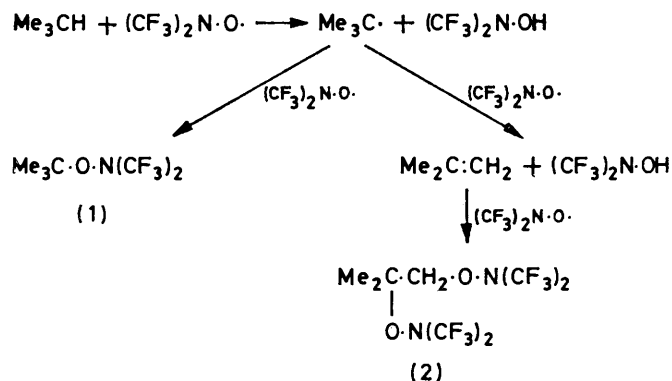


Nitroxide Chemistry. Part VIII.¹ Abstraction of Allylic Hydrogen from Isobutene by Bistrifluoromethyl Nitroxide

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Vapour-phase reaction of isobutene with bistrifluoromethyl nitroxide at 200 °C and low pressure leads to the formation of the 1 : 2 olefin-nitroxide adduct $\text{Me}_2\text{R}\cdot\text{CH}_2\text{R}$ and, mainly, the product arising from free-radical abstraction of allylic hydrogen, $\text{RCH}_2\cdot\text{CMe}\cdot\text{CH}_2$ [$\text{R} = (\text{CF}_3)_2\text{N}\cdot\text{O}$]. The former product is best prepared on a large scale by passing the nitroxide into the liquid olefin at *ca.* -60 °C. Acid-catalysed reaction of *NN*-bistrifluoromethylhydroxylamine with isobutene constitutes a convenient laboratory route to the amino-oxypropane Me_2CR .

We have reported previously that when a 2 : 1 molar mixture of bistrifluoromethyl nitroxide and isobutane is



allowed to warm from -196 °C to room temperature, rapid reaction leads to the formation of 2-(bistrifluoro-

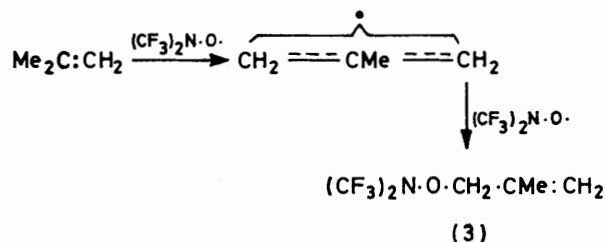
methylamino-oxy)-2-methylpropane (1) and 1,2-di(bistrifluoromethylamino-oxy)-2-methylpropane (2), together with *NN*-bistrifluoromethylhydroxylamine and a small amount of unidentified material.² In the presence of an inert solvent the conversion of isobutane into isobutene was 91%. The unidentified material must have arisen, at least in part, *via* hydrogen-atom abstraction by the nitroxide since the amount of *NN*-bistrifluoromethylhydroxylamine formed exceeded that required for the production of compounds (1) and (2). One of the components has now been found to be 3-(bistrifluoromethylamino-oxy)-2-methylpropene (3), formed by allylic nitroxylation of isobutene.

Yields of (3) of only 8–15% were obtained by low temperature reaction of bistrifluoromethyl nitroxide with isobutane without solvent or in carbon tetrachloride solution, but a 49% yield was obtained by passage of preheated isobutene and the nitroxide

¹ Part VII, R. E. Banks, K. C. Eapen, R. N. Haszeldine, A. V. Holt, T. Myerscough, and S. Smith, *J.C.S. Perkin I*, 1974, 2532.

² R. E. Banks, R. N. Haszeldine, and B. Justin, *J. Chem. Soc. (C)*, 1971, 2777.

separately into a mixing chamber at 200 °C and with *ca.* 1 cmHg pressure, a method suitable for larger scale



preparation; the yield of (2) at 200 °C was 40%. The marked effect of temperature on the yield of (3) was consistent with the results of parallel studies on the gas kinetics of the addition-abstraction reaction of bistrifluoromethyl nitroxide with isobutene.³

On a larger scale, (2) is conveniently prepared by bubbling the nitroxide into liquid isobutene at low temperatures; scale-up of the sealed-tube technique² can lead to explosive rupture of the Pyrex vessel and to charring.

An alternative convenient route to (1) in 85% yield was found in the reaction of *NN*-bistrifluoromethylhydroxylamine with isobutene in the presence of sulphuric acid.

EXPERIMENTAL

Reaction of Bistrifluoromethyl Nitroxide with Isobutene.—The nitroxide (1.18 g, 7.02 mmol) was condensed, *in vacuo*, into a cold (−196 °C) Pyrex tube (50 cm³) containing isobutane (0.41 g, 7.08 mmol). The tube was sealed, allowed to warm slowly to room temperature, then stored in the dark for 1 h. Work-up of the product by trap-to-trap fractional condensation *in vacuo*, followed by analysis of the fractions by i.r. and n.m.r. spectroscopy, g.l.c., and molecular weight determination (Regnault's method), showed it to comprise *NN*-bistrifluoromethylhydroxylamine (0.67 g, 3.94 mmol, 56%), 2-(bistrifluoromethylamino-oxy)-2-methylpropane (1) (0.15 g, 0.68 mmol, 33% based on isobutane consumed), 1,2-di(bistrifluoromethylamino-oxy)-2-methylpropane (2) (0.27 g, 0.68 mmol, 33%), 3-(bistrifluoromethylamino-oxy)-2-methylpropene (3) (0.036 g, 0.16 mmol, 8%), isobutane (0.29 g, 5.00 mmol, 71% recovery), and unidentified material (*ca.* 0.1 g).

