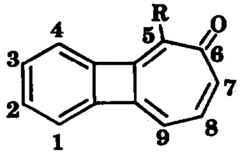
Tetrahedron Letters No. 2, pp 115 - 118, 1975. Pergamon Press. Printed in Great Britain.

BENZO[3,4]CYCLOBUTA[1,2-c]TROPONE

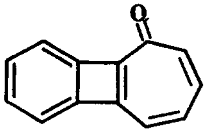
Luciano Lombardo and Dieter Wege*
Department of Organic Chemistry, University of Western Australia, Nedlands,
Western Australia 6009

(Received in UK 18 November 1974; accepted for publication 26 November 1974)

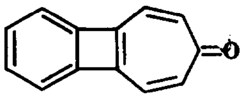
Following our synthesis of the benzo[3,4]cyclobuta[1,2]tropylium cation[1], we have been actively engaged in investigating routes to the three possible isomeric benzo[3,4]cyclobuta[1,2]tropones 1, 3, and 4. In each of these compounds the question of the extent of π-electron delocalisation in the 7-membered ring is of considerable interest. In particular, will 3 and 4 be reactive like benzocyclobutadiene[2], or possess sufficient stabilisation to be isolable? We report at this stage our synthesis of the title compound 1, and an approach to 3. A preparation of the chloro-derivative 2 has recently been recorded.[3]



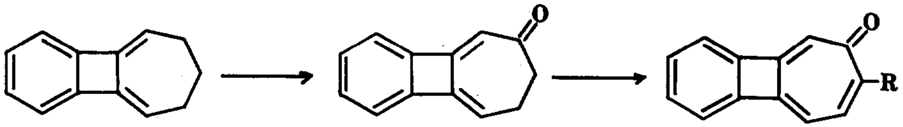
1 R=H
2 R=Cl



3



4

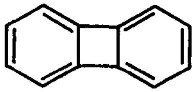


5

6

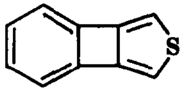
1 R=H
7 R=D

Allylic oxidation of diene 5[1] using CrO_3-pyridine-CH_2Cl_2 at 0° gave dienone 6[4] (21%), m.p. 92-4°, which with DDQ in refluxing benzene afforded 1 (9%), m.p. 97-8°; ^1H nmr δ ($CDCl_3$ 90 MHz) 7.2 (m, ArH), 6.61 (ddd, $J_{7,8}$ 12.0, $J_{8,9}$ 7.6, $J_{5,8}$ 0.5 H z, H_8), 6.46 (br s, H_5), 6.38 (ddd, $J_{7,8}$ 12.0. $J_{5,7}$ 1.3, $J_{7,9}$ 0.9 Hz, H_7), 6.27 (ddd, $J_{8,9}$ 7.6, $J_{5,9}$ 1.0, $J_{7,9}$0.9 Hz, H_9). Assignments were confirmed by preparing the deuterated derivative 7. The chemical shifts and coupling constants for H_7, H_8, and H_9 in 1 are very similar to the corresponding values reported[3] for the chlorotropone 2.[5] It is significant to note that the benzenoid protons in 1 resonate in the normal aromatic region at δ7.2. This is to be contrasted with biphenylene 8 and 2-thianorbiphenylene 9 where the benzenoid protons resonate at unusually high field[6]:



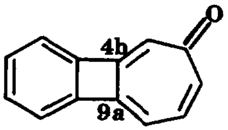
δ 6.7,6.6

8



δ 6.86

9



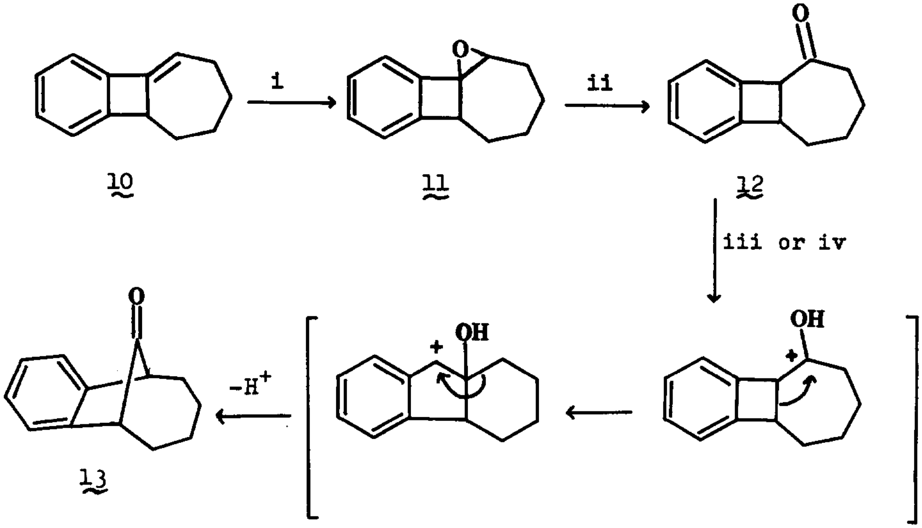
δ 7.2

1

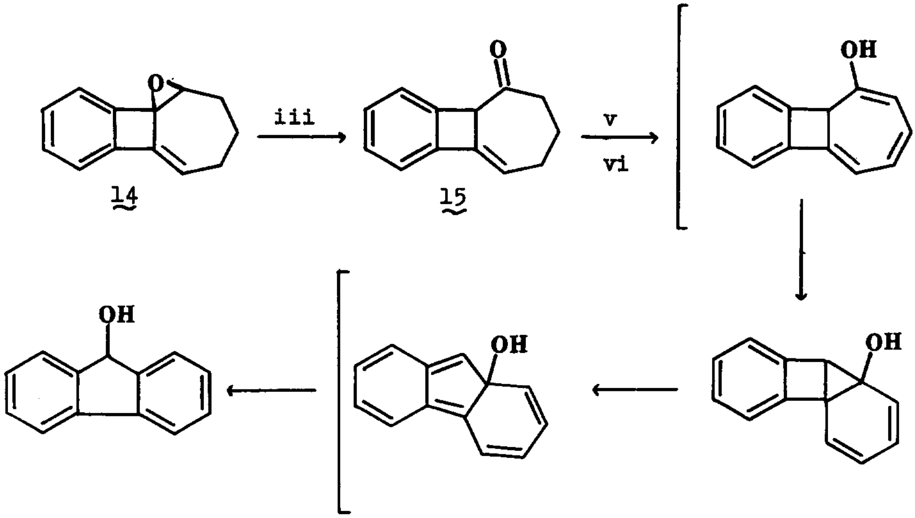
It has therefore been suggested[6] that the four-membered ring in 8 and 9 sustains a paramagnetic ring current, resulting in an upfield shift of the benzenoid protons. The fact that the benzenoid protons of 1 do not experience such shielding implies that in 1 there is no such paramagnetic contribution from the four-membered ring. Thus there must be a low π-bond order across the C_{4b}-C_{9a} bond in 1, and 1 must possess a highly localised dimethylenebenzocyclobutene system.

The crystal structure of tropone reveals marked bond alternation,[7] and the aromatic character usually attributed to tropone has been questioned.[8] The observation that the troponoid protons in 1 (and in 2) all resonate at higher field than in tropone (c δ7.0) suggests however that tropone does exhibit some diatropic[9] character.

Attempts to prepare the other two benzo[3,4]cyclobuta[1,2]tropones 3 and 4 have so far been unsuccessful. For example, ketone 12, a potential precursor for 3, proved to be extremely acid-sensitive, and underwent ready rearrangement to give the known[10] bridged ketone 13 in high yield (Scheme 1). A related rearrangement has recently been described by Caubere et al.[11] This type of rearrangement was completely suppressed in the unsaturated ketone 15, undoubtedly due to the poor migratory aptitude of the sp^2-hybridised carbon atom at the ring junction. However, bromination-dehydrobromination of 15 gave 9-fluorenol (25%) as the only isolable product. A possible mechanism, involving a 1,5-sigmatropic shift of a hydroxyl group, is shown in Scheme 2.



Scheme 1



Scheme 2

Reagents: i $\underline{m}$-Cl-C_6H_4-CO_3H ii BF_3 etherate-Na benzoate-benzene

iii BF_3 etherate iv acidic Al_2O_3 v NBS vi Et_4NBr-DMF-lutidine, 90°

References and Footnotes

1. L. Lombardo and D. Wege, *Tetrahedron Letters*, 4879 (1972).

2. M.P. Cava and M.J. Mitchell, "*Cyclobutadiene and Related Compounds*" Academic Press, New York 1967, p 180.

3. M. Sato, S. Ebine and J. Tsunetsugu, *JCS Chem. Comm.*, 846 (1974).

4. Satisfactory analytical and spectral data have been obtained for this and all other new compounds.

5. The numbering of these protons in the text of reference 3 does not correspond to the numbering used in the structural formula.

6. P.J. Garratt and K.P.C. Vollhardt, *J. Amer. Chem. Soc.*,*94*, 7087 (1972).

7. M.J. Barrow, O.S. Mills and G. Fillippini, *JCS Chem. Comm.*, 66 (1973).

8. D.J. Bertelli, T.G. Andrews and P.O. Crews, *J. Amer. Chem. Soc.*, *91*, 5286 (1969).

9. F. Sondheimer, *Acc. Chem. Research*, *5*, 81 (1972).

10. T. Miwa, M. Kato and T. Tamano, *Tetrahedron Letters*, 1761 (1969). We thank these workers for spectral data for compound **13**.

11. P. Caubere and M. S. Mourad, *JCS Chem. Comm.*, 1238 (1972); *idem*, *Tetrahedron*, *30*, 3439 (1974).