

SHORT COMMUNICATION

Proto-debromination of some Polybromopolyfluorobenzenes

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Debromination of hexabromobenzene by methanolic sodium methoxide in ethyl methyl ketone (EMK) [1,2] has been thought to involve nucleophilic attack upon bromine and not upon carbon [2]; some similarities can be found with the "halogen barn-dance" [3]. Nucleophilic attack upon carbon does not occur readily in hexabromo- and hexachlorobenzene [2,4,5], and the alternative displacement at halogen is only found [2] with polybromoarenes. This reaction might prevail because nucleophilic displacement at carbon is slow [4,5] when chloride or bromide ions are being expelled. This hypothesis might be tested by a study of the reaction of polybromopolyfluorobenzenes with methanolic sodium methoxide in EMK. The halogen substituents in these compounds facilitate both debromination (nucleophilic attack upon bromine) and defluorination (nucleophilic attack upon carbon).

Bromopentafluorobenzene, *p*-dibromotetrafluorobenzene, and fluoropentabromobenzene, were each (0.005 mole) boiled with sodium methoxide (0.005 mole) in methanol-EMK (50 ml.; 1:4) for one hour. The organic reaction products were characterised by ¹⁹F-NMR (56.4 MHz; Varian HA-60) and confirmed, where possible, by mass spectrometry.

Bromopentafluorobenzene gave pentafluorobenzene and *p*-bromotetrafluoroanisole (3:1); 60% of the starting material remained. GLC confirmed this and further identified a second bromotetrafluoroanisole. The relative yields of these isomers agreed with that found in the reaction of bromopentafluorobenzene with methanolic sodium methoxide [6]. *p*-Dibromotetrafluorobenzene gave entirely 2,3,5,6-tetrafluorobromobenzene; 30% of the starting material remained.

Fluoropentabromobenzene appeared to give 2,3,4,5-tetra- and 3,4,5-tri-bromofluorobenzene (see Table); the relative extents of loss of bromine and fluorine could not be assessed.

Fluorine displacement from *p*-dibromotetrafluorobenzene by methoxide ion does not occur appreciably under our conditions. Even with bromopentafluorobenzene, where the bromine substituent activates this nucleophilic displacement, anisole formation accounts for only one quarter of the reaction product. Bromine displacement occurs at a similar rate in both compounds, and seems to be less perturbed by substituent effects in the aromatic system than fluorine displacement. This is consistent with a mechanism of base-catalysed proto-debromination in which the rate-determining step is attack upon the exocyclic bromine substituent, rather than the ring carbon atom.

TABLE 1

^{19}F NMR chemical shifts used for identification *

Bromopentafluorobenzene	133.7	155.7	161.7	
	132.5	154.7	160.6	[7]
Pentafluorobenzene	139.3	155.5	164.6	
	139.1	154.0	162.6	[8]
<i>p</i> -Bromotetrafluoroanisole	135.9	156.8		
<i>p</i> -Bromotetrafluorophenetole	135.3	156.0		[9]
<i>p</i> -Dibromotetrafluorobenzene	132.55			
	131.7			[10]
2,3,5,6-Tetrafluorobromobenzene				
	134.3	138.0		
	132.8	137.5		[11]
2,3,4,5-Tetrabromofluorobenzene		97.8**		
3,4,5-Tribromofluorobenzene		107.0***		

*p.p.m. upfield of fluorotrichloromethane (solvent)

**1:1 doublet; $J = 7$ Hz

***1:2:1 triplet; $J = 7$ Hz

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