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A SOLVENT EFFECT UPON REACTION OF SULPHUR TETRAFLUORIDE
WITH 4-NITROBENZALDEHYDE

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SUMMARY

4-Nitrobenzaldehyde reacts with sulphur tetrafluoride in the absence of solvent to give a 94% yield of bis-(4-nitro- α -fluorobenzyl) ether. The reaction in benzene solution gives 4-nitrobenzylidene fluoride as the only product.

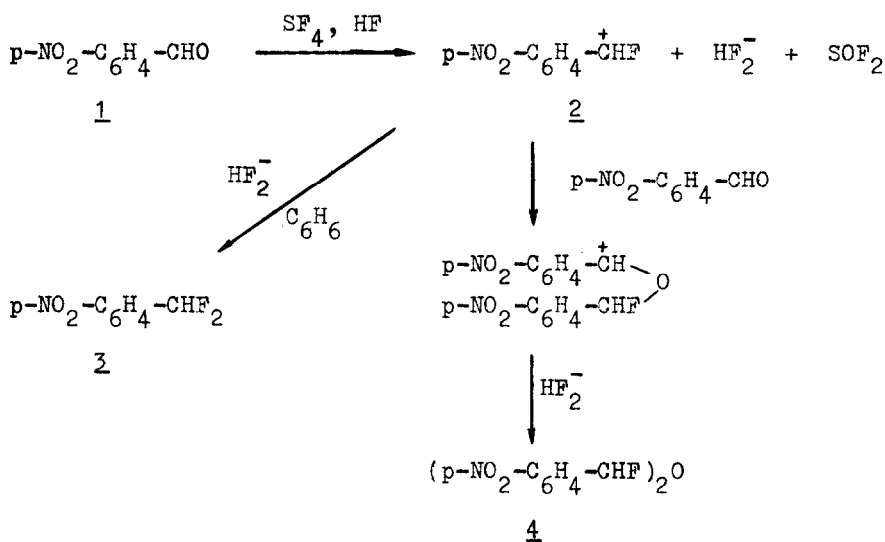
INTRODUCTION

Reactions of sulphur tetrafluoride with carbonyl compounds are generally conducted without solvent. Although, in some cases inert solvents have been used to moderate the vigour of the reaction [1], in no case was a solvent reported to alter the direction of the fluorination reaction. Experiments carried out in this laboratory showed that most aromatic aldehydes react with sulphur tetrafluoride in the usual way to give the corresponding benzylidene fluorides thus confirming the literature data [2].

Results obtained when 4-nitrobenzaldehyde was reacted with sulphur tetrafluoride without a solvent, and the influence of the solvent on the course of the reaction, are however exceptional.

RESULT AND DISCUSSION

4-Nitrobenzaldehyde 1, when treated with sulphur tetrafluoride at 150° without a solvent, gave bis-(4-nitro- α -fluorobenzyl) ether 4 with a 94% yield. However, when benzene was used as the reaction medium, the course of the reaction was totally altered and a 71% yield of 4-nitrobenzylidene fluoride 3 was obtained as the only product. According to the general carbocationic mechanism for the reaction of sulphur tetrafluoride with carbonyl compounds [3,4] formation of both products 3 and 4 may be explained as follows*:



The influence of the solvent on the reaction pathway may be interpreted statistically by considering decreased concentration of both carbocation 2 and aldehyde 1 (a 0.3 molar solution) or, in terms of solvation and therefore low reactivity of the former.

* Hydrogen fluoride is always present in the reaction medium due to reaction of SF₄ with moisture.

Attempted preparation of bis-(α -fluorobenzyl) ethers from other benzaldehydes under various reaction conditions failed. The most probable explanation is the instability of the ethers; benzyl ethers are known to decompose easily under acidic conditions [5]. Thus, it may be concluded that ether 4 is stable to the rather forcing conditions which are required for the reaction of aldehyde 1 with sulphur tetrafluoride, as a result of the stabilising effect of the nitro group.

EXPERIMENTAL

Melting and boiling points are uncorrected. NMR spectra were recorded with a JEOL INM-4H-100 spectrometer: chemical shifts are in ppm from internal CCl_3F for ^{19}F spectra (positive upfield) and from internal TMS for ^1H spectra (positive downfield). Sulphur tetrafluoride was prepared by a technique used in this laboratory [6]. 4-Nitrobenzaldehyde was pure grade commercial reagent.

Bis-(4-nitro- α -fluorobenzyl) ether 2 (nc)

A stainless steel autoclave (0.1 dm³ capacity) was charged with 4-nitrobenzaldehyde (19.0 g, 0.126 mole), cooled in a dry ice-acetone mixture, evacuated to 1-2 mm Hg and then sulphur tetrafluoride (30.0 g, 0.28 mole) was condensed in it. The autoclave was heated in a rocking muffle furnace at 150° for 6 hours. After completion of the reaction, the autoclave was allowed to cool to ambient temperature, gaseous products (SF_4 , SOF_2) were let off, and the solid residue was recrystallised from acetone to give 19.2 g of ether 2. Yield 94.2%, m.p. 120-121° (Found: C, 51.9; H, 3.1; F, 11.7%. $\text{C}_{14}\text{H}_{10}\text{F}_2\text{N}_2\text{O}_5$ requires C, 51.3; H, 3.0; F, 11.7%). ^1H and ^{19}F NMR (in $(\text{CD}_3)_2\text{CO}$): $\delta(\text{CHF}) = 7.17$ ppm (doublet of triplets), $\delta(\text{C}_6\text{H}_4) = 8.16$ ppm (AB quartet), $\delta(\text{CHF}) = 117.7$ and 124.4 ppm (doublet of triplets), $^2\text{J}(\text{HF}) = 63$ Hz, $^4\text{J}(\text{HF})$, $^4\text{J}(\text{FF})$ and $^4\text{J}(\text{HH}) = \text{ca. } 4\text{-}5$ Hz.

4-Nitrobenzylidene fluoride 3

4-Nitrobenzaldehyde (9.0 g, 0.06 mole), benzene (200 ml) and sulphur tetrafluoride (20.0 g, 0.19 mole) were placed in a 0.5 dm³ autoclave. The autoclave was heated in a rocking muffle furnace at 110-115° for 15 hours. The reaction mixture was washed with water, dried over MgSO₄ and benzene was distilled off. The residue was distilled under vacuum to give 7.3 g of **3**. Yield 71%, b.p. 80-84°/1.5 mmHg (Lit.: 83°/1 mmHg [7]), m.p. 23-24° (from toluene). ¹H and ¹⁹F NMR (in CCl₄): δ(CHF) = 7.02 ppm (triplet), δ(C₆H₄) = 8.14 ppm (AB quartet), δ(CHF₂) = 71.5 ppm (doublet), ²J(HF) = 55 Hz.

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