876. *Perfluoroalkyl Derivatives of Nitrogen. Part XVI.*[1] *Reaction of Trifluoronitrosomethane with Butadiene and with Isobutene*

By R. E. Banks, M. G. Barlow, and R. N. Haszeldine

Trifluoronitrosomethane reacts with butadiene at −78° to give 3,6-dihydro-2-trifluoromethyl-1,2-oxazine almost quantitatively; hydrogenation or bromination converts this into tetrahydro-2-trifluoromethyl-1,2-oxazine and its 4,5-dibromo-derivative, respectively. Trifluoronitrosomethane reacts with isobutene to give *N*-2-methallyl-*N*-trifluoromethylhydroxylamine.

AROMATIC nitroso-compounds or tertiary aliphatic nitroso-compounds containing electronegative α-substituents undergo what is formally a Diels–Alder reaction with hydrocarbon dienes to yield dihydro-1,2-oxazines.[2] Trifluoronitrosomethane similarly reacts with

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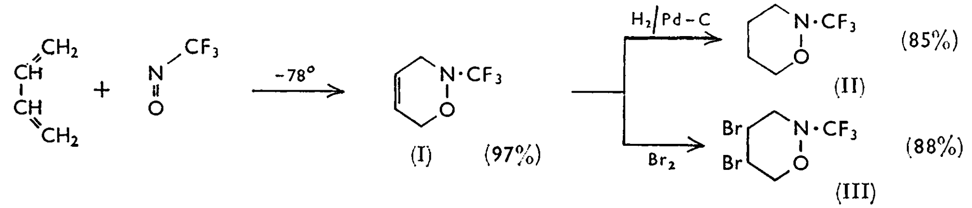
[1] Part XV, R. E. Banks, R. N. Haszeldine, H. Sutcliffe, and C. J. Willis, *J.*, 1965, 2506.

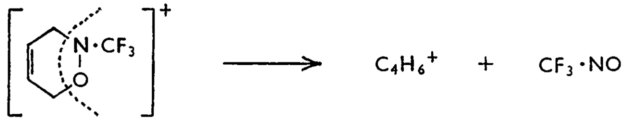
[2] S. B. Needleman and M. C. Chang Kuo, *Chem. Rev.*, 1962, **62**, 407; A. L. McKee in " The Chemistry of Heterocyclic Compounds," R. H. Wiley, ed., Interscience Publishers, Inc., New York, 1962, p. 332.

butadiene to give 3,6-dihydro-2-trifluoromethyl-1,2-oxazine (I) which is readily hydrogenated or brominated to give (II) or (III):



3,6-Dihydro-2-trifluoromethyl-1,2-oxazine (I) is a colourless liquid, the spectrum of whose vapour shows a C:C band of weak intensity at 1653 cm.$^{-1}$ (*cf.*[3] cyclohexene, 1646 cm.$^{-1}$). Its p.m.r. spectrum consists of three bands of equal intensity at τ-values of 3·99, 5·59, and 7·40, which are assigned on the basis of chemical shifts to the hydrogen nuclei of the CH:CH, CH_2·O, and CH_2·N groups, respectively; each band gives evidence of unresolved multiplet structure. In contrast, the dihydro-derivative (II) gives a spectrum containing bands at τ 6·14, 7·31, and 8·43 of relative intensities 1 : 1 : 2; these bands are assigned to the hydrogen nuclei of the CH_2·O, CH_2·N, and C·CH_2·C (two) groups, respectively. The bands at τ 6·14 and 7·31 are 1 : 2 : 1 triplets (splitting of 3·8 c./sec. for both bands), while that at τ 8·43 is a complex unresolved multiplet.

The mass spectrum of (I) shows prominent peaks at *m*/*e* values (relative abundances and assignments in parentheses) of 153 (61·6; parent ion), 69 (47·4; CF_3^+), *54* (*100·0*; $C_4H_6^+$), 39 (36·2; $C_3H_3^+$), 29 (20·5; CHO^+), and 27 (14·2; $C_2H_3^+$). The base peak at 54 corresponds to the $C_4H_6^+$ ion, and presumably arises through the retro-Diels–Alder cleavage:[4]



Oxazines have recently been found to result from the interaction of trichloronitrosomethane with butadienes.[5]

Trifluoronitrosomethane reacts extremely slowly with ethylene[1] at 20°/7 atm. to give an elastomer, while in a similar very slow reaction at 100°/8 atm. an unidentified compound containing a 2 : 1 molar ratio of trifluoronitrosomethane : ethylene is obtained. Isobutene was therefore examined to determine whether its greater nucleophilic character would facilitate reaction. Trifluoronitrosomethane reacts rapidly with isobutene at —78° to give a compound believed to be *N*-2-methylallyl-*N*-trifluoromethylhydroxylamine (IV) in 96% yield; this product is thus different in type from either of those obtained from ethylene.

