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# HOMOLYTIC REACTIONS OF POLYFLUOROAROMATIC COMPOUNDS IX.* ABSTRACTION REACTIONS OF SOME *p*-SUBSTITUTED TETRAFLUOROPHENYL RADICALS

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## Summary

The decomposition of pentafluoroaniline, 2,3,5,6-tetrafluoroaniline and its 4-bromo and 4-methoxy analogues by pentyl nitrite gives the corresponding aryl radicals which, when generated in the presence of chloroform, carbon tetrachloride, or bromotrichloromethane, remove atoms from these solvents to give substituted benzenes. The ease of removal of X from $XCCl_3$ decreases in the order X = Br,H > Cl.

The yield of substituted benzene product depends upon the *p*-substituent of the polyfluoroaniline and is greatest for tetrafluoro-*p*-anisidine.

## Introduction

Aryl radicals generated by the decomposition of either benzoyl peroxide or of aryldiazonium species will abstract atoms from some aliphatic molecules and are also able to attack aromatic systems to give biaryls [2]. A recent modification of the Gomberg reaction [3] involves the interaction of pentyl nitrite and aromatic amines in suitable substrates to give biaryls [4]. This process is thought to involve aryldiazonium intermediates. It has been used successfully to prepare a number of polyfluorinated biaryls from the appropriate anilines [5], and aryl radicals thus generated have been used in abstraction reactions involving chloroform or bromotrichloromethane when the high yields of some products made the reaction attractive as a preparative route [6].

Abstraction reactions involving polyfluorinated radicals also seem to be of interest, both in giving further information on the properties of aryl radicals and in possible synthetic potentialities. We now report a study of the abstraction reactions of the pentafluoro-2,3,5,6-tetrafluoro-, 4-bromo-2,3,5,6-tetrafluoro- and 4-methoxy-2,3,5,6-tetrafluoro-phenyl radicals in chloroform and in bromotrichloromethane.

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* For Part VIII, see ref. 1.

TABLE 1

Yields of abstraction products from chloroform or bromotrichloromethane

| | $CHCl_3$ | $BrCCl_3$ | |
|---|---|---|---|
| Aryl radical (Ar•) | ArH (%) | ArCl (%) | ArBr (%) |
| $C_6F_5$ | 18 | 0.5 | |
| $C_6F_5$ | | 1.1 | 43 |
| $4H$—$C_6F_4$ | 21 | 9 | |
| $4H$—$C_6F_4$ | | 11 | 22 |
| 4Br—$C_6F_4$ | 18 | 1 | |
| 4Br—$C_6F_4$ | | 3 | 32 |
| 4MeO—$C_6F_4$ | 47 | 3 | |
| 4MeO—$C_6F_4$ | | 8 | 72 |

## Results and discussion

When either chloroform or bromotrichloromethane were used, two possible abstraction products were formed (Table 1). Hydrogen is removed more readily than chlorine from chloroform and bromine is similarly preferred in abstraction from bromotrichloromethane.

$$Ar\cdot + HCCl_3 \rightarrow ArH + \cdot CCl_3 \qquad (1)$$

$$Ar\cdot + BrCCl_3 \rightarrow ArBr + \cdot CCl_3 \qquad (2)$$

$$Ar\cdot + Y\text{—}CCl_3 \rightarrow ArCl + \cdot CCl_2Y \ (Y = Br \text{ or } H) \qquad (3)$$

The relative yields of these products reflect the relative rates of the abstraction reactions. The selectivity of the radicals is evidently dependent upon the bond being broken since bromine is removed more easily than chlorine; the stability of the resulting radical fragment is also important for hydrogen is removed preferentially to chlorine from chloroform, although the bond strengths of the C—Cl and C—H bonds would suggest otherwise. Arguments based upon bond strengths alone cannot be completely satisfactory for carbon tetrachloride appears to be less reactive than either chloroform or bromotrichloromethane.

The relative extents of reaction depend upon the aryl radical as well as the substrate. For instance, hydrogen is removed at 36 times the rate of chlorine from chloroform by the pentafluorophenyl radical, but this ratio diminishes to about two when the 2,3,5,6-tetrafluorophenyl radical is involved. Figure 1 shows, however, that the relative reactivities of the aryl radicals in the various abstracting reactions are proportional regardless of the atom removed, for the graph of two relative rates of abstraction is sensibly linear although not of unit slope.

Although the relative rates of abstraction may be satisfactorily described in this way, the absolute yields of products vary considerably. A detailed

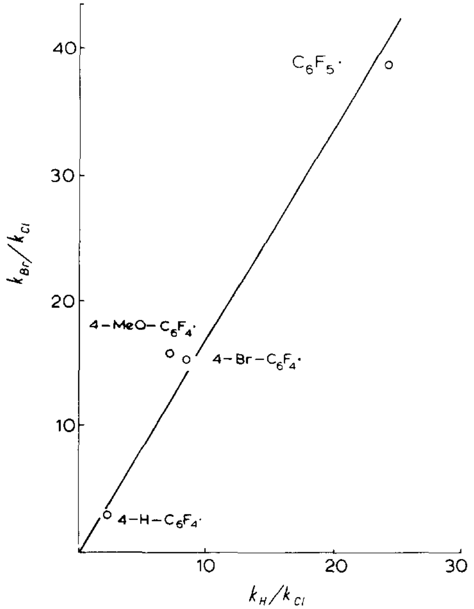

Fig. 1. Relative rates of abstraction reactions of some aryl radicals, as measured by product yields.

