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SHORT COMMUNICATION

Nitroxide Chemistry. Part XVI. Reactions Between Bistrifluoromethyl Nitroxide and Some Aliphatic Derivatives of Sulphur

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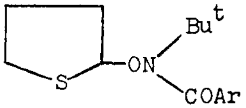
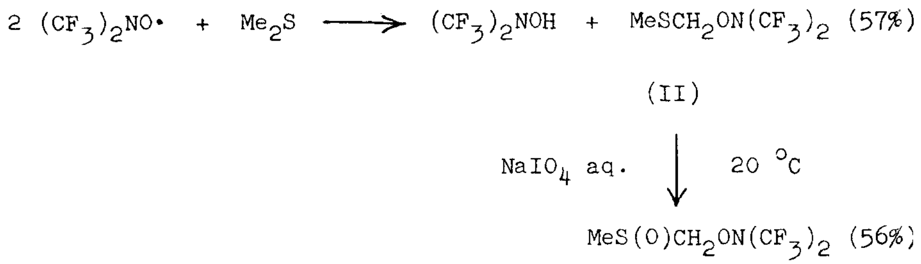
The recent claim [1] that benzoyl t-butyl nitroxide and its 3,5-dinitrobenzoyl analogue readily attack tetrahydrothiophen to yield the corresponding hydroxamic acids and α-(aroylbutylamino-oxy)tetrahydrothiophens (I) prompts us to disclose the results of a cursory study of reactions between bistrifluoromethyl nitroxide and the sulphur derivatives Me_2S, $MeSCH{=}CH_2$, $MeS(O)_{\underline{x}}CH{=}CH_2$ ($\underline{x}$ = 1,2), and $(CH_2{=}CH)_2SO_2$ completed seven years ago.



Ar = C_6H_5, $C_6H_3(NO_2)_2$-3,5 [2]

(I)

Dimethyl sulphide reacts instantaneously with bistrifluoromethyl nitroxide at *ca*. -30 °C to give an equimolar mixture of *NN*-bistrifluoromethyl-hydroxylamine and (bistrifluoromethylamino-oxy)methyl methyl sulphide (II) plus much unidentified multi-component material; oxidation of the mixed sulphide with aqueous sodium metaperiodate provides the corresponding sulphoxide:



$$2\ (CF_3)_2NO\cdot + Me_2S \longrightarrow (CF_3)_2NOH + MeSCH_2ON(CF_3)_2\ (57\%)$$

(II)

$$MeSCH_2ON(CF_3)_2 \xrightarrow[20\ ^{\circ}C]{NaIO_4\ aq.} MeS(O)CH_2ON(CF_3)_2\ (56\%)$$

The sulphoxide $MeS(O)CH[ON(CF_3)_2]CH_2ON(CF_3)_2$ can be obtained virtually quantitatively by allowing a 2:1 molar mixture of bistrifluoromethyl nitroxide and methyl vinyl sulphoxide to warm from -196 °C to room temperature, the addition reaction typical of the nitroxide [3] occurring exothermically when the reactants melt. The parent sulphide $MeSCH[ON(CF_3)_2]CH_2ON(CF_3)_2$ can be prepared similarly, but in lower yield (73%) by application of the same technique to methyl vinyl sulphide. The sulphones $MeS(O)_2CH{=}CH_2$ and $(CH_2{=}CH)_2SO_2$ react much more slowly with the nitroxide, giving the expected derivatives $MeS(O)_2CHRCH_2R$ and $(CH_2RCHR)_2SO_2$ [$R = -ON(CF_3)_2$] in 88 and 93% yield respectively. Caesium fluoride-initiated addition of the elements of NN-bistrifluoromethyl-hydroxylamine across the C=C bond in methyl vinyl sulphoxide yields the monosubstituted compound $MeS(O)CH_2CH_2ON(CF_3)_2$; this reaction will be discussed later when work on Michael condensation (addition) reactions involving the hydroxylamine is complete.