$CH_2{:}CMe{\cdot}CH_2{\cdot}N(OH){\cdot}CF_3$ (IV)

$CH_2{:}CMe{\cdot}CH_2{\cdot}O{\cdot}NH{\cdot}CF_3$ (V)

The reaction product from trifluoronitrosomethane and isobutene is a white crystalline solid at —78°, but at *ca.* —30° it melts to a colourless liquid, which decomposes slowly in glass at 20°, forming carbon dioxide, silicon tetrafluoride, and an amber gum. Its p.m.r. spectrum consists of four bands (τ 3·88, 5·00, 6·54, and 8·23) of relative intensities 1 : 2 : 2 : 3, which are assigned to the hydrogen nuclei of OH, :CH_2, N·CH_2, and CH_3 groups, respectively. The band at τ 8·23 appears to be a doublet (*J*=0·7 c./sec.). The band due to the :CH_2 group is particularly broad (width at half-height *ca.* 3·9 c./sec.) and shows signs

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[3] R. C. Lord and R. W. Walker, *J. Amer. Chem. Soc.*, 1954, **76**, 2518.

[4] K. Biemann, " Mass Spectrometry," McGraw-Hill, New York, 1962, p. 103.

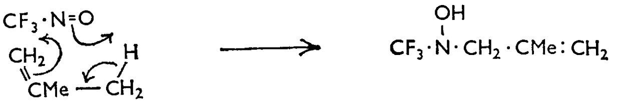
[5] D. Klamann, P. Weyerstahl, and M. Fligge, *Angew. Chem., Internat. Edn.*, 1964, **3**, 146.

of unresolved multiplet structure, which may be due to (i) weak coupling to the other hydrogen nuclei in the molecule, and (ii) the fact that the hydrogen nuclei in this group are in different environments and hence should give rise to an AB-type pattern. On this basis, the doublet structure of the methyl group band is ascribed to the coupling to one of the hydrogen nuclei of the $:CH_2$ group. The spectrum provides good evidence for the presence of a methallyl group in the 1 : 1 adduct, and is consistent with both structure (IV) and (V), except that the sharpness of the band at τ 3·88 (width at half-height *ca.* 2·7 c./sec.) militates against the presence of an NH group which might be expected to give rise to a broader band *via* the nitrogen-14 quadrupole effect.

Few of the peaks present in the mass spectrum of the compound can be assigned with certainty to only one ion specie, but on the whole the spectrum is again more consistent with the structure (IV) than (V). The parent-ion is fairly prominent, and isotopic analysis confirms the molecular formula $C_5H_8F_3NO$, while the base peak corresponds to the $C_3H_5^+$ ion, and an intense peak corresponding to the ion $C_4H_7^+$ is present. Strong evidence in favour of structure (IV) is provided by peaks corresponding to OH^+ and OH_2^+ ions and by the occurrence of a peak corresponding to $C_5H_7F_2N^+$, formation of which from (V) would require very extensive rearrangement to occur. The last ion arises from the parent-ion by loss of 36 mass units, which is most reasonably accounted for by the loss of the fragments F and OH, since (i) loss of carbon-containing fragments is impossible to reconcile with mass numbers, and (ii) loss of a nitrogen-containing fragment appears highly improbable without concurrent loss of the CF_3 group.

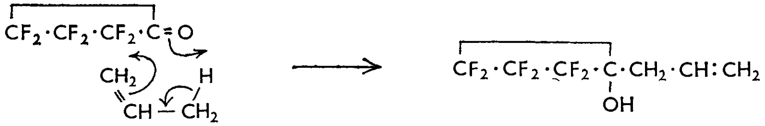
The infrared spectrum of the liquid 1 : 1 adduct appears to be consistent with both structures (IV) and (V). It shows bands that can be assigned to C–H and C–F bonds, and to the C:C bond (1661 cm.$^{-1}$), and also a broad band (*ca.* 3406 cm.$^{-1}$) with a sharp shoulder at 3571 cm.$^{-1}$, which, in view of the p.m.r. and mass spectroscopic evidence, may be due to bonded and free O–H stretching frequencies, respectively.

