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1-CHLORO-1-FLUOROBENZOCYCLOPROPENE

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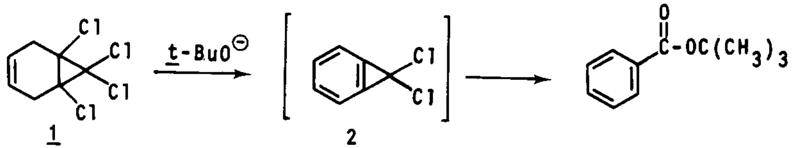
While 1,1-difluorobenzocyclopropene has been prepared more than 10 years ago by two independent routes,[1] all attempts to synthesize the analogous 1,1-dichloro compound (2) failed.[2]

Halton[3] has found that elimination of 1,6,7,7-tetrachlorobicyclo[4.1.0]hept-3-ene (1) with potassium-*t*-butoxide leads to *t*-butylbenzoate in 16% yield as the only isolable product,

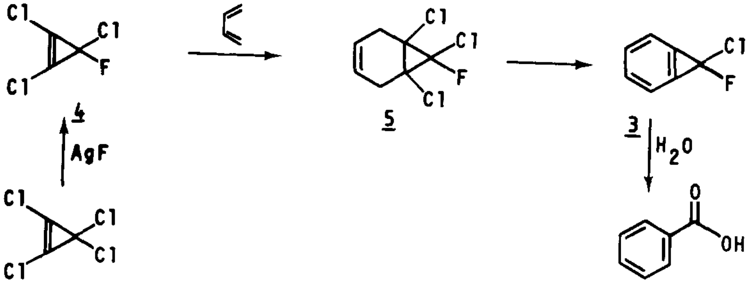


1 2

the formation of which is best accounted for by formation of the desired dichloro compound as a highly reactive, not isolable intermediate. In contrast, 1,1-dichloro-2,5-diphenylbenzocyclopropene is isolable at room temperature although it decomposes under very mild conditions.[4]

We now report the preparation of 1-chloro-1-fluorobenzocyclopropene (3), the first benzocyclopropene carrying two different halogen substituents. This compound is of interest in view of its use as precursor for the preparation of 1-fluorobenzocyclopropene and of the unsubstituted benzocyclopropenium ion.[5]

Our scheme for the preparation of 3 is shown below. 1,2,3-Trichloro-1-fluorocyclopropene was readily obtained in 40-60% yield by refluxing tetrachlorocyclopropene with silver fluoride. Cycloaddition of 2 with butadiene, as described by Tobey,[6] afforded 1,6,7-trichloro-7-fluorobicyclo[4.1.0]hept-3-ene (5) in 65% yield. Treatment of 3 with excess potassium *t*-butoxide in THF at -70 to 20° for 7 hours gave 3 (40%) together with polymeric material. 1-Chloro-1-fluorobenzocyclopropene was separated by preparative VPC (Apiezon column, 80°). The structure of 3



follows from its NMR and mass spectral data: The ^1H-NMR shows a multiplet at $\delta = 7.6$ which, upon F-decoupling, collapses to a symmetrical AA'BB' system. The ^{19}F signal appears as a triplet with $^4J_{HF} = 2.0$ Hz, at 97.5 ppm downfield from C_6F_6, in good agreement with the signal of 1-chloro-1-fluoro-2,5-diphenylbenzocyclopropene (97.8 ppm).[5] The characteristic cyclopropene IR-frequency is found at 1730 cm^{-1}.

Hydrolysis of 1-chloro-1-fluorobenzocyclopropene with water affords benzoic acid. This reaction is analogous to that of other dihalogenobenzocyclopropenes, which form benzoic acid derivatives *via* 1-halogenobenzocyclopropenium ion intermediates.[3,7]

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