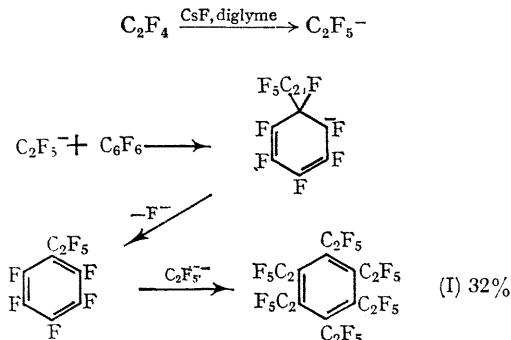


Benzocyclobutene and Stable Xylylene Formation from Hexakis(pentafluoroethyl)benzene

W. T. FLOWERS, R. N. HASZELDINE,* and J. E. G. KEMP

(Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD).

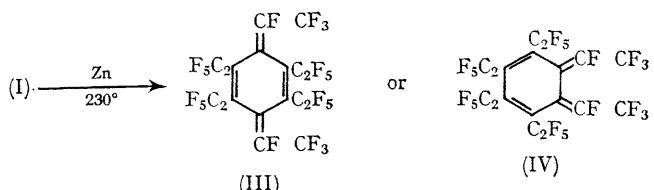
THE reaction of hexafluorobenzene with tetrafluoroethylene in the presence of fluoride ion at 135° has been found to give hexakis(pentafluoroethyl)benzene (I), m.p. 198–199° [^{19}F n.m.r. chemical shifts:[†] CF_3 (18F) –2·1; CF_2 (12F) +14·1; M^+ 786]



Perfluoroethylbenzene is more susceptible than hexafluorobenzene to nucleophilic substitution so that polyalkylation occurs in satisfactory yield, and without major concurrent anionic polymerisation of tetrafluoroethylene. A recent patent¹ describes independent work with dimethylformamide as solvent, but the yield of (I) so obtained is *ca.* 3%. Our own studies on dimethylformamide as solvent have failed to give (I), but have led to the isolation of the benzocyclobutene (II) m.p. 95° in 8% yield [CF_3 , (6F) –4·8, (6F) –3·0, (6F) –0·3; CF_2 (8F) +2 to +32 (complex); CF (2F) +81·4; λ_{max} 278 nm. (760), M^+ 748].

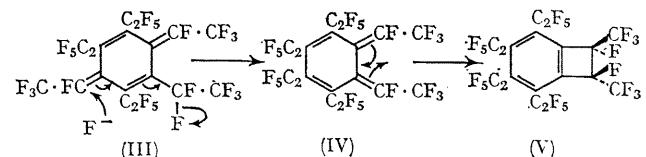
The reactivity of the benzylic fluorines in hexakis(pentafluoroethyl)benzene (I), possibly caused by steric strain, is sufficient to allow defluorination by zinc under relatively mild conditions. The product (m.p. 129°, 65% yield; M^+ 748) is not a styrene [*cf.* the defluorination of perfluoroethylbenzene²], but is either the *p*-xylylene (III) or the *o*-xylylene (IV), and not a mixture of (III) or (IV).

Neither the n.m.r. spectrum of the product [CF_3 , (6F) –8·0, (6F) –0·4, (6F) +3·1; CF_2 , (4F) +22·4, (4F) +31·1; CF , (2F) +23·1] nor its chemical reactions enable the structure to be assigned unambiguously to either (III) or (IV), and it will be noted that (III) and (IV) would readily be



interconverted by fluoride ion addition–elimination reactions. This, the first example of a stable monocyclic xylylene (*cf.* ref. 2), exhibits i.r. absorptions at 1590 and 1690 cm^{-1} and a u.v. maximum at 266 nm. (8050) [*cf.* octafluorostyrene,³ 1793 cm^{-1} ; 265 nm. (1400)]. The benzocyclobutene (II) is obtained in 58% yield by fluoride-ion isomerisation of the xylylene. One stereoisomer of (II) is obtained, and on steric grounds this is considered to have *trans*- CF_3 groups.

Satisfactory elemental analyses and mass spectra have been obtained for the compounds mentioned.



(Received, December 23rd, 1968; Com. 1773.)

[†] Chemical shifts are p.p.m. from $\text{CF}_3\text{CO}_2\text{H}$, measured on the liquid phase at 200°; the fine structure of most of the bands is complex due to restricted rotation of the fluoro-alkyl groups and long-range coupling and will be discussed in detail in the full publication.

¹ I.C.I. Ltd., B.P. 1,076,357/1967.

² R. F. Hill and G. H. Mitchell, *Chem. Comm.*, 1968, 1243, and references therein.

³ B. F. Letchford, C. R. Patrick, M. Stacey, and J. C. Tatlow, *Chem. and Ind.*, 1962, 1472.