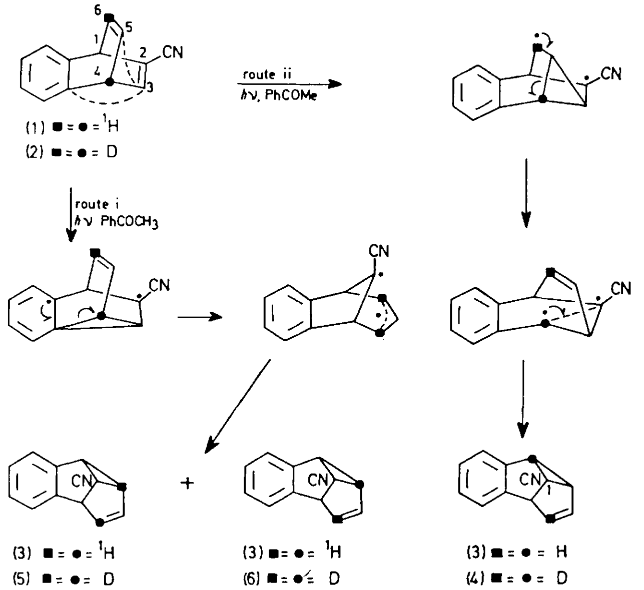
Summary Deuterium labelling reveals that 1-cyanobenzosemibullvalene derived from the sensitized irradiation of 2-cyanobenzobarrelene is formed by a di-π-methane rearrangement initiated by vinyl–vinylcyano-bridging and not by the benzo–vinylcyano-mechanism proposed by Houk.

RECENTLY Houk reported a molecular orbital model to account for the direction of preferred di-π-methane bridging in benzonorbornadiene and benzobarrelene systems with polar substituents.[1] One case which was claimed to be in accord with the bonding predictions was that of 2-cyanobenzobarrelene (**1**) which gives 1-cyanobenzosemibullvalene (**3**) from the triplet-excited manifold.[2]

Although there are two *a priori* di-π-methane rearrangements capable of furnishing (**3**) (Scheme: route i initiated by benzo-vinylcyano-bridging, and route ii initiated by vinyl–vinylcyano-bridging) Houk invoked exclusively route i. In order to distinguish between these two alternatives we have examined the photochemistry of the deuteriated mixture (**2**) of barrelenes.

The mixture (**2**), prepared by the addition of benzyne to *m*-deuteriobromobenzene, followed by treatment of the bromobarrelene with CuCN, consisted of an equal amount of two singly labelled isomers, one incorporating deuterium (92 ± 3%) at C-4 and the other deuterium (92 ± 3%) at C-6; within experimental error no deuterium isotope effects were discernable in the benzyne addition stage or in the subsequent photoisomerizations. Under conditions of triplet sensitization (450 W medium-pressure Hanovia lamp, Pyrex filter, acetophenone sensitizer, cyclohexane solution, nitrogen degassing) the barrelene mixture (**2**) gave only 1-cyanosemibullvalene (ϕ 0·36), the ^{1}H n.m.r. spectrum of which [τ (100 MHz, CCl_4) 2·66—3·05 (m, 4·00H, ArH), 4·34 (dd, 0·53 ± 0·04H, 6-H, $J_{5,6}$ 2·5, $J_{6,7}$ 5·0 Hz), 4·78—4·87 (m, 0·97 ± 0·04H, 7-H), 5·83 (br s, 1·02 ± 0·03H, 5-H), 6·37 (d, 0·56 ± 0·03H, 2-H, $J_{2,8}$ 7·0 Hz), and 6·67—6·78 (m, 1·03 ± 0·04H, 8-H)] is in accordance solely with the presence of mixture (**4**), since the labels appear exclusively and equally at C-2 and C-6.

Possible scrambling of the label in the mixture (**4**), *e.g. via* a degenerate photochemical vinyl-cyclopropane rearrangement, was examined. Direct irradiation of (**4**) (Corex filter, 80% conversion) gave a deuteriated mixture of 6-cyanobenzocyclo-octenes containing equal amounts of deuterium at C-5 and C-9 (ϕ 0·13), but the distribution of the label in recovered (**4**) was unchanged. Irradiation with acetophenone or acetone as sensitizer results in the disappearance of (**4**) ($\phi_{\text{dis}} < 0{\cdot}05$) to give unidentified products, but there was no change in the labelling pattern in (**4**) after 85% consumption. Thus the example reported in ref. 3 remains the only case of a semibullvalene observed to undergo a photochemical vinyl-cyclopropane rearrangement.[3]



SCHEME. Individual structures represent a 50:50 two-component mixture, each singly labelled with deuterium at the positions designated by ■ and ●.

Therefore Houk's account of the initial bonding process (route i) involved in the di-π-methane rearrangement of (**1**) is not in accord with our findings.

We thank the Spectroscopic Services Laboratory of the University of Alberta for the 100 MHz n.m.r. spectra, and acknowledge the financial support of the National Research Council of Canada, and the University of Lethbridge Research Committee.

(*Received*, *7th September* 1976; *Com.* 1042.)

---

[1] C. Santiago and K. N. Houk, *J. Amer. Chem. Soc.*, 1976, **98**, 3380.

[2] C. O. Bender and S. S. Shugarman, *J.C.S. Chem. Comm.*, 1974, 934.

[3] C. O. Bender and J. Wilson, *Helv. Chim. Acta*, 1976, **59**, 1469.