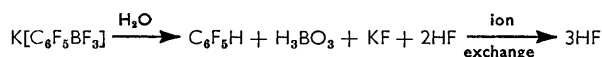


955. *Polyfluoroaryl Organometallic Compounds. Part III.*¹
Potassium Pentafluorophenyltrifluoroborate

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PENTAFLUOROPHENYLBORON DIHALIDES,^{1,2} tris(pentafluorophenyl)boron,³ and derivatives of the former compounds are the first stable perfluorocarbon derivatives of tervalent boron which have been prepared, and the only stable perfluoroalkylboron compounds are salts of the anion $[\text{CF}_3\text{BF}_3]^-$, obtained by the reaction $\text{Me}_3\text{SnCF}_3 + \text{BF}_3 \longrightarrow \text{Me}_3\text{Sn}[\text{CF}_3\text{BF}_3]$.⁴ The analogous reaction of trimethylpentafluorophenyltin gave pentafluorophenylboron difluoride¹ but we have found that potassium pentafluorophenyltrifluoroborate is precipitated by condensing pentafluorophenylboron difluoride into an aqueous solution of potassium fluoride, $\text{C}_6\text{F}_5\text{BF}_2 + \text{KF} \longrightarrow \text{K}[\text{C}_6\text{F}_5\text{BF}_3] \downarrow$, a method used to obtain $\text{K}[\text{CH}_2=\text{CHBF}_3]$.⁵ Surprisingly, the complex ions mentioned above, together with $[\text{Ph}_3\text{BF}]^-$, appear to be the only ions of this type which have been investigated.⁶

As indicated, potassium pentafluorophenyltrifluoroborate was only sparingly soluble in water at 20° and on heating the aqueous solution, hydrolysis occurred. Thus, the salt was hydrolysed by boiling water to give, after ion-exchange of the product, three equivalents of acid,



Hydrolysis was not rapid below 40–50° since the potassium salt was conveniently purified by recrystallisation from aqueous ethanolic solution after heating to this temperature and, furthermore, the titre, after ion-exchange of aliquot portions of the aqueous ethanolic solution, did not change significantly (<3%) over five days. However, the value of the titre was significantly higher (~30%) than required for the exchange, $\text{K}[\text{C}_6\text{F}_5\text{BF}_3] \longrightarrow \text{H}[\text{C}_6\text{F}_5\text{BF}_3]$, suggesting that the free acid is hydrolytically very unstable. This was tested by titrating aliquot portions of a solution of the acid, made by the exchange process, after various intervals of time and it was observed that the titre changed only very slowly, *i.e.*, only ~6% increase of the total in 4 hr. and ~13% after 13 hr. Thus, the hydrolysis of the salt which does take place during the ion-exchange process must occur in contact with the resin and does not reflect the instability of the salt or the free acid in aqueous solution. The ease of hydrolysis of pentafluorophenyl derivatives of tervalent boron has already been illustrated¹ but the instability of the quatercovalent boron derivative, $\text{K}[\text{C}_6\text{F}_5\text{BF}_3]$, to boiling water is surprising, especially in the light of the comparative inertness to hydrolysis of the ion $[\text{CF}_3\text{BF}_3]^-$.⁴

Barium and silver pentafluorophenyltrifluoroborates could not be precipitated from aqueous ethanolic solution and the solubilities of these salts thus parallel those of the tetrafluoroborates⁷ but, in contrast with this, addition of $\text{K}[\text{C}_6\text{F}_5\text{BF}_3]$ to a cooled solution of

¹ Part II, R. D. Chambers and T. Chivers, *J.*, 1965, 3933.

² R. D. Chambers and T. Chivers, *J.*, 1964, 4782.

³ A. G. Massey and A. J. Park, *J. Organometallic Chem.*, 1964, 2, 245.

⁴ R. D. Chambers, H. C. Clark, and C. J. Willis, *J. Amer. Chem. Soc.*, 1960, 82, 5298.

⁵ S. L. Stafford, *Canad. J. Chem.*, 1963, 41, 807.

⁶ D. L. Fowler and C. A. Kraus, *J. Amer. Chem. Soc.*, 1940, 62, 1143.

