

SYNTHESIS AND PROPERTIES OF BENZO[3,4]CYCLOBUTA[1,2-c]TROPOLONE  
DERIVATIVES

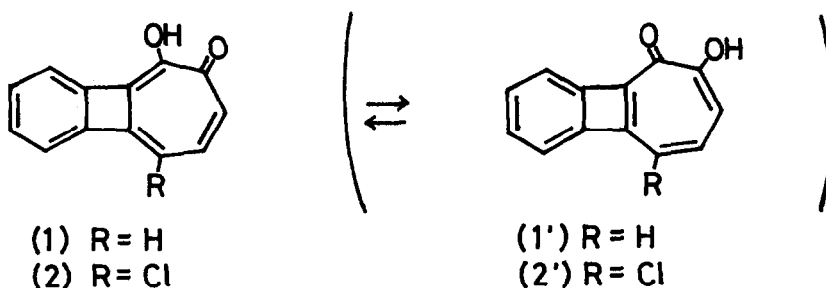
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(Received in Japan 22 January 1977; received in UK for publication 31 January 1977)

Considerable interest has recently been focused on the properties of fused polycyclic compounds containing both  $4n\pi$ - and  $(4n+2)\pi$ -electron ring systems. Of these compounds, biphenylene analogues, where one benzene ring of biphenylene is replaced by nonbenzenoid  $(4n+2)\pi$ -electron system, have been accumulated. A group of compounds includes norbiphenylene anion,<sup>1</sup> homobiphenylene cation,<sup>2</sup> benzo[3,4]cyclobuta[1,2-a]benzo[d]tropylium cation,<sup>3</sup> benzo[3,4]cyclobuta[1,2-c]-tropone derivatives,<sup>4,5</sup> and benzo[3,4]cyclobuta[1,2-a]dibenzo[d,e]cyclooctatetraenyl dianion.<sup>6</sup> Benzo[3,4]cyclobuta[1,2-c]tropolone (1) is a novel and unknown member of this type of compounds.

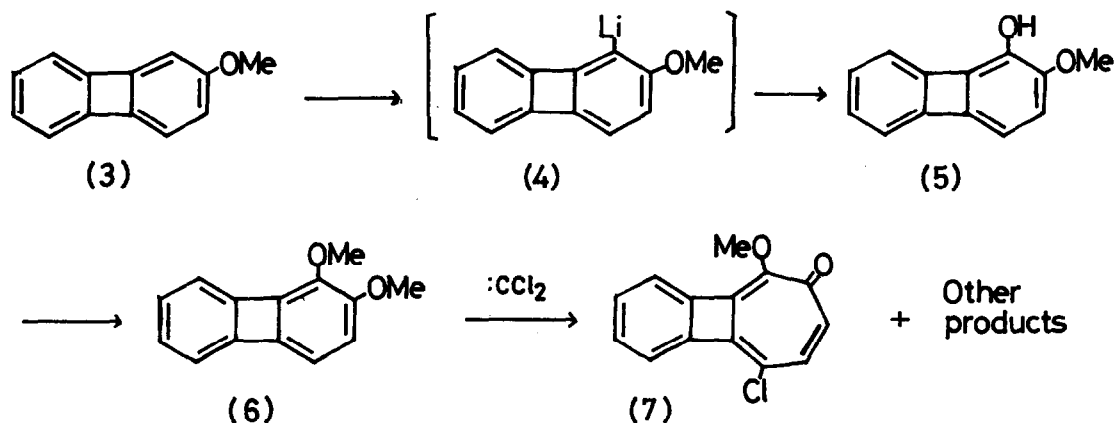


Much of the interest in this ring system centers around the question of the presence of the tautomerism  $(1) \rightleftharpoons (1')$ , and the extent of  $\pi$ -electron delocalization in the tropolone ring and hence on the degree of antiaromatic character of the central four-membered ring. We now wish to report the synthesis and some

properties of the 9-chloro derivatives (2) of benzo[3,4]cyclobuta[1,2-c]-tropolone (1).

