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REACTIONS OF TETRAFLUOROBENZYNE WITH [2,2]-PARACYCLOPHANE

J. P. N. Brewer, H. Heaney and B. A. Marples
Department of Chemistry, The University of Technology, Loughborough, Leicestershire

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Abstract—Tetrafluorobenzyne reacts with [2.2]-paracyclophane to give a mono-, and a bis-adduct. The structures of these compounds are reported and their mass spectra briefly discussed.

WE HAVE previously reported[2] the reactions of tetrafluorobenzyne with benzene and other simple aromatic hydrocarbons. Whereas mixtures of 1,4-cyclo-adducts are obtained with many alkyl-substituted benzenes *p*-xylene only affords one product. It was logical therefore to extend our work to include [2,2]-paracyclophane, and we report now our results of reactions of tetrafluorobenzyne with this hydrocarbon. Ciganek[3] has reported the results of reactions of dicyanoacetylene with aromatic hydrocarbons, including *p*-xylene and [2,2]-paracyclophane, and our results complement these.

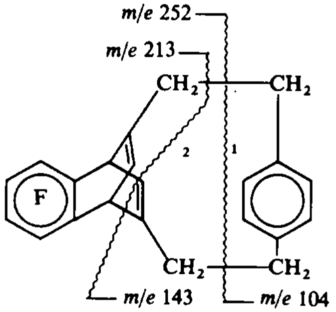
Tetrafluorobenzyne, generated from pentafluorophenyl-magnesium bromide (1·5 moles), at 80° in the presence of [2,2]-paracyclophane, gave compound I, m.p. 197°, in 44% yield. The product was separated from unchanged starting material by TLC on silica impregnated with silver nitrate. The structure is evident from PMR and mass spectra. The former shows signals at τ 3·01 (four aromatic protons), singlet; τ 4·18 (two vinylic protons), doublet ($J \simeq 6$ c/s) further broadened by allylic coupling to —CH_2— and C—H; τ 5·60 (two bridgehead protons), doublet ($J \simeq 6$ c/s) further broadened by allylic coupling to =C—H and by long-range coupling to fluorine; and at τ 6·68–7·89 (eight methylene protons), complex multiplet. The UV spectrum shows $\lambda_{max}^{cyclohexane}$ 218 (ε 25,250), 233 (inf) (ε 21,150), 284·5 (ε 950), and 294 mμ (ε 750). The mass spectrum (Table 1) shows the molecular ion peak at *m/e* 356 and the base

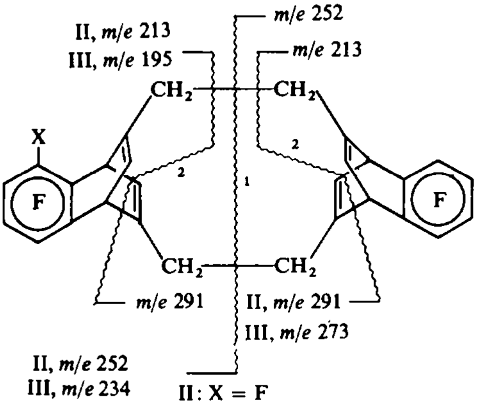
TABLE 1

Adduct	*m/e*	Relative abund. %	Adduct	*m/e*	Relative abund. %	Adduct	*m/e*	Relative abund. %
I	356	64	II	504	45	III	486	62
	252	23		291	52		291	42
	213	31		252	14		273	42
	187	23		213	100		252	16
	143	29		187	68		234	16
	104	100					213	100
							196	100
							187	71
							169	67

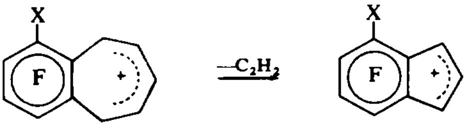
peak resulting from cleavage 1, appears at m/e 104. The same cleavage may occur with charge retention by the fluorinated fragment to give m/e 252. Cleavage 2 gives ions of m/e 213 and m/e 143. It seems likely that the former fragment corresponds to the tetrafluorobenzotropyllium ion (IVa) which has previously been reported[2c] to lose acetylene and give the tetrafluorobenzocyclopentadienyl ion (Va; m/e 187). This latter ion is observed in the spectrum (Table 1).

