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REACTIONS OF BROMOTRIFLUOROMETHANE AND RELATED HALIDES

PART VII [1] CONDENSATIONS WITH THIOCYANATES AND ISOCYANATES IN THE PRESENCE OF ZINC

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SUMMARY

Reaction of zinc and bromotrifluoromethane, or perfluoroalkyliodides, with thiocyanates and isocyanates gives respectively trifluoromethylsulfides and substituted trifluoroacetamides, as well as their long chain analogs.

INTRODUCTION

We described recently some new reactions of bromotrifluoromethane in the presence of zinc. We prepared trifluoromethanesulfonic acid from bromotrifluoromethane and sulfur dioxide [2] in dimethylformamide. The reaction with carbonyl compounds in pyridine led to trifluoromethyl-substituted methanols [3] . Arylamines were transformed, in the presence of sulfur dioxide, to their ortho and para-trifluoromethyl derivatives in a mixture of dimethylformamide and pyridine [4] . Simple esters like ethylbenzoate induced the formation of trifluoromethylzinc derivatives, in dimethylformamide or pyridine, whereas the Barbier condensation occurred with activated esters and cyclic anhydrides in pyridine [5] . The reactions with sulfur dioxide required the use of a polar aprotic solvent like DMF ; however, a donor solvent, like pyridine, led to better yields for carbonyl and carboxyl condensations. Moreover, for these latter reactions, an induction time, up to three hours, was observed in DMF, but not in pyridine.

In this paper, we have examined the behaviour of nitrogen derivatives, thiocyanates and isocyanates, in the perfluoroalkylhalides-zinc-solvent mixtures.

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Thiocyanates

We obtained perfluoroalkylsulfides by a Barbier reaction ; all the reagents were mixed together at the beginning of the reaction.

$$R_FX + RSCN \xrightarrow[2)\ H_3O^+]{1)\ Zn/pyridine} RSR_F$$

R_F=CF_3, C_4F_9, C_8F_{17}

X=Br,I R=CH_3, $C_6H_5CH_2$

The condensation with CF_3Br was performed under a slight pressure (3-5 bars) at ambient temperature ; the long chain perfluoroalkyliodides R_FI reacted at atmospheric pressure ; the reaction time was about 2 hours. The results are reported in Table I.

TABLE I

N°	RSCN	R_FX	Products	Yield*
1	$C_6H_5CH_2SCN$	CF_3Br	$C_6H_5CH_2SCF_3$	22 %
2	$C_6H_5CH_2SCN$	C_4F_9I	$C_6H_5CH_2SC_4F_9$	73 %
3	CH_3SCN	CF_3Br	CH_3SCF_3	16 %
4	CH_3SCN	$C_8F_{17}I$	$CH_3SC_8F_{17}$	54 %**

* Calculated from thiocyanates in the case of CF_3Br (in excess) and from R_FI for the other examples.

** 30 % of R_FI did not react and 10 % of R_FH was also obtained.

Among these perfluoroalkylsulfides [6] , the trifluoromethyl example can be easily transformed to trifluoromethanesulfonic acid derivatives. Oxidative chlorination of benzyltrifluoromethylsulfide to trifluoromethanesulfonylchloride was carried out with chlorine in water at a pressure of 4 bars and gave a 70 % yield.

$$C_6H_5CH_2SCF_3 \xrightarrow[H_2O]{Cl_2} \underset{70\ \%}{CF_3SO_2Cl} + C_6H_5CH_2Cl$$

Cleavage of the carbon-sulfur bond was easy because the benzyl group is able to stabilize a positive charge [7] . On the other hand, methyltrifluoromethylsulfide was oxidized to methyltriflone by potassium permanganate following the procedure described by Haszeldine et al. [8] .

$$CH_3SCF_3 \xrightarrow[AcOH\ 0\text{-}20°C]{KMnO_4} \underset{63\ \%}{CF_3SO_2CH_3}$$

