Journal of Fluorine Chemistry, 12 (1978) 153–158

Received: December 22, 1977

SHORT COMMUNICATION

Perfluoroalkyl Derivatives of Nitrogen. Part XLV . Synthesis and Some Reactions of α-Trifluoromethyl-N-t-butylnitrone

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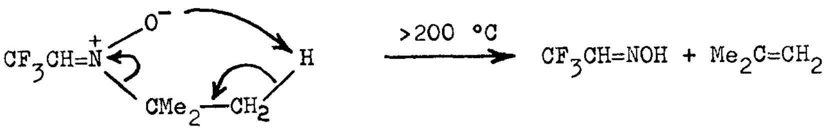
The scarcity of published information on fluorinated nitrones prompts us to report details of work on the chemistry of α-trifluoromethyl-N-t-butylnitrone, a compound readily obtained [1] via a von Pechmann-Staudinger reaction [2]:

$$CF_3CHN_2 + Me_3CNO \longrightarrow CF_3CH{=}\overset{+}{N}(\overset{-}{O})CMe_3 \quad (81\%)$$

α-Trifluoromethyl-N-t-butylnitrone is a colourless solid, m.p. 35 °C, which decomposes at elevated temperatures into trifluoroacetaldoxime and isobutene, presumably via a Cope-type elimination (see the Scheme) [3]. In other respects too, the behaviour of the nitrone conforms with general aldonitrone chemistry: it yields the 2,4-DNP derivative of trifluoroacetaldehyde when treated with 2,4-dinitrophenylhydrazine, is converted into the hydroxylamines $CF_3CH_2N(OH)CMe_3$ and $CF_3CHEtN(OH)CMe_3$ by lithium aluminium hydride



SCHEME

and ethylmagnesium iodide, respectively, and photo-isomerises to the amide $CF_3CONHCMe_3$.

EXPERIMENTAL

2,2,2-Trifluorodiazoethane was prepared by nitrosation of 2,2,2-trifluoroethylamine [4]. N.m.r. spectra were obtained with a A.E.I. RS2 instrument, ^{19}F chemical shifts being measured relative to external $CF_3.CO_2H$ (downfield shifts positive).

Preparation of α-trifluoromethyl-N-t-butylnitrone

2-Methyl-2-nitrosopropane (8.60 g, 98.9 mmole) was added (30 min.) to a cold (0 °C) stirred solution of 2,2,2-trifluorodiazoethane (10.9 g, 98.2 mmole) in dry diethyl ether (125 cm^3) under nitrogen; the resulting solution was heated under reflux for 2 h, then filtered and the filtrate was evaporated *in vacuo*. The residue was recrystallised from light petroleum (b.p. 30-40 °C) to give needless of α-trifluoromethyl-*N*-t-butylnitrone (nc) (13.4 g, 79.3 mmole; 81% [Found: C, 42.4; H, 6.2; N, 8.6%; *M* (mass spec.), 169. $C_6H_{10}F_3NO$ requires C, 42.6; H, 6.0%; N, 8.3%; *M*, 169], m.p. 35 °C, $\lambda_{max.}$ (me) 6.25 μm (C:N str.), $\lambda_{max.}$ (hexane) 244 nm (ε 9300), δ_F (60 MHz) +12.8 p.p.m. (d, J_{HF} 6 Hz), δ_H (60 MHz) τ2.95 (q; $CHCF_3$) and τ8.5 (s; CMe_3) (rel.int. 1:9), and *m/e* 169 ($C_6H_{10}F_3NO^{+\cdot}$,<1%), 153 ($C_6H_{10}F_3N^+$,<1%), 82 ($C_2HF_3^+$, 1%), 57 ($C_4H_9^+$, 100%), and 43 ($CHNO^+$, 10%).

Reactions of α-trifluoromethyl-N-t-butylnitrone

(a) Pyrolysis

A sample (4.50 g, 26.6 mmole) of the nitrone was heated at 50 °C *in vacuo* and its vapour allowed to enter the mouth (rate:

ca. 1 g/h) of a hot (500 °C) platinum tube (100 x 1 cm; heated length 50 cm) which was evacuated continuously *via* two traps cooled to -78 and -196 °C. Distillation of the material which condensed in the cold traps provided isobutene (1.36 g, 24.3 mmole; 91%) [Found: *M* (Regnault's method), 57. Calc. for C_4H_8: *M*, 56], shown to be pure by i.r. spectroscopy and g.l.c. analysis, and a white solid which was sublimed, *in vacuo*, to yield trifluoroacetaldoxime (2.64 g, 23.4 mmole; 88%) [Found: C, 20.5; H, 1.9; N, 12.5%; *M* (Regnault) 117.5. $C_2H_2F_3NO$ requires C, 21.2; H, 1.8; N, 12.4%; *M*, 113], m.p. 48-53 °C, $\lambda_{max.}$ (melt) 2.76 (O-H str.) and 6.05 µm (C:N str.), δ_F ($CDCl_3$ soln.) +11.0 p.p.m. (d, J_{HF} 5 Hz), δ_H (same soln.) τ0.42 (br.s; NOH) and τ3.05 (q; $CHCF_3$), and *m/e* 114 [$C_2H_3F_3NO^+$ (*M*+H^+), 25%], 113 ($C_2H_2F_3NO^{+\cdot}$, 49%), 94 ($C_2H_2F_2NO^+$, 15%), 69 (CF_3^+, 96%), 50 (CF_2^+, 25%), and 44 (CH_2NO^+, 100%).

