$S_{RN}1$ Substitutions of Halogenoperfluoroalkanes (CF_3Br or CF_2Cl_2) under Pressure

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Radical chain fluoroalkylation of arenethiolates by CF_3Br or CF_2Cl_2, performed under slight pressure in a glass apparatus, gives aryl polyfluoromethyl sulphides.

Halogenoperfluoroalkanes (Freons) are noted for their inertness.[1] In the case of CF_3Br and CF_2Cl_2, some reactivity has been observed when powerful nucleophilic reagents such as organolithium derivatives are used. These condensations often lead to partial (or even total) decomposition of the perfluoroalkyl group.[2,3]† We describe here the reactivity of these perhalogenomethanes with arenethiolates under special conditions.

The gaseous trifluoromethyl bromide does not react if it is simply bubbled through a solution of arenethiolates in dimethylformamide (DMF). We obtained only very small amounts of the sulphides (**1**) by carrying out the reaction in an autoclave at 80 °C. We report here that the condensation can be achieved in glass apparatus at room temperature when a pressure of about 2 atm is used, and under these conditions the trifluoromethyl aryl sulphides (**1**) were obtained in 62% yield for Ar = Ph, 75% for Ar = *p*-MeC_6H_4, and 83% for Ar = *p*-$MeOC_6H_4$ [reaction (1)].

$$\underset{}{ArSK + CF_3Br \longrightarrow \underset{(\mathbf{1})}{ArSCF_3}} \qquad (1)$$

Inhibition experiments with nitrobenzene (0.025—0.1 mol of inhibitor for 0.1 mol of arenethiolate in 100 ml of DMF) are clear cut‡ and show that a radical chain mechanism, similar to the one described by Kornblum and Bunnett for benzyl and aryl halides, is involved.[4] The chain process can be written as in reactions (2)—(5).

$$ArS^- + CF_3Br \longrightarrow ArS^{\cdot} + [CF_3Br]^{\cdot-} \qquad (2)$$

$$[CF_3Br]^{\cdot-} \longrightarrow CF_3^{\cdot} + Br^- \qquad (3)$$

$$ArS^- + CF_3^{\cdot} \longrightarrow [ArSCF_3]^{\cdot-} \qquad (4)$$

$$[ArSCF_3]^{\cdot-} + CF_3Br \longrightarrow ArSCF_3 + [CF_3Br]^{\cdot-} \qquad (5)$$

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† It has been possible to introduce a fluoroalkylgroup ($-CF_2Br$) from the more reactive CF_2Br_2 or CF_2BrCl by capture of the intermediate difluorocarbene (ref. 7). The introduction of a halogenoperfluoroalkyl group can also be achieved with these reagents through a radical chain process similar to the one observed with iodoperfluoroalkanes (D. Cantacuzene, C. Wakselman, and R. Dorme. *J. Chem. Soc., Perkin Trans. 1*, 1977, 1365) as shown in the condensation with uncharged nucleophiles (I. Rico, D. Cantacuzene, and C. Wakselman, *Tetrahedron Lett.*, 1981, **22**, 3405).

‡ We have also observed a clear-cut inhibition by nitrobenzene in the condensation of benzenethiolate with perfluorohexyl bromide in DMF at atmospheric pressure. The inhibition by nitrobenzene of the similar condensation with perfluorohexyl iodide is not so efficient. However in that case inhibition by styrene has been reported recently (A. E. Feiring, *J. Fluorine Chem.*, 1984, **24**, 191).

The initiation step is likely to be the electron transfer (2) from the arenethiolate to the trifluoromethyl bromide. Radical anions $[CF_3X]^{\cdot}$ (with X = Cl, Br, or I) have been observed as stable species by e.s.r. spectroscopy at very low temperature; their breakdown to give a trifluoromethyl radical and a halide ion has also been followed by e.s.r.[5] The slight pressure used for the condensation can easily be obtained in a Parr apparatus. This pressure seems to increase the concentration of CF_3Br in the solution and the chain process can occur.

Therefore, the use of the expensive CF_3I and u.v. irradiation[6] is not necessary for the trifluoromethylation of arenethiolates.

The behaviour of CF_2Cl_2 has also been examined under these conditions.§ The major compound obtained is the chlorodifluoromethyl aryl sulphide (**2**) [yield: (**2**) 62%, (**3**) 8%, (**4**) 7% with PhSK; yield: (**2**) 44%, (**3**) 8%, (**4**) 6% with p-MeC_6H_4SK; reaction (6)].

$$\mathrm{ArS^- + CF_2Cl_2 \longrightarrow \underset{(\mathbf{2})}{ArSCF_2Cl} + \underset{(\mathbf{3})}{ArSCF_2H} + \underset{(\mathbf{4})}{ArSCF_2SAr}} \qquad (6)$$

Inhibition of the substitution by nitrobenzene shows that the mechanism with CF_2Cl_2 is similar to the one proposed for CF_3Br. The radical anion $[CF_2CL_2]^{\cdot -}$ has also been observed.[5] The formation of the side product (**4**) can be explained by the decomposition of the radical anion $[ArSCF_2Cl]^{\cdot -}$ to the radical $ArSCF_2^{\cdot}$ which can react further with the arenethiolate anion.[7]

The condensation of arenethiolates with CF_3Br or CF_2Cl_2 gives aryl polyfluoromethyl sulphides in fair to good yields. The method used is cheap and can be applied to polyhalogenosulphides in the agrochemical field,[8] the properties of which are due to their high lipophilicity.[9]

This type of condensation is the first example of monosubstitution of these poorly reactive reagents by a radical chain process.

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§ We have observed previously a partial condensation of CF_2Cl_2 with benzenethiolate under u.v. irradiation; however, the main product obtained was the disubstituted product (**4**) (ref. 7).