EXPERIMENTAL

N.m.r. data

N.m.r. absorptions to low field of reference signals have been assigned positive chemical shift values; ^{19}F shifts are quoted relative to trifluoroacetic acid.

Reactions involving bistrifluoromethyl nitroxide (see the Table)

Except for the reaction involving dimethyl sulphide, the nitroxide was condensed, *in vacuo*, into a cold (-196 °C) Pyrex ampoule (120 cm^3) containing the substrate [and carbon tetrachloride as inert solvent in the case of divinyl sulphone] under examination; the ampoule was then sealed with a Rotaflo PTFE valve and allowed to warm slowly to room temperature. Volatile product was transferred to a Pyrex vacuum system and examined by standard techniques; residual material was also dealt with conventionally. Details are given in Table 1.

Preparation of (bistrifluoromethylamino-oxy)methyl methyl sulphoxide

(Bistrifluoromethylamino-oxy)methyl methyl sulphide (5.73 g, 25.0 mmol) was stirred with a solution of sodium metaperiodate (5.36 g, 25.3 mmol) in water (70 cm^3) at room temperature for 4 days. The product was filtered, and the filtrate and the precipitate were shaken separately with methylene chloride (4 x 50 cm^3). The methylene chloride solutions were combined, dried ($MgSO_4$), and evaporated at reduced pressure; the pale yellow residue was sublimed (35 °C at 1 mmHg) to provide (bistrifluoromethylamino-oxy)methyl methyl sulphoxide (nc) (3.40 g, 13.9 mmol, 55.5%) (Found: C, 19.8; H, 2.0; N, 5.8. $C_4H_5F_6NO_2S$ requires C, 19.6; H, 2.0; N, 5.7%), m.p. 38-40 °C, δ_F (soln. in $CDCl_3$; 56.5 MHz) + 10.45 (s) p.p.m., and δ_H (60 MHz; ext. TMS ref.) + 2.68 (s; CH_3) and + 4.93 (br. s; CH_2) p.p.m.

Notes to Table 1

[a] The nitroxide was passed slowly (2 h) into the cold (*ca*. -30 °C) sulphide; an instantaneous reaction occurred.

[b] Isolated by precise distillation (micro spinning-band column) as an oil (Found: C, 20.9; H, 2.4, 2.4. $C_4H_5F_6NOS$ requires C, 21.0; H, 2.2%), b.p. 94 °C, δ_F (neat liq.; 94.1 MHz) + 8.5 (s) p.p.m., δ_H (100 MHz; TMS lock) + 4.59 (s; CH_2) and + 1.77 (s; CH_3) p.p.m. [c] Identified by i.r. spectroscopy.

[d] A complex [at least 8 components according to g.l.c. (2 m SE30, 86 °C)] pale yellow oil, mainly (*ca*. 4 g) recovered from the reaction vessel after transfer of the volatile product to a vacuum system. [e] An oil (Found: C, 20.5; H, 1.6; N, 6.9. $C_7H_6F_{12}N_2O_2S$ requires C, 20.5; H, 1.5; N, 6.8%), isolated

TABLE 1

Reactions of bistrifluoromethyl nitroxide with derivatives of sulphur

Substrate (g, mmol)	$(CF_3)_2NO\cdot$ (g, mmol)	Reaction period and temp. (°C)	Products [R = $(CF_3)_2NO-$] (g, mmol, %)
Me_2S (1.80, 29.0)	10.0, 59.5	[a]	$MeSCH_2R$(nc)(3.53, 15.4, 53)[b] RH (2.67, 15.8, 27)[c] $\left.\begin{array}{l}(CF_3)_2NH\\CF_3NO_2\end{array}\right\}$ traces unidentified (ca. 5 g)[d]
$MeSCH{=}CH_2$ (0.36, 4.86)	1.69, 10.1	2 min, 20	$MeSCHRCH_2R$(nc)(1.45, 3.54, 73)[e] RH (0.21, 1.24, 12)[c,f] R. (trace)[c]
$MeS(O)CH{=}CH_2$ (0.80, 8.90)	3.13, 18.6	2 min, 20	$MeS(O)CHRCH_2R$(nc)(3.65, 8.57, 96)[g]
$MeS(O)_2CH{=}CH_2$ (1.84, 17.4)	5.88, 35.0	6 days, 20	$MeS(O)_2CHRCH_2R$(nc)(6.75, 15.3, 88)[h]
$(CH_2{=}CH)_2SO_2$ (0.78, 6.61)	4.49, 26.7 (CCl_4, 2 cm^3)	7 days, 20	$(CH_2RCHR)_2SO_2$(nc)(4.88, 6.17, 93)[i]