Formation of (IV) from trifluoronitrosomethane and isobutene is visualised as nucleophilic attack by the olefin on the nitrogen of the nitroso-compound, followed, or accompanied, by transfer of an allylic hydrogen atom to the oxygen:



(IV)

The same type of scheme can be used to account for formation of tertiary alcohols from polyfluoroketones and hydrocarbon olefins containing allylic hydrogen atoms,[6] *e.g.*,



and nucleophilic attack on the nitrogen of a polyfluoroalkylnitroso-compound is well established.[7]

EXPERIMENTAL

Products were separated by trap-to-trap fractional condensation *in vacuo* and by precise distillation, and were identified by molecular weight determination (Regnault's method), infrared spectroscopy (Perkin-Elmer spectrometer model 21 with sodium chloride or calcium fluoride optics), proton magnetic resonance spectroscopy (A.E.I. RS2 spectrometer operating

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[6] D. C. England, *J. Amer. Chem. Soc.*, 1961, **83**, 2205; H. R. Davis, *Abs. 140th Meeting Amer. Chem. Soc.*, Chicago, Sept. 1961, p. 25M; I. L. Knunyants and B. L. Dyatkin, *Izvest. Akad. Nauk S.S.S.R.*, 1962, 355.

[7] See earlier Papers in this Series.

at 60 Mc./sec.; chemical shifts were measured relative to tetramethylsilane as internal standard), gas–liquid chromatography (Perkin-Elmer "Vapor Fraktometer," model 116), and mass spectrometry (A.E.I. MS/2H instrument).

Trifluoronitrosomethane was prepared by photolysis of a trifluoroiodomethane–nitric oxide mixture,[8] and by pyrolysis of trifluoroacetyl nitrite.[9] Butadiene was a purified commercial sample, and isobutene was obtained by dehydrating t-butyl alcohol in the presence of oxalic acid.

Reaction of Trifluoronitrosomethane with Butadiene.—Trifluoronitrosomethane (8·55 g., 86·4 mmoles) and butadiene (4·64 g., 85·8 mmoles), kept at −78° for 40 min. in a 450-ml. Dreadnought ampoule, gave unchanged starting materials ($CF_3\cdot NO$, 2·3 mmoles; C_4H_6, 2·0 mmoles) and 3,6-*dihydro*-2-*trifluoromethyl*-1,2-*oxazine* (12·82 g., 83·8 mmoles; 97%) (Found: C, 39·2; H, 3·9; N, 8·9%; *M*, 154. $C_5H_6F_3NO$ requires C, 39·2; H, 3·9; N, 9·1%; *M*, 153), b. p. (Siwoloboff) 108°/748 mm.

NOTE. When the above reaction, which was carried out several times without mishap, was repeated but the temperature of the reaction mixture was allowed to rise from −196° (temperature at which the reactants were condensed into the Dreadnought ampoule) to −5°, a violent explosion completely destroyed the reaction vessel.

Properties and Reactions of 3,6-*Dihydro*-2-*trifluoromethyl*-1,2-*oxazine*.—(a) *Physical properties*. The infrared spectrum of 3,6-dihydro-2-trifluoromethyl-1,2-oxazine vapour contains bands characteristic of the $\cdot CH_2\cdot CH{:}CH\cdot$ group at 3052 (:C–H str.), 2958, 2905, 2860 (·C:C·CH–H str.), 1653 (C:C str.), and 1435 cm.$^{-1}$ (CH_2 def.). The mass spectrum of the oxazine shows prominent peaks at *m/e* values (relative abundances in parentheses) of 153 (61·6), 69 (47·4), *54* (*100·0*), 42 (12·0), 40 (12·1), 39 (36·2), 29 (20·5), and 27 (14·2).

(b) *Hydrogenation*. When a solution of 3,6-dihydro-2-trifluoromethyl-1,2-oxazine (7·57 g., 49·5 mmoles) in ether (40 ml.) containing a 5% Pd–C catalyst (1·0 g.) was shaken at 0° in the presence of hydrogen at 1 atm. pressure, the theoretical amount of hydrogen was absorbed (1110 ml.) to give *tetrahydro*-2-*trifluoromethyl*-1,2-*oxazine* (6·48 g., 41·8 mmoles; 85%) (Found: C, 38·7; H, 5·0; N, 8·9%; *M*, 155. $C_5H_8F_3NO$ requires C, 38·7; H, 5·2; N, 9·0%, *M*, 155), b. p. 111—112°.