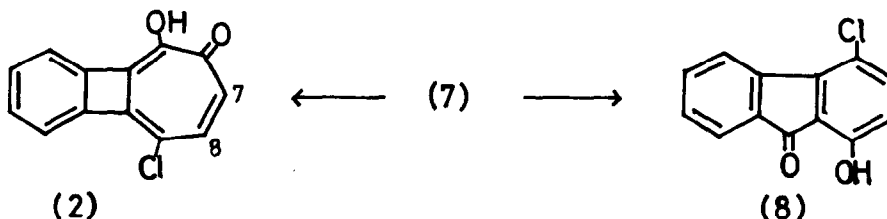
2-Methoxybiphenylene (3)<sup>7</sup> was metalated with *n*-butyllithium and the lithio intermediate, presumably (4), was allowed to react with *n*-butylborate, and the resulting biphenyleneboronic acid was subsequently oxidised with hydrogen peroxide to give 1-hydroxy-2-methoxybiphenylene (5)<sup>8,9</sup> (mp 94-95°, 61%). (5) was methylated with dimethyl sulfate and alkali to afford 1,2-dimethoxybiphenylene (6) (pale yellow needles, mp 132.5-133.5°) in nearly quantitative yield:

$\delta$  (CDCl<sub>3</sub>) 3.77 (s, 3H), 3.98 (s, 3H), 6.13 (d, 1H, J=8.0 Hz), 6.28 (d, 1H, J=8.0 Hz), and 6.5-6.83 (m, 4H). The reaction of (6) with dichlorocarbene, generated from chloroform, aqueous sodium hydroxide and a phase-transfer catalysis,<sup>10</sup> gave a complex mixture,<sup>11</sup> from which 9-chloro-5-methoxybenzo[3,4]cyclobuta[1,2-c]-tropolone (7) (yellow needles, mp 135-136°) was isolated by silica gel chromatography in 5.6% yield:  $\nu_{\text{CO}}$  (KBr) 1602 cm<sup>-1</sup>,  $\delta$  (CDCl<sub>3</sub>) 4.08 (s, 3H), 6.71 (d, 1H, J=13.2 Hz), 6.37 (d, 1H, J=13.2 Hz), and 7.12-7.4 (m, 4H),  $\lambda_{\text{max}}$  (EtOH) 312 nm (log $\epsilon$  4.54).



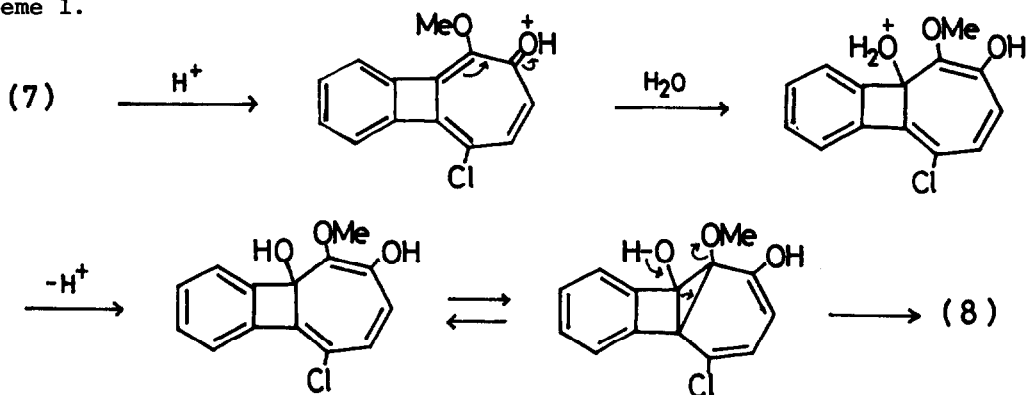
Attempt to hydrolyze the tropolone methyl ether (7) with concentrated hydrochloric acid in boiling ethanol led to the hydroxy fluorenone derivative (8) (yellow needles, mp 108-110°):<sup>12</sup>  $\nu_{\text{CO}}$  (KBr) 1690 cm<sup>-1</sup>. The facile rearrangement of (7) to (8) may be due to the release of the central four-membered ring strain, according to the route shown in Scheme 1. (7) was treated with boron tribromide in dichloromethane at -65° and subsequently hydrolyzed to give 9-chlorobenzo-