Treatment of a sample of the trifluoroacetaldoxime (0.90 g, 7.96 mmole) with phosphorus pentoxide (3 g) at 110 °C for 24 h in an evacuated Pyrex ampoule (100 cm^3) gave trifluoroacetonitrile (0.53 g, 5.58 mmole; 70%) [Found: *M* (Regnault), 94.5. Calc. for C_2F_3N: *M*, 95], with a correct i.r. spectrum.

(b) Reduction

A mixture of α-trifluoromethyl-*N*-t-butylnitrone (1.0 g, 5.9 mmole), diethyl ether (40 cm^3), and lithium aluminium hydride (0.25 g, 6.6 mmole) was heated under reflux (2 h) then cooled (20 °C) and stirred with 4M-hydrochloric acid (40 cm^3, added dropwise) for 1 h. The aqueous layer was made strongly alkaline (NaOH) and extracted with diethyl ether (5 x 20 cm^3); the extracts plus the original ethereal layer were dried ($MgSO_4$) and saturated with hydrogen chloride to cause the precipitation of N-t-butyl-N-2,2,2-trifluoroethylhydroxylamine hydrochloride (nc) (0.79 g, 3.81 mmole; 65%) (Found: C, 35.0; H, 6.6; N, 6.9. $C_6H_{13}ClF_3NO$ requires C, 34.7; H, 6.3; N, 6.7%), a white solid, m.p. 155 °C.

(c) With ethylmagnesium iodide

α-Trifluoromethyl-N-t-butylnitrone (5.0 g, 29.6 mmole) in diethyl ether (25 cm^3) was added slowly (0.5 h) to a stirred solution of the Grignard reagent prepared by adding ethyl iodide (4.5 g, 28.8 mmole) to magnesium turnings (0.72 g) in diethyl ether (20 cm^3) The mixture was heated under reflux (0.5 h), cooled to 20 °C, and then stirred with 20% aqueous ammonium chloride (50 cm^3). The ethereal layer was removed and the aqueous layer was extracted with diethyl ether (2 x 25 cm^3); the combined ethereal material was dried ($Na_2SO_4/MgSO_4$) and saturated with hydrogen chloride to provide N-t-butyl-N-1-(trifluoromethyl)propylhydroxylamine hydrochloride (nc) (4.3 g, 18.4 mmole; 63%) (Found: C, 41.1; H, 7.4; N, 5.9. $C_8H_{17}ClF_3NO$ requires C, 40.8; H, 7.2; N, 5.9%), m.p. 132 °C.

(d) With 2,4-dinitrophenylhydrazine

Concentrated hydrochloric acid was added dropwise to a solution of 2,4-dinitrophenylhydrazine (1.17 g) in ethanol (8 cm^3) until it became clear. The solution was cooled to 20 °C and mixed with a solution of α-trifluoromethyl-N-t-butylnitrone (1.00 g) in ethanol (4 cm^3); after 5 min., the mixture was heated gently until it started to boil then filter . The filtrate was stored for 24 h and the orange-yellow needles of trifluoroacetaldehyde 2,4-dinitrophenylhydrazone which formed were recrystallised from ethanol to provide a sample with m.p. 148 °C (lit.,[5] 149 °C).

(e) Photolysis

A solution of α-trifluoromethyl-N-t-butylnitrone (3.0 g) in dioxan (50 cm^3), contained in a silica ampoule (300 cm^3) from which air had been removed, was exposed for 2 days to u.v. light from a Hanovia S.500 medium-pressure mercury vapour lamp placed 20 cm distant. Evaporation of the product under reduced pressure to remove dioxan provided a colourless oil (2.85 g), shown by i.r. spectroscopy to contain much N-t-butyltrifluoroacetamide. Treatment of the oil with boiling 4M-NaOH aq. (20 cm^3) for 1 h followed by standard work-up procedures gave t-butylamine [isolated as the hydrochloride (0.75 g)] and trifluoroacetic acid [isolated as the S-benzylthiouronium salt (0.2 g)].

An authentic sample of N-t-butyltrifluoroacetamide (Found: C, 42.2; H, 5.9; N, 8.4. $C_6H_{10}F_3NO$ requires C, 42.6; H, 6.0; N, 8.3%), m.p. 42-43 °C, was prepared (for i.r. comparison purposes) by treating trifluoroacetyl chloride with a two-molar proportion of t-butylamine in conventional fashion.

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