Octafluorodibenzothiophen

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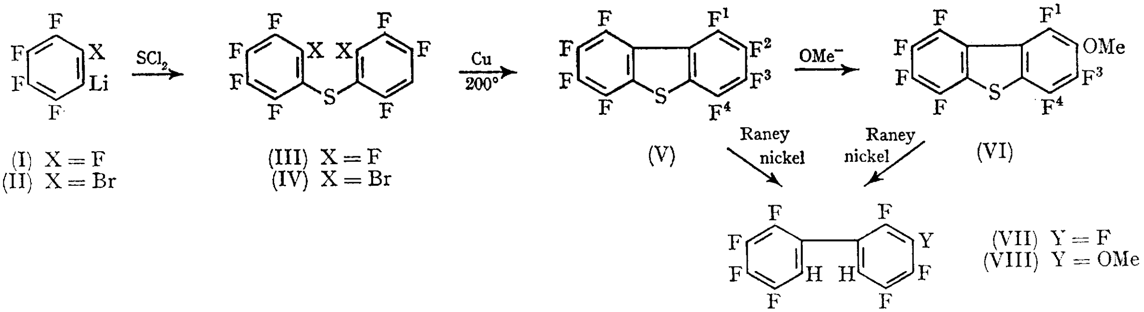
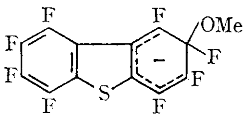
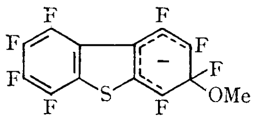
No fully fluorinated condensed-ring compounds containing one hetero-atom have previously been reported. We now describe the synthesis of octafluorodibenzothiophen. The latter, and other polyfluoroaryl–sulphur compounds can be conveniently prepared by using the known reaction of aryl-lithiums with sulphur dichloride. Pentafluorophenyl-lithium (I) reacts with sulphur dichloride giving bis(pentafluorophenyl) sulphide (III), a compound which, when this work began, had itself evaded synthesis[1] but has now been reported.[2] Correspondingly, 2-bromotetrafluorophenyl-lithium (II) in hexane–ether solution at $-75°$ with sulphur dichloride gave bis-(2-bromotetrafluorophenyl) sulphide (IV) and the latter compound on reaction with copper, in an evacuated sealed tube at 200° gave an almost quantitative yield of octafluorodibenzothiophen, m.p. 99—100°.



Octafluorodibenzothiophen showed considerable thermal stability, being recovered unchanged after 4 days at 420° in the presence of copper, but reaction with Raney nickel proceeded smoothly giving 2,2′-dihydro-octafluorobiphenyl (VII).

Nucleophilic substitution in this new class of fluoroaromatic compound was of considerable interest. With sodium methoxide in methanol, (V) gave a monoether (VI) which was cleaved by Raney nickel to give the biphenyl (VIII). The


(IX)


(X)

orientation of substitution was conveniently established by the ^{19}F and ^{1}H n.m.r. spectra on the basis of chemical-shift data and coupling respectively, and the spectrum of (VI) can only be accounted for with the methoxyl in the 2 position. This orientation indicates that sulphur stabilises the intermediate (IX) with respect to (X) and is consistent with the stabilisation of carbanions by sulphur which has been observed in other systems.[3]

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[1] P. Robson, M. Stacey, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1960, 4754.

[2] J. Burdon, P. L. Coe, and M. Fulton, *J. Chem. Soc.*, 1965, 2094; L. J. Belf, M. W. Buxton, and G. Fuller, *ibid.*, p. 3372.

[3] D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, 1965, p. 71.