[3,4]cyclobuta[1,2-c]tropolone (2) (bright yellow needles, mp 207–208°) in 93% yield:  $\nu_{\text{CO}}$  (KBr) 1569 and  $\nu_{\text{OH}}$  3250  $\text{cm}^{-1}$ ,  $\delta$  ( $d_6$ -DMSO) 6.49 (d, 1H,  $J=13.3$  Hz), 7.02 (d, 1H,  $J=13.3$  Hz), 7.2–7.45 (m, 4H), and 10.3 (broad, 1H),  $\lambda_{\text{max}}$  (EtOH) 312 nm ( $\log \epsilon$  4.64), and  $m/e$  (60 eV) 230 (62%,  $M^+$ ), 202 (100%,  $M^+ - \text{CO}$ ), and 139 (62%,  $M^+ - 2\text{CO} - \text{Cl}$ ).



The tautomerism  $(2) \rightleftharpoons (2')$ , like monocyclic tropolone derivatives, is potentially expected. The equilibrium, however, has proved to be imposed predominantly or exclusively to the former tautomer (2) by the following facts: the electronic spectrum of (2) is extremely similar to that of the methyl ether (7). The nmr coupling constant between H-7 and H-8 ( $J=13.3$  Hz) of (2) is nearly the same as that ( $J=13.2$  Hz) of the corresponding protons of (7). If the equilibrium  $(2) \rightleftharpoons (2')$  exists, the coupling constant  $J_{7,8}$  in (2) should be reduced to the corresponding value ( $J_{6,7}=10.9$  Hz) of tropolone.<sup>13</sup> The high-field shift, which would be caused by the paramagnetic ring current of the central four-membered ring if (2') exists, is not observed in the benzenoid protons of (2). The tautomer (2') would be more unstable because of the partial contribution of antiaromatic cyclobutadiene structure in the central four-membered ring. The benzocyclobuta-tropolone (2) gave a red coloration in chloroform layer with aqueous ferric chloride, like monocyclic tropolone derivatives. (2) cannot be extracted with aqueous sodium bicarbonate but reacted with aqueous sodium carbonate to give a red precipitate from which (2) was recovered by neutralization with 2N-hydrochloric acid, suggesting that (2) has a considerable acidity. (2) was treated with diazomethane to give the methyl ether (7),<sup>14</sup> an alternate methyl ether of the tautomer (2') not being found after careful research of the reaction mixture.

Scheme 1.



## References and footnotes

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2. P. J. Garratt and K. P. C. Vollhardt, *Chem. Comm.*, 1143 (1971).
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6. C. S. Baxter, P. J. Garratt, and K. P. C. Vollhardt, *J. Amer. Chem. Soc.*, 91, 7783 (1969).
7. W. Baker, J. W. Barton, and J. F. W. McOmie, *J. Chem. Soc.*, 2658 (1958).
8. Satisfactory elemental analyses were obtained for all new compounds.
9. It should be noted that the  $\alpha$ -metalation of (3) is in contrast to the  $\beta$ -metalation of 2-methoxynaphthalene (e.g., See R. A. Barnes and W. M. Buch, *J. Amer. Chem. Soc.*, 81, 4705 (1959)).
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11. Another paper will be soon published concerning with the component compounds of this reaction mixture.
12. The structure of (8) has been also established by the independent synthesis.<sup>11</sup>
13. D. J. Bertelli, T. G. Andrews, Jr., and P. O. Crews, *J. Amer. Chem. Soc.*, 91, 5286 (1969).
14. A halo-2,3-benzotropolone shows a similar behavior on treatment with diazomethane: J. W. Cook, A. R. M. Gibb, and A. R. Somerville, *J. Chem. Soc.*, 603 (1952); S. Ebine, *Bull. Chem. Soc. Jpn.*, 35, 117 (1962).