The infrared spectrum of tetrahydro-2-trifluoromethyl-1,2-oxazine shows only two resolved bands in the C–H stretching region, at 2958 and 2917 cm.$^{-1}$ (CaF_2 prism). The mass spectrum shows prominent ions at *m/e* (relative abundance) 155 (30·8), 114 (61·9), 69 (34·9), *55* (*100·0*), 54 (14·1), 42 (10·0), 41 (22·8), 39 (12·2), 29 (26·4), and 27 (15·1). The rearrangement ion $C_2H_3F_3NO^+$ is assigned to the process $C_5H_8F_3NO^+ \longrightarrow C_2H_3F_3NO^+ + C_3H_5$, and this is confirmed by the presence of a metastable peak at *m/e* = 83·9.

(c) *Bromination*. A mixture, prepared by dropwise addition of bromine (1·10 g., 6·9 mmoles) in carbon tetrachloride (5 ml.) to 3,6-dihydro-2-trifluoromethyl-1,2-oxazine (1·00 g., 6·54 mmoles) at 0°, was left at 20° overnight and then evaporated *in vacuo*. The crystalline residue was sublimed at 23° *in vacuo* to give 4,5-*dibromotetrahydro*-2-*trifluoromethyl*-1,2-*oxazine* (1·80 g., 5·75 mmoles; 88%) (Found: C, 19·2; H, 1·9; N, 4·8%. $C_5Br_2H_6F_3NO$ requires C, 19·2; H, 1·9; N, 4·5%) as a white crystalline solid, m. p. 32—32·5°.

Reaction of Trifluoronitrosomethane with Isobutene.—Trifluoronitrosomethane (4·45 g., 45·0 mmoles) and isobutene (2·52 g., 45·0 mmoles), kept at −78° for 30 min. in a 300-ml. Dreadnought ampoule, gave N-2-*methallyl*-N-*trifluoromethylhydroxylamine* (6·74 g., 43·5 mmoles; 96%) [Found: C, 38·6; H, 5·4; N, 9·1%; *M*, 155 (mass spectrometry). $C_5H_8F_3NO$ requires C, 38·7; H, 5·2; N, 9·0%; *M*, 155], b. p. (Siwoloboff) 110°/757 mm.

N-2-Methallyl-*N*-trifluoromethylhydroxylamine is unstable in glass at room temperature (80% decomposition in 4 weeks), forming carbon dioxide, silicon tetrafluoride, and an amber gum [Found: C, 41·2; H, 6·2; N, 9·1% $(C_5H_8F_3NO)_n$ requires C, 38·7; H, 5·2; N, 9·0%]. The infrared spectrum (liquid film) of the hydroxylamine contains bands at 3571 (sh., O–H str.), 3406 (broad, O–H str.) 3077 (:CH–H str.), 2976 (asym. CH_3 str.), 3946, 2920, and 2857 (C–H str. of CH_2 and CH_3 groups), 1828 (overtone of 909 cm.$^{-1}$ band), 1661 (C:C str.), 1453 (CH_2 def. and CH_3 asym. def.), 1381 (sym. CH_3 def.), 1314, 1287, 1227, 1152, 1091, 1073, 1056, 1033, 997, 970, 909 (:CH_2 o.o.p. def.), 825, 719, 692, and 680 cm.$^{-1}$. The mass spectrum shows peaks at *m/e* values (relative abundances in parentheses) of 155 (7·2), 140 (1·5), 119 (1·7), 118 (2·7),

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[8] Part XII, A. H. Dinwoodie, and R. N. Haszeldine, *J.*, 1965 1675.

[9] R. E. Banks, R. N. Haszeldine, and M. K. McCreath, *Proc. Chem. Soc.*, 1961, 64; R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, publication in preparation.

114 (4·4), 113 (2·9), 104 (5·6), 98 (2·3), 97 (2·7), 96 (3·7), 92 (1·7), 91 (1·0), 82 (4·5), 81 (5·3), 78 (4·2), 77 (3·2), 70 (1·4), 69 (15·2), 68 (1·9), 67 (1·4), 64 (1·4), 56 (56·4), 55 (67·8), 54 (12·5), 53 (12·0), 52 (2·6), 51 (6·1), 50 (7·2), 49 (1·8), 47 (2·4), 45 (1·3), 44 (7·1), 43 (1·9), 42 (9·9), *41*, (*100·0*), 40 (11·9), 39 (60·8), 38 (7·9), 37 (4·1), 33 (2·0), 31 (1·2), 30 (2·8), 29 (26·2), 28 (22·6), 27 (23·6), 26 (5·0), 18 (5·6), 17 (1·2), and 15 (3·1).

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