Preparation of 7,7-Difluoro-2,5-diphenylbenzocyclopropene by Halide Exchange

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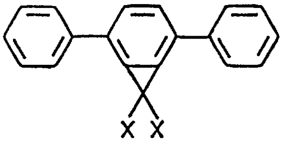
Summary 7,7-Dichloro-2,5-diphenylbenzocyclopropene (**1**) undergoes exchange with silver fluoride under mild conditions to yield 7,7-difluoro-2,5-diphenylbenzocyclopropene (**2**); a substituted benzocyclopropenium ion (**3**) is proposed as an intermediate of the reaction.

Solvolysis of 7,7-dichloro-2,5-diphenylbenzocyclopropene (**1**) in methanol results in cleavage of the cyclopropene ring to give methyl-2,5-diphenylbenzoate.[1] The reaction could proceed by direct addition of solvent to a single bond of the benzocyclopropene.[1] An alternative mechanism involves a substituted benzocyclopropenium ion (**2**) as an intermediate.[2] Theoretical calculations[3,4] ascribe aromatic stabilisation to benzocyclopropenium ions. These calculations are supported by the mass spectral fragmentation pattern of (**1**)[4] and of benzocyclopropene[2] itself, both showing important fragments corresponding to the respective benzocyclopropenium ions. Benzocyclopropenium ion has been postulated to be an intermediate in the reaction of trityl fluoroborate with benzocyclopropene.[2] The observation that halide exchange with (**1**) occurs under mild conditions and with preservation of the benzocyclopropene skeleton provides further evidence for the existence of benzocyclopropenium ions as reactive intermediates.

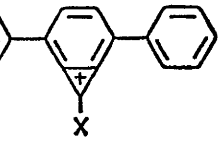
7,7-Dichloro-2,5-diphenylbenzocyclopropene (**1**) was stirred in the dark for 24 h at room temperature with a large excess of silver fluoride, suspended in dry acetonitrile. The difluoro-compound (**2**) was obtained (85%) after chromatography, m.p. 161—163°.†

The ready halide exchange of (**1**) is best explained by proceeding *via* substituted benzocyclopropenium ions (**3a**) and (**3b**). An analogous exchange mechanism has been demonstrated for tetrahalogenocyclopropenes in the presence of Lewis acids.[6] In the absence of Lewis acids an S_N2' or carbanion mechanism has been invoked to rationalise the experimental results.[7] The latter mechanisms would require participation of the cyclopropene double bond and skeletal rearrangements which are not compatible with the preservation of the benzocyclopropene structure in going from (**1**) to (**2**). The S_N2 mechanism is unlikely with halogenocyclopropenes[7] and with benzocyclopropene because of the strain that would develop in the transition state.[7]



(1) X=Cl

(2) X=F



(3)

a; X=Cl

b; X=F

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† The n.m.r., u.v., i.r., and mass spectral data are consistent with structure (**2**).

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