by trap-to-trap fractional condensation of the volatile product at 1-2 mmHg (-45 °C trap), δ_F (neat liq.; 56.46 MHz) + 9.7 (s) and + 8.2 (s) p.p.m. (rel. int. 1:1), and δ_H (60 MHz; ext. C_6H_6 ref.) -1.59 (t; CH), -2.40 (d; CH_2), and -4.58 (s; CH_3) p.p.m. [f] Condensed in a -78 °C trap, and shown by g.l.c. (2m SE30, 95 °C) to be contaminated with at least 4 unknown compounds. [g] Isolated by sublimation (45 °C and *ca*. 1 mmHg) of the crude reaction product as a mixture (m.p. 62-66 °C) of diastereoisomers {[Found: C, 20.0; H, 1.5; N, 6.3%; *M*, 42 6. $C_7H_6F_{12}N_2O_3S$ requires C, 19.7; H, 1.4; N, 6.6%; *M*, 426]; δ_F (20% soln. in $CDCl_3$; 94.1 MHz) + 10.05 (s) and + 10.10 (s) (rel. int. *ca*. 4:3), and + 10.9 (br. s) and + 11.1 (br. s) (rel. int. of the two groups of absorptions 1:1) p.p.m., δ_H (100 MHz; TMS lock) + 2.60 (s; CH_3) and + 2.70 (s; CH_3) (rel. int. *ca*. 4:3) and + 4.4 to + 5.25 (complex; CH_2 and CH) (rel. int. of the two groups of absorptions 1:1) p.p.m.}. [h] A hygroscopic solid [Found: C, 19.2; H, 1.5. $C_7H_6F_{12}N_2O_4S$ requires C, 19.0; H, 1.4%], δ_F (*ca*. 30% soln. in $CDCl_3$; 56.46 MHz) + 9,3 (s) and + 10.4 (br. s) p.p.m. (rel. int. 1:1), δ_H (60 MHz; ext. C_6H_6 ref.) -1.48 (t; CH), -1.78 (d; CH_2), and -3.49 (s; CH_3) p.p.m.], m.p. 35-37 °C, isolated by sublimation (45 °C at *ca*. 1 mmHg) of the crude reaction product. [i] Isolated as an oil [Found: C, 18.4; H, 0.8; N, 6.9. $C_{12}H_6F_{24}N_4O_6S$ requires C, 18.2; H, 0.8; N, 7.1%], δ_F (neat liq.; 56.46 MHz) + 8.0 (s) and + 9.4 (s) (rel. int. 1:1) p.p.m., δ_H (60 MHz; ext. C_6H_6 ref.) -1.25 (vbr. s; CH) and -1.9 (vbr. s; CH_2) p.p.m.

1 S.A. Hussain, T.C. Jenkins, and M.J. Perkins, J.C.S. Perkin Trans. I, (1979) 2809.

2 Only the benzoyl compound was characterised: the 3,5-dinitrobenzoyl compound decomposed during attempted isolation.

3 R.E. Banks, R.N. Haszeldine, and M.J. Stevenson, J. Chem. Soc.(C), (1966) 901; R.E. Banks, R.N. Haszeldine, and B. Justin, *ibid*., (1971) 2777.