Isocyanates

Reactions of perfluoroalkylhalides with zinc and isocyanates took a longer time than those with thiocyanates. In the case of bromotrifluoromethane, we noticed an induction time of 1 to 4 hours and the reaction needed 2 to 4 hours to go to completion. The Barbier conditions were also necessary. We had to use dimethylformamide because the reaction in pyridine gave an intractable grey solid. We obtained, after hydrolysis, perfluoroalkanecarboxamides in yields of 20 to 50 % approximately.

$$R_FX + R\text{-}N{=}C{=}O \xrightarrow[2)\ H_3O^+]{1)\ Zn/DMF} R_FCONHR$$

R_F:CF_3, C_2F_5, C_4F_9 X:Br, I   R:CH_3, C_6H_5

These two reactions allowed us to develop the chemistry of derivatives of trifluoromethanesulfonic and trifluoroacetic acids as well as those of their long chain analogs [9].

EXPERIMENTAL

Proton magnetic resonance spectra were recorded on a Varian EM360L spectrometer. Shifts are in ppm downfield from tetramethylsilane. Fluorine 19 magnetic resonance spectra were obtained on the same spectrometer at 56,4 MHz and are recorded in ppm (δ_F) downfield from trichlorofluoromethane. The infrared spectra were recorded on a 1420 Perkin Elmer spectrometer. The thiocyanates and isocyanates were purchased from Aldrich, Zn from Prolabo, CF_3Br from Setic Labo. DMF and pyridine (Aldrich) were distilled before use.

Benzyltrifluoromethylsulfide

A pressure-safe glass bottle, containing 8 g (0,054 mole) of benzylthiocyanate, 4 g of zinc powder and 25 ml of pyridine was placed under vacuum. Then, the bottle was charged with bromotrifluoromethane to a pressure of 3.7 bars and shaken at 20°C. The gas absorption began at once and the pressure was kept between 4 and 2.5 atmospheres for about one hour until gas absorption ceased.

The crude product was filtered, the organic layer was hydrolyzed with 20 ml of 10 % hydrochloric acid and left for 30 minutes. After extraction with ether, the organic layer was washed with water, dried on magnesium sulfate and evaporated. The residue was distilled to give 2.3 g of benzyltrifluoromethylsulfide b.p. 54-56°C/11 mmHg, (b.p. lit. 76-77°C/30 mmHg [6c]). Yield 22 %. δ_F:-41.3 ppm (s) ; δ_H:7.2-7.5 ppm (m, 5H), 4.1 ppm (s, 2H).

Trifluoromethanesulfonylchloride

A pressure-safe glass bottle containing 1.6 g of benzyltrifluoromethylsulfide and 10 ml of water was placed under vacuum. Then, the bottle was charged with chlorine gas to a pressure of 4 atmospheres and was shaked for two hours at 5°C.

The lower layer was distilled to give 1 g of trifluoromethanesulfonylchloride b.p. 29-32°C δ_F:-74 ppm(s), yield 70 %.

Methyltrifluoromethylsulfide

A pressure-safe glass bottle containing 7.3 g (0.01 mole) of methyl thiocyanate, 6.5 g of zinc powder and 25 ml of pyridine was placed under vacuum. The bottle was charged with bromotrifluoromethane to a pressure of 3.7 atmospheres. It was shaken for 3 hours and the pressure was kept between 5 and 2.5 atmospheres. Volatile products were recovered under 30 mmHg in a dry-ice trap. The bromotrifluoromethane was distilled first at -30°C and then 1.9 g of methyltrifluoromethylsulfide was distilled [6a] ; b.p. 10°C/760 mmHg. Yield 16 % ; δ_F:-43 ppm (s) ; δ_H 2.4 ppm (s).

Methyltrifluoromethylsulfone [6d]

1.5 g of methyltrifluoromethylsulfide was oxidized by 4 g of potassium permanganate in 40 ml of acetic acid according to [8] . After neutralization and extraction with ether, the organic layer was dried over magnesium sulfate. The ether was distilled with a spinning band apparatus. The residue was distilled from a microdistillation unit to give the sulfone (63 % from the methyl trifluoromethylsulfide) B.p.: 127°C.

Benzylnonafluorobutylsulfide (n.c.)