⁷ A. G. Sharpe, *Adv. Fluorine Chem.*, 1960, 1, 63.

benzenediazonium chloride did not give a precipitate in a way analogous to that in which benzenediazonium tetrafluoroborate is precipitated, as indicated by a control experiment. Both the infrared and the fluorine-19 n.m.r. spectra of the potassium salt were complicated by the pentafluorophenyl group. The infrared spectrum had bands at 1056 and 1027 cm^{-1} , probably due to B-F stretch but not distinctive as in the case of tetrafluoroborates which absorb at 1050 and 1075⁷ cm^{-1} ; and the n.m.r. spectrum gave only three well resolved areas of absorption, approximately in the ratio 5 : 1 : 2, the low-field area thus containing overlapping B-F and *ortho* C-F fluorine resonances.

Thermal decomposition of the potassium salt occurred quite sharply *in vacuo*, in the region of 300°, although the results were variable. The residue always contained potassium tetrafluoroborate, which was extracted with aqueous ethanol, and the infrared spectrum of the organic residue showed bands at 1487 cm^{-1} , characteristic of a polyfluoroaryl system, at 1075 cm^{-1} , characteristic of an *ortho*-⁸ or *meta*-linked⁹ perfluoropolyphenylene, and at 961 cm^{-1} , characteristic of a corresponding *para*-linked system.¹⁰ Also, during one pyrolysis, a small amount of a lower-molecular-weight perfluoropolyphenylene sublimed and the carbon analysis corresponded to a terphenyl but the infrared spectrum differed from that of *para*-perfluoroterphenyl. Thus, production of potassium tetrafluoroborate and perfluoropolyphenylenes represents a very unusual polymerisation process, $\text{K}[\text{C}_6\text{F}_5\text{BF}_3] \xrightarrow{\Delta} \text{KBF}_4 + -[\text{C}_6\text{F}_4-]_n-$. A benzyne mechanism could account for *ortho*-links, and it is significant to note that no perfluorobiphenylene could be isolated, but a process leading to the formation of other links is difficult to formulate.

Experimental.—*Potassium pentafluorophenyltrifluoroborate.* Pentafluorophenylboron difluoride (5.19 g., 24 mmoles) prepared by the fluorination of pentafluorophenylboron dichloride with antimony trifluoride¹ was transferred under vacuum into a solution of potassium fluoride (1.4 g., 24 mmoles) in water (20 ml.). A solid was precipitated (4.1 g., 62%) which was recrystallised from aqueous ethanol (the solution not being heated above 40–50°) and gave *potassium pentafluorophenyltrifluoroborate*, m. p. 324° (Found: C, 27.1; F, 55.8. $\text{C}_6\text{BF}_5\text{K}$ requires C, 26.3; F, 55.5%). A portion of the salt was heated in aqueous solution under reflux for one hour and then passed through a cation-exchange column; titration of the resulting solution gave 3.1 equivalents of acid (required, 3.0 equivalents). The fluorine-19 n.m.r. spectrum showed only three resolved peaks, in the ratio 5 : 1 : 1.8, at 134.25 (*ortho* C-F and B-F), 159.89 (*para* C-F), and 164.22 (*meta* C-F), measured from trifluoroacetic acid as external reference.

Pentafluorophenyltrifluoroboric acid. An aqueous ethanolic solution of $\text{K}[\text{C}_6\text{F}_5\text{BF}_3]$ was passed through a cation-exchange column and the resulting solution titrated with standard sodium hydroxide. Variable results, requiring between 1.3 and 1.4 equivalents of base, were obtained but the titre still remained at this level (1.4 equivalents) after the solution of the potassium salt had been standing for 5 days.

Pyrolysis of $\text{K}[\text{C}_6\text{F}_5\text{BF}_3]$. The salt was carefully dried *in vacuo* and then ground in a mortar; a portion of this material was heated *in vacuo* in a small-scale sublimation apparatus. The temperature was raised slowly and decomposition occurred in the region of 300°. The residue was extracted under reflux with portions of aqueous ethanol and distillation of the extracts left potassium tetrafluoroborate (correct infrared spectrum).

In one experiment a small amount of material sublimed (Found: C, 44.9. Calc. for $\text{C}_{18}\text{F}_{14}$: C, 44.8%) and the infrared spectrum contained strong bands at 1504, 1466 (doub.) cm^{-1} and medium bands at 1007, 970, 934, and 706 cm^{-1} . The spectrum differed from that of an authentic sample of *para*-perfluoroterphenyl and the material melted over a broad temperature range, 150–170°, indicating a mixture of terphenyls.

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⁸ R. A. Faulk, *Sperry Engineering Review*, 1963, 16, (No. 3), 24.

⁹ J. Thrower, personal communication.

¹⁰ J. Thrower and M. A. White, Abs. of the 148th Meet., Amer. Chem. Soc., Aug.–Sept. 1964, K39.