Journal of Fluorine Chemistry, *26* (1984) 161–164

Received: January 5, 1984; accepted: April 5, 1984

PREPARATION OF PERFLUOROALKYLTHIOHYDROXIMATES FROM PERFLUOROALKYL NITRILES

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SUMMARY

S-Methyl(Z)-2,2,2-trifluorothioacetohydroximate (1), S-methyl(Z)-2,2,3,3,3-pentafluorothiopropiohydroximate (2), and S-methyl(Z)-2,2,3,3,4,4,4-heptafluorothiobutyrohydroximate (3) were prepared by reaction of the corresponding perfluoroalkyl nitriles 4, 5, and 6 with methanethiol and hydroxylamine hydrochloride.

INTRODUCTION

The consideration of S-Methyl(Z)-2,2,2-trifluorothioacetohydroximate (1)[1] as a potential agrichemical intermediate necessitated the development of a short and efficient synthesis from readily available non-fluorine containing starting materials. As methodology existed for the conversion of acetonitrile to trifluoroacetonitrile (4) by chlorination [2] followed by halogen exchange with hydrogen fluoride [3], 4 appeared to be a reasonable material for conversion to the hydroximate 1.

RESULTS AND DISCUSSION

It is well known that nitriles will undergo a Pinner reaction [4] with thiols to form thioimidates. This has been demonstrated for perfluoroalkylnitriles [5] as well. Thus treatment of trifluoroacetonitrile with excess methanethiol and potassium carbonate catalyst (Scheme 1) afforded the S-methyltrifluoroacetimidate (7) (mixture of E and Z isomers).

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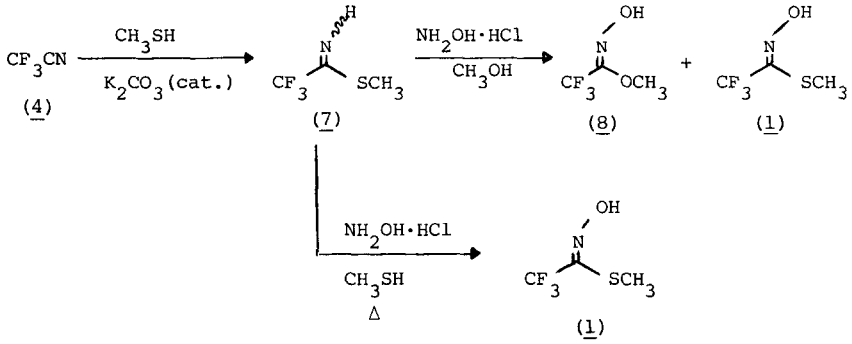
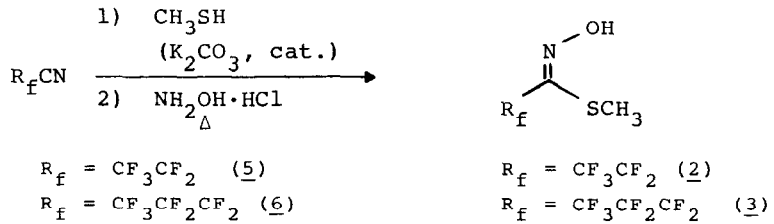


Scheme 1

To convert this material to 1 then required only exchange with hydroxylamine. However, treatment of the thioimidate 7 with a methanol solution of hydroxylamine hydrochloride or hydroxylamine itself resulted in formation of the O-methyl thiohydroximate derivative 8 due to exchange of methanethiol with methanol along with the desired product 1 (Scheme 1).

This problem was circumvented by utilizing methanethiol as the solvent with heating required to dissolve the hydroxylamine hydrochloride (Scheme 1). Thus treatment of trifluoroacetonitrile with methanethiol as solvent (potassium carbonate catalyst) followed by addition of hydroxylamine hydrochloride without isolation of the intermediate thioimidate and heating afforded a 60% yield of 1 identical in all respects with material prepared by an alternate route [1]. The process was also found to be generally applicable and allowed the preparation of the penta and heptafluoro derivatives 2 and 3 (Scheme 2)



Scheme 2

The Z- configuration of the S-Methyl-2,2,2-trifluorothioacetohydroximate (1) was established by X-ray crystal structure. [1] Attempts to carry out the same sequence with trichloroacetonitrile resulted in displacement of chlorine by methanethiol.

