Dichlorocarbene Addition to 1-Methoxybiphenylene. Formation of a Benzo[3,4]cyclobuta[1,2-*c*]tropone Derivative

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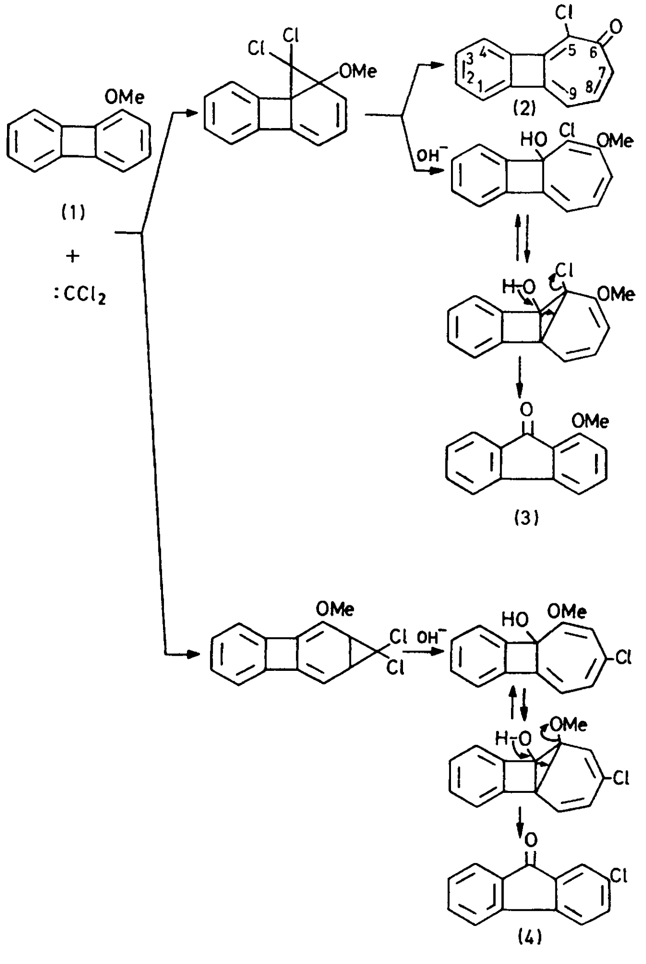
Summary 1-Methoxybiphenylene (**1**) reacts with dichlorocarbene to give 1-chlorobenzo[3,4]cyclobuta[1,2-*c*]tropone (**2**) and two fluorenone derivatives (**3**) and (**4**).

The compounds derived from fusion of the $4n\pi$-electron cyclobutadiene ring to $(4n + 2)$ π-electron non-benzenoid aromatic systems are of considerable interest with regard to aromatic character.[1,2] We now report the preparation and properties of the benzocyclobutatropone derivative (**2**).

Reaction of 1-methoxybiphenylene (**1**) with dichlorocarbene (3 mol. equiv.), generated by action of alkali on $CHCl_3$ in the presence of trimethyloctylammonium chloride, at room temperature for 2 h and chromatographic separation of the products afforded the chloro-compound (**2**) as pale yellow needles, m.p. 172—173°, in 1·7% yield with 55—65% recovery of the starting biphenylene. Elemental analyses and spectral properties are in agreement with the assigned structure; *m/e* 214 (M^+) and 186 (100%) ($M^+ -$ CO); $\delta(CDCl_3$; 100 MHz) 6·31 (1H, dd, $J_{4,5}$ 6·9, $J_{3,5}$ 1·4 Hz, 5-H), 6·51 (1H, dd, $J_{3,4}$ 12·6 Hz, 3-H), 6·72 (1H, dd, 4-H), and 7·1—7·5 (4H, m, benzenoid); ν_{max} (KBr) 1613 and 1603 cm^{-1} (CO and C = C); λ_{max} (EtOH) 294 nm (ϵ 47,000). The fusion of the cyclobutadiene ring with the tropone ring should result in π-electron localization in both rings, and the n.m.r. spectrum should provide information about the character of both the four- and seven-membered rings. The benzene ring protons move a little to higher field, in constrast to the case of biphenylene[3] and thianorbiphenylene[1] whose benzenoid protons show a large upfield shift. This may be accounted for if the four-membered ring is in the tetramethylenecyclobutane (or dimethylenecyclobutene) form and hence has little paramagnetic ring current effect arising from the cyclobutadiene structure. The upfield shift of the seven-membered ring protons in (**2**), compared with tropone ring protons (δ 7·0),[4] may be due to increased π-electron localization of the tropone ring rather than a paramagnetic ring current effect of the four-



Scheme

membered ring. $J_{4,5}$ in (**2**) is significantly smaller than $J_{3,4}$ (8·3 Hz)[5] in tropone itself, suggesting that the seven-membered ring in (**2**) has some distortion from planarity.

1-Methoxyfluorenone (**3**)[6] (0·8%) and 2-chlorofluorenone (**4**)[7] (1·3%) were also isolated from the reaction mixture by column chromatography. These were identical (mixed m.p. and i.r. spectra) with authentic samples.

A possible reaction mechanism is given in the Scheme.

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