study of the abstraction reactions of bromotrichloromethane by pentafluorophenyl radical failed to account for substantial amounts of the reagents other than by abstraction. Trace amounts of decafluorobiphenyl and hexachloroethane could be detected, but the bulk of the reagents were destroyed to form orange-red tars from which no identifiable components could be completely separated. A phenolic fraction and a basic fraction could be separated by the use of aqueous sodium hydroxide or dilute acid but none of these fractions (or others arising from column chromatography) gave crystalline material. Doubtless such side-products arose in part from nucleophilic attack upon the radical precursors; phenols may arise either from displacement of the diazonium ion or of fluorine in such reactions.

While the discrete steps between the primary aromatic amine and the derived aryl radical have not been elucidated, the simplest scheme accounting for the experimental observations is shown in equations (4) and (5).

$$\mathrm{ArNH_2 + RONO = ArN{=}NOR + H_2O} \tag{4}$$

$$\mathrm{ArN{=}NOR = Ar\cdot + N_2 + \cdot OR} \tag{5}$$

The diazo ether is thought to undergo homolysis, in a similar manner to a number of analogous species [7], to give aryl radicals [8]. This conclusion remains true whether the covalent diazo ether or the free diazonium ion is involved. The latter is suggested by the formation of azo dyes [5] and of phenols but this is not unequivocal evidence of their presence. It is certainly true that when the amino substituent is replaced by $-N_2^+$, the aromatic system providing the aryl radical is activated towards nucleophilic attack; displacement can involve not only the diazonium group itself, but also suitable groups (*e.g.* F, Cl, Br, $NO_2$) *ortho* or *para* to the diazonium group. The precursor of the aryl radicals is therefore more vulnerable to nucleophilic attack than the parent amine or the final product, and attack both by water and by the aromatic amine must remove radical precursor and hence lower the yields of the products of reaction of the aryl radical.

If it is assumed that the four fluorine substituents show a constant electronic effect regardless of the substituent in the *para* position, the resistance of these precursors to nucleophilic displacement of the diazonium group would lie in the order $p$-OMe $<$ $p$-H $<$ $p$-F $<$ $p$-Br, which is the order of increasing electron withdrawal [9]. This is also the order in which the groups would be expected to assist displacement of fluorine atoms, to judge from relative rates of displacement in some pentafluorophenyl derivatives [10]. While the observations only approximate these expectations, nucleophilic attack of the radical precursors does offer a consistent explanation of the variations in the yields of abstraction products.

Our results show that abstraction reactions do occur with polyfluorophenyl radicals and polyhalogenomethanes but that with a few exceptions the yields of these products do not make this method competitive with existing routes for the introduction of halogen or hydrogen into polyfluoroaromatic systems.

## Experimental

Pentafluoroaniline and 2,3,5,6-tetrafluoroaniline were commercial products (I.S.C. Avonmouth). 4-Bromo-2,3,5,6-tetrafluoroaniline [11] was prepared by conventional methods, although in low yield. 4-Chloro-2,3,5,6-tetrafluorobenzene, b.p. 122 - 124 °C/757 mmHg, was obtained from chloropentafluorobenzene through the corresponding chlorotetrafluorophenylhydrazine [12]; the bromo analogue was similarly prepared. 4-Chloro- and 4-bromo-2,3,5,6-tetrafluoroanisole were obtained by nucleophilic displacement of fluorine by methoxide ions from the appropriate halogeno-pentafluorobenzene. 4-Chloro-2,3,5,6-tetrafluorobromobenzene, b.p. 178 - 180 °C, was prepared by bromination ($Br_2/Ag_2SO_4$) [13] of 2,3,5,6-tetrafluorochlorobenzene; other methods of bromination [14] failed in our hands. Pentafluorobromobenzene and pentafluorochlorobenzene were commercial samples as were 1,4-dibromotetrafluorobenzene and 2,3,5,6-tetrafluoroanisole. All compounds were purified by crystallisation or by fractional distillation until gas chromatography showed no impurities.

Decompositions were carried out in purified chloroform or bromotrichloromethane at reflux temperature and under an atmosphere of nitrogen. The products were identified by gas chromatographic analysis either *via* their retention times relative to an internal standard or by adding known amounts of authentic material. The amounts of these components were determined both by comparison with known weights of added authentic material and by comparison with the internal standard; calibration graphs were necessary to compare the response of the instrument (Perkin–Elmer F21) towards the various compounds.

Detailed investigation of the orange-red residue left after distillation of the solvent and the products of abstraction gave no crystalline material. Column chromatography ($Al_2O_3$) gave much tarry red material whose physical properties and UV and IR spectra yielded little except evidence for the presence of azo linkages and of a polyfluorophenyl system. Part of the residue was soluble in dilute sodium hydroxide but gave material which again showed little except the presence of (phenolic?) hydroxyl groups and of a polyfluoroaromatic system; the acid-soluble fraction of the tar similarly showed the presence of N—H groups and C—F bonds.

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