Di-adducts (possibly mixtures) were obtained in similar reactions using excess pentafluorophenylmagnesium bromide (4 moles). We have previously observed the presence of compounds derived from bromotrifluorobenzyne in reactions of tetrafluorobenzyne generated from the above Grignard reagent.[2c] We were unable to separate compounds containing bromine by preparative TLC. The mixture of adducts was therefore treated in ethereal solution with n-butyl lithium (the amount added was estimated from the GLC of the mixed di-adducts). Rechromatography on silica gel impregnated with silver nitrate gave compounds II, m.p. 314°, and III, m.p. 297°, in 39 and 15% yield respectively. The PMR spectrum of II shows the presence of four olefinic protons as a doublet ($J \simeq 6$ c/s) of multiplets at τ 3·7; four bridgehead protons as a doublet ($J = 6$ c/s) of multiplets at τ 5·2; and eight methylene protons as a multiplet at τ 7·18–7·68. In the mass spectra of II and III cleavages 1 and 2, similar to those observed in compound I, are important. Charge retention by either fragment of these cleavages is again observed. In compound II, the molecular ion peak occurs at m/e 504 and cleavage 1 gives the ion of m/e 252, observed for compound I. The base peak corresponds to the tetrafluorobenzotropyllium ion (IVa; m/e 213) which arises from cleavage 2, as does the ion at m/e 291. The ion IVa, as expected, loses acetylene to give Va. In compound III, the molecular ion peak is observed at m/e 486 and ions at m/e 273, 234, 195 (IVb) and 169 (Vb) accompany those at m/e 291, 252, 213 (IVa) and 187 (Va) due to the unsymmetrical nature of III.





II: X = F
III: X = H



IV a: X = F, m/e 213
b: X = H, m/e 195

V a: X = F, m/e 187
b: X = H, m/e 169

EXPERIMENTAL

Reaction of tetrafluorobenzyne (1·5 *mole*) *with* [2.2]-*paracyclophane*. [2.2]-Paracyclophane (2 g) and cyclohexane (50 ml) were added to a soln of pentafluorophenylmagnesium bromide from pentafluorobromobenzene (3·6 g) in ether. The ether was removed by distillation until the vapour temp reached 79°. The mixture was then heated under reflux for 5 hr, cooled, and hydrolysed with 4N HCl. The solvents were removed, and the residue was taken into chloroform and dried ($MgSO_4$). Removal of the solvent gave a light-brown solid (4·1 g). Preparative TLC, first on silica (eluting with benzene–light petroleum, 1:9) and then on silica:silver nitrate (9:1) gave I (44%, 1·6 g) m.p. 197°, from chloroform–ether: ν_{max} 3065, 3020, 2985, 2920, 2850, 1490, 1288, 1070, 1000 and 784 cm^{-1}. (Found: C, 73·9; H, 4·65; F, 21·2. $C_{22}H_{16}F_4$ requires: C, 74·15; H, 4·35; F, 21·35%).

Reaction of tetrafluorobenzyne (4 *moles*) *with* [2.2]-*paracyclophane*. A similar reaction using pentafluorophenylmagnesium bromide (4M) gave a mixture of products (9 g) which were partially separated by PLC on silica by elution with light petroleum:benzene (92:8) to give a mixture (4·5 g). Analytical gas chromatography showed the presence of two compounds in the ratio of 5·5:4·5 in order of increasing retention time. This mixture was treated with n-BuLi in ether (45% of one equiv) at 0°. The solution was allowed to warm to room temp and after 4 hr was hydrolysed with HCl. The organic layer was dried ($MgSO_4$) and the solvents removed to leave a residue which was rechromatographed on silica containing 10% $AgNO_3$ eluting with benzene:light petroleum (9:1). Two fractions were obtained and shown to be the *adduct* II (1·9 g) (39%) m.p. 314°: ν_{max} 3060, 2980, 2940, 2915, 2850, 1495, 1485, 1070, 1000, 845 and 775 cm^{-1}. (Found: C, 66·4; H, 3·1; F, 29·8. $C_{28}H_{16}F_8$ requires: C, 66·65; H, 3·15; F, 30·15%).

The second fraction (0·75 g) which was not obtained analytically pure was shown, by mass spectrometry, to be the adduct III contaminated with material still containing bromine.

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