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PRELIMINARY NOTE

A New Approach to Di(perfluoroaryl)methanes Utilising Sulphone-Stabilised Carbanions

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SUMMARY

Phenylsulphonyl stabilised carbanions react with fluorinated aromatic compounds forming aryl- and diaryl-methyl sulphone derivatives. These are reductively cleaved to give aryl- and diaryl-methane derivatives.

The reactions of various carbanions with unsaturated fluorocarbons have been previously investigated (e.g. fluorocarbanions [1], and the carbanions derived from nitriles and esters [2-4]). The generation of sulphone-stabilised carbanions is also well known but the reactions of these species with unsaturated fluorocarbons have not been reported.

Phenylsulphonyl stabilised carbanions are of particular interest. These species are known to react cleanly and efficiently with a wide range of alkyl halides and carbonyl compounds to form new carbon-carbon bonds [5-7]. Furthermore, the phenylsulphonyl fragment can often be reductively cleaved from the rest of the molecule later on in the synthetic sequence [7].

This process therefore presents an intriguing approach to making carbon-carbon bonds to perfluorinated aromatics via nucleophilic aromatic substitution and hence a route to the corresponding mono-methyl derivatives (7) and di(perfluoroaryl)methanes (6) (Scheme 1).

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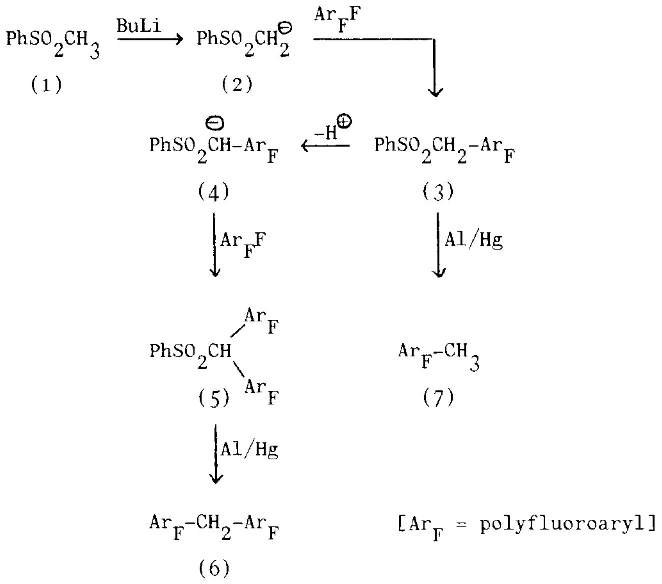
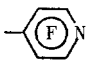
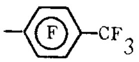


Scheme 1

Our investigation showed that when sulphone (1) was treated with ca. one equivalent of butyl lithium, followed by 2 - 3 equivalents of the perfluorinated aromatic compound (C_6F_6, $C_6F_5CF_3$, fluorinated heterocycles both mono- and di-substitution occurred, indicating that carbanion (4) is rapidly formed by proton exchange of (3) with (2) to give the more stable anion. The results are shown in Table 1.

Table 1

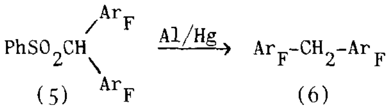
$$(1)\ \xrightarrow{\text{i) BuLi}\quad\text{ii) }Ar_FF}\ (3)\ +\ (5)$$

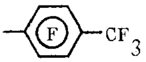
Ar_F	(3) % yield	(5) % yield
C_6F_5	17 - 23	18*
	13 - 28	42 - 60
	26	49
	26	–

* crude product treated with Al/Hg and isolated as $CH_2(C_6F_5)_2$

The reductive cleavage of the phenylsulphonyl fragment from the disubstituted product (5) occurred smoothly at room temperature on treatment with aluminium amalgam to give the corresponding di(perfluoroaryl)methane (6) in high yield (Table 2).

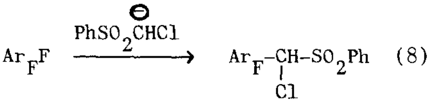
Table 2

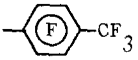
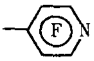


(5) Ar_F	(6) % yield
	74
	92

When $PhSO_2CH_2Cl$ was converted to the corresponding carbanion [8] and treated with perfluorinated aromatic compounds, it was found that the monosubstituted product (8) could be isolated in fair to good yields (Table 3).

Table 3



Ar_F	(8) % yield
C_6F_5	29
	74
	64

Work is currently being carried out to extend the scope of this nucleophilic substitution reaction to other unsaturated fluorocarbons. Also, the chemistry of the series of novel α-chlorosulphones (8) is being investigated.

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