1.5 g of benzylthiocyanate, 10 ml of pyridine, 1 g of zinc powder and 3.5 g of iodononafluorobutane were stirred together for 12 hours under argon. After hydrolysis as above, the benzylperfluorobutylsulfide was distilled. B.p. 92°C/17 mmHg. Yield:73 % ; δ_F=-82.5 ppm (3F) -88.8 ppm (2F) -121.5 ppm (2F) -126.5 ppm (2F) ; δ_H 7.3 ppm (s, 5H), 4.2 ppm (s, 2H). m/e 342 (M^+) ; 309 (M^+-SH) ; 91 ($C_6H_5CH_2^+$).

Methylperfluorooctylsulfide [10]

The previous experiment was repeated with 1 ml of methylthiocyanate, 10 ml of pyridine, 1 g of zinc and 8 g of iodoperfluorooctane.

^{19}F NMR analysis of the crude product showed that 30 % of iodoperfluorooctane had not reacted and 10 % of hydridoperfluorooctane was formed. Methylperfluorooctylsulfide was distilled bp:44°C/19 mmHg. Yield : 54%

δ_F:-82.6 ppm (3F), -92.3 ppm (2F), -121.2 ppm (2F), -123.9 ppm (8F), -128.6 ppm (2F) ; δ_H:2.4 ppm (s).

N-phenyl-trifluoroacetamide

The pressure-safe glass bottle containing 10 ml of phenylisocyanate, 30 ml of DMF and 6 g of zinc powder was placed under vacuum. The bottle was then charged with bromotrifluoromethane to a pressure of 3.7 atmospheres and shaken at 20°C. The gas absorption began after several hours. The pressure was then maintained between 5 and 3.5 atmospheres for 3 hours.

The crude product was then filtered. The organic layer was hydrolyzed with 40 ml of 10 % hydrochloric acid. After extraction with chloroform, the organic layer was washed with 1N hydrochloric acid, water and dried over magnesium sulfate. After removal of the solvent, the N-phenyltrifluoro2,2 acetamide was sublimed at 40°C/20 mmHg ; m.p. 87°C (mp [11] 86-90°C), yield from isocyanate : 17 %. δ_F=-75.7 ppm (s) ; δ_H:9.3 ppm ($N\underline{H}$), 7.1-6.3 ppm (m, 5H); IR:1730 cm^{-1}.

N-phenyl-pentafluoropropanamide

The previous experiment was repeated with pentafluoroethyliodide at one atmosphere pressure. The N-phenyl-pentafluoropropanamide obtained was sublimed. m.p. 96°C (mp [12] 97.5-98.5°C), yield from isocyanate : 33 % ; δ_F=-81.7 ppm (3F), -121 ppm (2F) ; δ_H 9.2 ppm (NH), 7.1-6.3 ppm (m, 5H) ; IR 1730 cm^{-1}.

N-methyl-nonafluoropentanamide(n.c.)

1 ml of methyl isocyanate, 1 g of zinc powder, 10 ml of DMF and 3.5 g iodoperfluorobutane were stirred under argon for 24 hours. After hydrolysis as above, N-methyl-nonafluoropentanamide was sublimed at 60°C/0.2 mmHg, mp 35°C, conversion yield from R_FI : 40 %.

δ_F:-81 ppm (3F), -120.7 ppm (2F), -124 ppm (2F), -127 ppm (2F) ; δ_H 3 ppm (s) 2.93 ppm (s) ; IR (CCl_4) 1730 cm^{-1}.

C calc. 26.01 %	H 1.48 %
C found 25.88 %	H 1.78 %

ms:m/e:278 ($M-H^+$), 258, 230

N-phenyl-nonafluoropentanamide (n.c.)

The previous experiment was repeated with 1.8 g of phenylisocyanate. After sublimation, 1.8 g of N-phenyl-nonafluoropentanamide was obtained ; m.p. 65° C ; conversion yield from R_FI : 53 %.
δ_F:-81 ppm (3F), -120 ppm (2F), -124 ppm (2F), -126 ppm (2F) ; δ_H 7.6-7.1 ppm (m) ; IR (CCl_4) 1730 cm^{-1} ; ms:m/e:339 (M^+), 120 (C_6H_5NHCO).

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