The reaction was repeated exactly except that the nitroxide was condensed onto a homogeneous mixture of carbon tetrachloride (5.0 g) and isobutane. The product comprised *NN*-bistrifluoromethylhydroxylamine (0.63 g, 3.72 mmol, 53%), isobutane (0.29 g, 5.00 mmol; 71% recovery), compounds (1) (0.09 g, 0.40 mmol, 19%), (2) (0.435 g, 1.11 mmol, 53%), and (3) (0.07 g, 0.32 mmol, 15%), and unidentified material.

Reaction of Bistrifluoromethyl Nitroxide with Isobutene.—(a) *At* −60 °C. During 1 h, bistrifluoromethyl nitroxide (17.97 g, 107 mmol) was bubbled at a constant rate into isobutene (3.03 g, 54.1 mmol) contained in a flask cooled to −60 °C and fitted with a cold-finger (−72 °C) condenser.

Distillation of the product afforded 1,2-di(bistrifluoromethylamino-oxy)-2-methylpropane (17.57 g, 44.8 mmol, 84%), b.p. 129.5 °C, which was identified by i.r. spectroscopy and found to be >99% pure by g.l.c. analysis.

(b) *At* 200 °C. The reactor comprised a Pyrex tube (80 × 2.0 cm) fitted with two parallel inlet tubes (47 × 0.6 cm) that acted as preheaters for the reactants; the reactor was heated to 200 °C over 50 cm of its length, being placed in a 64 cm furnace so that the heated reaction zone below the point where the inlet tubes terminated had a length of 15 cm, and the exit was connected to a vacuum system *via* a cold trap (−196 °C). The apparatus was evacuated, then isolated from the pump while bistrifluoromethyl nitroxide (35.5 g, 0.211 mol) and isobutene (15.0 g, 0.27 mol) were metered simultaneously and at constant rates into the reactor during 5.25 h; the pressure in the reactor during this period was *ca.* 1 cmHg. The product that condensed in the cold trap was passed at *ca.* 2 mmHg pressure through a train of cold traps comprising three cooled to −78 and one to −196 °C; isobutene (11.85 g, 0.212 mol, 79%) was recovered from the −196 °C trap, and the material (38.5 g) from the −78 °C traps was washed with 4*M*-sodium hydroxide to remove *NN*-bistrifluoromethylhydroxylamine (9.37 g, 55.4 mmol, 53%), dried (MgSO₄), and distilled in a 45 × 0.6 mm Nester Faust spinning-band apparatus to provide 3-(bistrifluoromethylamino-oxy)-2-methylpropene (11.5 g, 51.6 mmol, 49%) (Found: C, 31.8; H, 3.0; F, 50.7; N, 6.0%; *M*⁺, 223. C₆H₇F₆NO requires C, 32.3; H, 3.1; F, 51.1; N, 6.3%; *M*, 223), b.p. 75 °C, λ_{max} (vapour) 3.23 (CH₂ asym. str.), 6.00 (C=C str.), and 9.52 μm (N—O str.), δ_F (neat liq.) 7.88 (s) downfield from ext. CF₃·CO₂H, τ 8.20 (m, :C·CH₃), 5.58 (s, :C·CH₃), and 5.00 (m, :CH₂) (rel. int. 3 : 2 : 2); and 1,2-di(bistrifluoromethylamino-oxy)-2-methylpropane (16.3 g, 41.6 mmol, 40%), b.p. 129 °C, i.r. spectrum identical with that of an authentic sample.

Reaction of NN-Bistrifluoromethylhydroxylamine with Isobutene.—A mixture of the hydroxylamine (5.28 g, 31.4 mmol) and isobutene (1.78 g, 31.8 mmol) was stored in a Pyrex ampoule (300 cm³) at room temperature for 24 h. The reactants were recovered virtually quantitatively by standard techniques.

The hydroxylamine (5.14 g, 30.4 mmol) and isobutene (1.76 g, 31.4 mmol) were condensed, *in vacuo*, into a cold (−196 °C) Pyrex tube (300 cm³) containing 18*M*-sulphuric acid (*ca.* 0.05 cm³). The tube was sealed and stored at room temperature for 3 days. Work-up by standard techniques gave *NN*-bistrifluoromethylhydroxylamine (2.66 g, 15.7 mmol, 52% recovery); 2-(bistrifluoromethylamino-oxy)-2-methylpropane [2.82 g, 12.5 mmol, 85% based on (CF₃)₂N·OH consumed] (Found: C, 32.3; H, 4.2; N, 6.0. Calc. for C₆H₉F₆NO: C, 32.0; H, 4.0; N, 6.2%), isolated by g.l.c. and possessing an i.r. spectrum identical with that of an authentic sample; and polymeric material.

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³ P. E. Coles, R. N. Haszeldine, and P. J. Robinson, unpublished results.