Synthesis of a Cyclopropa[*b*]naphthalene

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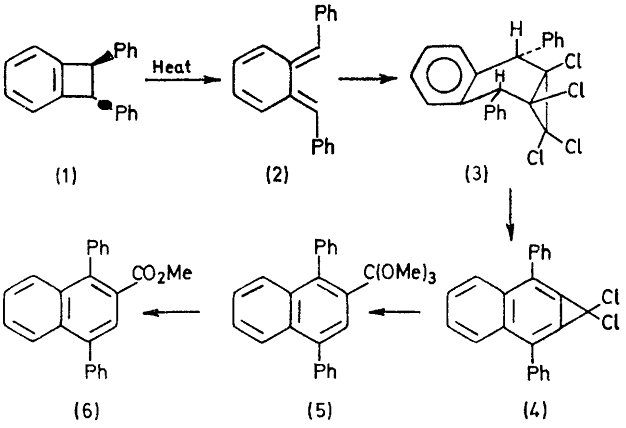
Summary Dehydrochlorination of the benzobicycloheptene (**3**) gives 1,1-dichloro-2,7-diphenylcyclopropa[*b*]naphthalene (**4**) in low yield; the three-membered ring is readily cleaved by protic solvent.

While the chemistry of cyclopropabenzene is well established,[1] no other aromatic system incorporating a linearly fused cyclopropene ring has been reported. Although cyclopropa[*b*]naphthalene is expected to have a high degree of π-bond localisation,[2,3] prior attempts to obtain derivatives of this ring system have failed.[3] We now report the synthesis of a cyclopropa[*b*]naphthalene derivative.



Of the synthetic methods available for the synthesis of cyclopropabenzenes,[1] the dehydrohalogenation of substituted bicyclo[4,1,0]hept-3-enes[4,5] appeared to be the most amenable to modification for the synthesis of cyclopropa[*b*]napthalenes. The electrocyclic ring-cleavage product (**2**) of the cyclobutabenzene (**1**) is known[6] to undergo $[_{\pi}4 + {}_{\pi}2]$cycloaddition and this consequently offers a simple synthesis of the desired benzobicycloheptene (**3**). Indeed, thermolysis of (**1**)[7] in the presence of tetrachlorocyclopropene[8] gives (**3**)† (80%), m.p. 171—172°. De-

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† Satisfactory microanalytical and spectral data were obtained for all new compounds reported.

hydrochlorination of (**3**) with a slight excess of $KOBu^t$ in tetrahydrofuran, in a manner strictly analogous to that used to obtain the corresponding *gem*-dichlorocyclopropabenzene,[5] resulted in discolouration and formation of the cyclopropanaphthalene (**4**)‡ [25%; m.p. 177—179°; δ ($CDCl_3$) 7·51—7·53 p.p.m. (complex m), ν_{max} (KBr) 1675, 1358, 1000, 770, 755, 715, and 695 cm^{-1}] which was isolated by fractional crystallisation.

The chemistry of (**4**) parallels that of the *gem*-dichlorocyclopropabenzene analogue. For example, treatment of (**4**) with methanol results in cleavage of the three-membered ring and formation of the naphthoate (**6**)[9] *via* the orthoester (**5**). An *X*-ray structure determination of (**4**) is being undertaken.

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‡ A mass value accurate to 1·6 p.p.m. was obtained for $C_{23}H_{14}{}^{35}Cl^{37}Cl$.

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