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Isomerisation Accompanying Fluorodenitration of Trifluoromethyl Activated Diphenyl Sulfones

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Abstract: Fluorodenitration of 2-(4-chlorobenzene sulfonyl)-5-nitrobenzotrifluoride using tetramethyl ammonium fluoride affords a mixture of 2-fluoro-5-nitrobenzotrifluoride and two isomers of (4-chlorobenzene sulfonyl)-fluorobenzotrifluoride

In our present work,[1] we are interested in the use of ortho-trifluoromethyl substituted diphenyl sulphones to modify the thermal, electrical, mechanical and hydrophobic properties of poly (aryl ether) sulphones.

Synthesis of poly (aryl ether) sulphones requires halide ended monomers [2] which may readily be prepared from their nitro analogues. In this work, we have used tetramethyl ammonium fluoride (TMAF) as the fluorinating agent, which has been shown to be more effective than the traditional KF/PTC system.[3]

2-(4-Chlorobenzene sulfonyl)-5-nitrobenzotrifluoride was prepared by heating 5.0g (25 mmol) sodium 4-chlorobenzene sulfinate[4] and 8.0g (35 mmol) 2-chloro-5-nitrobenzotrifluoride in 30 mls N,N-Dimethyl Acetamide (DMAc) for 10 minutes.[5] Fluorodenitration on a 5 mmol scale with 1.1 equivalent of TMAF[3] at 80°C was followed by g.c. and after five minutes, no starting material was detected. The ratios of the reaction products identified by g.c.-m.s.; 2-fluoro-5-nitrobenzotrifluoride (1), 2-(4-chlorobenzenesulfonyl)-5-fluorobenzotrifluoride (2) and its isomer (3) were monitored (fig.1).

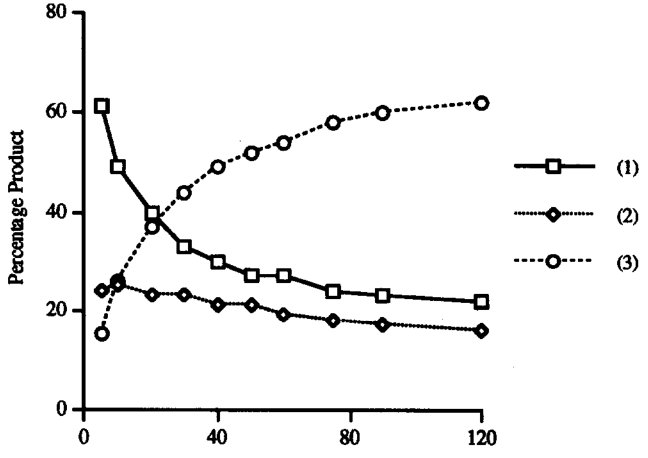

Figure 1. Reaction of 2-(4-chlorobenzenesulfonyl)-5-nitro benzotrifluoride with TMAF

A similar reaction profile was observed at lower temperatures (60°C) whereas using five equivalents of TMAF gave 4-nitro-2-trifluoromethylphenol. This is presumably due to the activation of residual water by fluoride.[6]

In the fluorodenitration of 2-(4-chlorobenzenesulfonyl)-5-nitrobenzotrifluoride, initial attack would either give fluorodenitration (to produce 2-(4-chlorobenzenesulfonyl)-5-fluorobenzotrifluoride), (**2**) or fluorodesulfonylation,[6] with the latter being favoured on electronic grounds.

4-Chlorobenzenesulfinate is sufficiently activate to react with 2-fluoro-5-nitrobenzotrifluoride[1], the expected reaction being nucleophilic substitution of the aryl fluoride, regenerating the substrate. However, since starting material is not observed during the course of the reaction, we assume that it rapidly re-reacts. An alternative reaction is the nucleophilic substitution of the nitro group to produce 5-(4-chlorobenzenesulfonyl)-2-fluorobenzotrifluoride), (**3**), the isomer of (**2**). Since neither of these isomers are nitro activated, further reaction is not favoured. However, during substrate synthesis, the isomer (**3**) is not observed in significant quantities so this route seems unlikely. A side product observed during substrate synthesis was identified as 2,5-di-(4-chlorobenzenesulfonyl)benzotrifluoride (**4**) which accounted for up to 10% of the reaction mixture.

(**4**) was prepared separately by heating 5g (25 mmol) sodium 4-chlorobenzenesulfinate and 5.67g (25 mmol) 5-chloro-2-nitrobenzotrifluoride, in 30 mls DMAc for 15 minutes, with no 2-nitro-5-(4-benzenesulfonyl)-benzotrifluoride being detected.[5] Fluorodenitration of this substrate using 1.1 equivalent of TMAF at 80°C resulted in total conversion to (**3**) in under 5 minutes. Formation and subsequent fluorodenitration of this intermediate therefore seems the most likely route to this second isomer (figure 2).

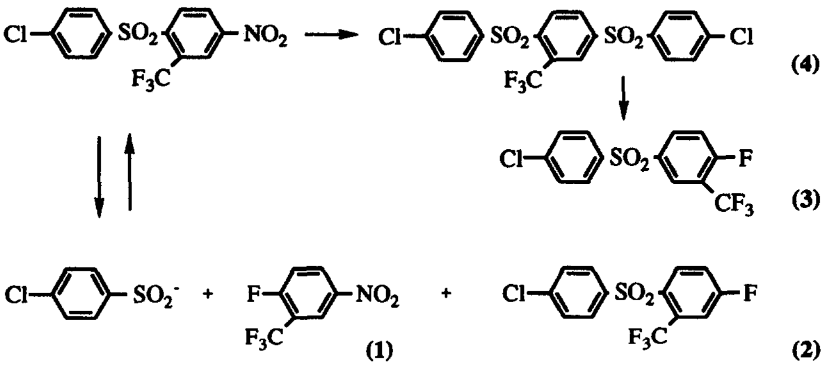

Figure 2. Mechanism of fluorodenitration of 2-(4-chlorobenzenesulfonyl)-5-nitrobenzotrifluoride.

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References and Notes

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5. Substrates were isolated by pouring onto crushed ice, filtering and recrystallisation from ethanol. They were characterised by G.C.-M.S., ^{19}F NMR, and gave satisfactory elemental analysis.
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