EXPERIMENTAL

Preparation of S-Methyl-2,2,2-trifluoroacetimidate (7)

A polymer tube was charged with trifluoroacetonitrile (2 mL), methanethiol (2 mL), and potassium carbonate (2 mg) and allowed to stand at room temperature for 3 days. The mixture was then distilled under vacuum yielding a colorless volatile liquid (3.05 g, bp = 50°-52°C, 200 mm); ^{1}H NMR (90 MHz, $CDCl_3$) δ 2.37 (s, 1.27H, SCH_3), 2.47 (s, 1.73H, SCH_3), 10.00 (b, 1H, NH); ^{19}F NMR (94.1 MHz, $CDCl_3$) δ -71.01 (d, J = 2.5Hz, 1.27F, CF_3), -72.44 (s, 1.73F, CF_3).

Preparation of S-Methyl(Z)-2,2,2-trifluorothioacetohydroximate (1)

A polymer tube was charged with trifluoroacetonitrile (5.52 g, 58.1 mmole), methanethiol (10 mL), and potassium carbonate (20 mg) and allowed to stand at room temperature for 4 days. The tube was cooled (liquid nitrogen), opened under nitrogen, hydroxylamine hydrochloride (8.0 g, 116.2 mmole) was added, and the tube resealed. The mixture was then heated at 125°C for 15 hrs. Excess methanethiol was allowed to evaporate, the reaction mixture was diluted with ether (200 mL), filtered, the solvent removed under reduced pressure, and the remaining liquid purified by flash column chromatography (silica, methylene chloride) to yield the product as a crystalline solid (5.49 g, 60%). mp = 49°-53°C; IR(KBr) ν_{max} (cm^{-1}) 3305 (b, OH), 1428 (m), 1290(m), 1188(s), 1150(s), 1135(s), 1050(s), 980(s), 960(s); ^{1}H NMR (90 MHz, $CFCl_3$) δ 2.53 (m, 3H, SCH_3), 9.70 (s, 1H, OH); ^{19}F NMR (94.1 MHz, $CFCl_3$) δ -65.10 (m, 3F); High resolution mass spectrum calculated for $C_3H_4F_3NOS$: 158.9965; Found: 158.9956.

Preparation of S-Methyl(Z)-2,2,3,3,3-pentafluorothiopropiohydroximate (2)

The procedure was identical with that described in the preparation of 1, using pentafluoropropionitrile (3.38 g, 23.3 mmole), methanethiol (10 mL), potassium carbanate (20 mg) and hydroxylamine hydrochloride (3.24 g, 46.6 mmole). The product was isolated as a colorless liquid (1.98 g, 41%). IR(liquid film) ν_{max} (cm^{-1}) 3375 (b, OH), 1205(s), 1112(m), 1080(m), 995(m), 985(m), 885(m), 738(m); ^{1}H NMR (90 MHz, $CFCl_3$) δ 2.57 (s, 3H, SCH_3), 9.55 (s, 1H, OH); ^{19}F NMR (94.1 MHz, $CFCl_3$) δ-81.80 (t, J = 1.5 Hz, 3F, CF_3), -110.75 (q, J = 1.5 Hz, 2F, CF_2); Analysis calc. for $C_4H_4F_5NOS$: 22.97% C, 1.92% H; Found: 23.14% C, 2.72% H.

Preparation of S-Methyl(Z)-2,2,3,3,4,4,4-heptafluorothiobutyrohydroximate (3)

The procedure was identical with that described in the preparation of 1 using heptafluorobutyronitrile (5.25 g, 26.9 mmoles), methanethiol (10 mL), potassium carbonate (20 mg), and hydroxylamine hydrochloride (3.74 g, 53.8 mmoles). The product was isolated as a white solid (2.93 g, 42%). Sublimation (0.5 mm, 35°C) afforded white crystals. mp = 36°-38°C; IR(KBr) ν_{max} (cm^{-1}) 3330 (b, OH), 1232(s), 1185(m), 1125(m), 1058(w), 980(m), 820(w), 738(w); ^{1}H NMR (90 MHz, $CFCl_3$) δ 2.57 (s, 3H, SCH_3), 9.57 (s, 1H, OH); ^{19}F NMR (94.1 MHz, $CFCl_3$) δ -80.86 (t, J = 9Hz, 3F, CF_3), -109.38 (q, J = 9 Hz, 2F, CF_2), -125.44 (m, 2F, CF_3CF_2); Analysis calc. for $C_5H_4F_7NOS$: 23.17% C, 1.56% H, 5.40% H; Found: 22.99% C, 1.67% H, 5.75% N.

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