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NITROXIDE CHEMISTRY. PART XIV [1]. REACTIONS OF TRIFLUORO-
METHYL 2,3-DIMETHYLBUT-3-EN-2-YL AND TRIFLUOROMETHYL
2,3-DIMETHYLBUT-2-YL NITROXIDES

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SUMMARY

The nitroxide $\text{CF}_3\text{N}(\dot{\text{O}})\text{CMe}_2\text{CMe}=\text{CH}_2$ abstracts the aldehydic hydrogen from benzaldehyde, yielding the benzoyl compound $\text{PhCO}_2\text{N}(\text{CF}_3)\text{CMe}_2\text{CMe}=\text{CH}_2$ (82%), the benzylic hydrogen from cumene, yielding $\text{PhCMe}_2\text{ON}(\text{CF}_3)\text{CMe}_2\text{CMe}=\text{CH}_2$ (80%), and the methylene group hydrogen from fluorene, oxidises benzoin to benzil, and hydroquinol to quinone, attacks the Si-H bond of trimethylsilane, and adds to tetrafluoroethylene to give the compound $\text{R}^1\text{N}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{ON}(\text{CF}_3)\text{R}^1$ ($\text{R}^1 = \text{CMe}_2\text{CMe}=\text{CH}_2$, 97%), and to hexafluoropropene to give the 2:1-adduct.

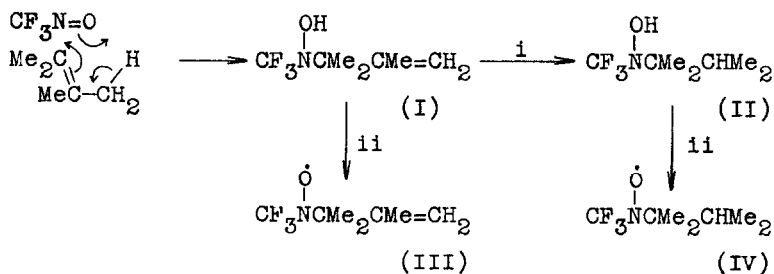
In a similar manner, the nitroxide $\text{CF}_3\text{N}(\dot{\text{O}})\text{CMe}_2\text{CHMe}_2$ adds to tetrafluoroethylene to give the compound $\text{R}^2\text{N}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{ON}(\text{CF}_3)\text{R}^2$ ($\text{R}^2 = \text{CMe}_2\text{CHMe}_2$, 75%) and to hexafluoropropene to give a similar adduct (71%), and abstracts a benzylic hydrogen from toluene.

INTRODUCTION

Reactions of bistrifluoromethyl nitroxide have been extensively studied; it is a reactive and versatile compound [2]. The 'ene' reaction of trifluoronitrosomethane with

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2,3-dimethylbut-2-ene provided a hydroxylamine (I), which, along with the corresponding saturated compound (II), could readily be oxidised by silver(II) oxide to a stable nitroxide (see Scheme 1) [3]. These nitroxides (III) and (IV) are of a novel class [4], containing both a fluorocarbon and hydrocarbon grouping [5].

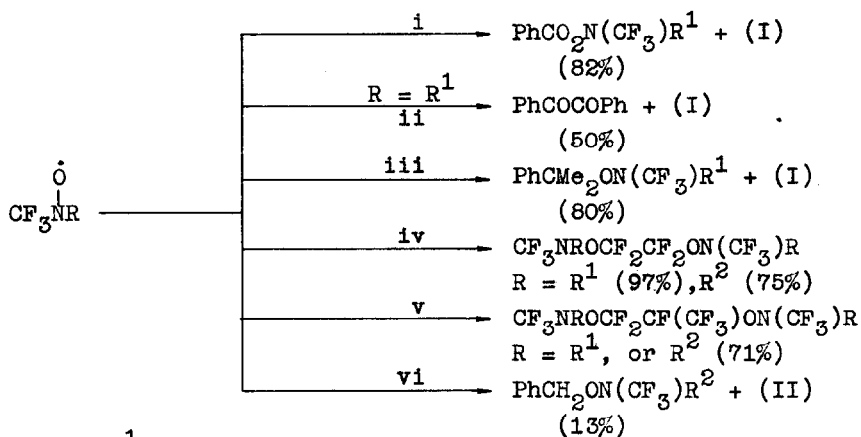


Scheme 1: Reagents: i, H₂, Pd/C (5%) in Et₂O; ii, AgO at room temperature.

RESULTS

It appeared opportune to survey the reactivity of these nitroxides. The results are shown in Scheme 2. The high yields of adducts with tetrafluoroethylene indicate that both nitroxides are efficient scavengers for free radicals. Addition to hexafluoropropene occurs somewhat less readily. Hydrogen atoms are readily abstracted from activated C-H bonds, and the resultant radical is efficiently trapped. In addition to the reactions shown, the nitroxide (III) attacked the CH₂ group of fluorene to give fluorenone and probably a fluorenyl hydroxylamine, and attacked the Si-H bond of trimethylsilane probably giving the compound Me₃SiON(CF₃)CMe₂CMe=CH₂, but this was not separated from the hydroxylamine (I). It oxidises hydroquinol to p-benzoquinone. The nitroxide (IV) formed an unstable compound, presumably the o-nitroso-compound, with nitric oxide at low temperatures, and attacked mercury.

The nitroxides (III) and (IV) thus undergo reactions similar to those of bistrifluoromethyl nitroxide, but less rapidly, perhaps because of steric and inductive effects of



$\text{R} = \text{R}^1 = \text{CMe}_2\text{CMe}=\text{CH}_2$
 or $\text{R} = \text{R}^2 = \text{CMe}_2\text{CHMe}_2$

Scheme 2. Reagents: i, PhCHO, room temperature, 3 h; ii, PhCH(OH)COPh in CH_2Cl_2 , reflux, 7 h; iii, PhCHMe₂, room temperature, 9 h; iv, C_2F_4 , room temperature; v, $\text{CF}_2=\text{CFCF}_3$, room temperature; and vi, PhMe , 48 °C, 20 h.

the alkyl groups. For example, bistrifluoromethyl nitroxide reacts exothermically with benzaldehyde [2], and with toluene at room temperature [6], and adds to hexafluoropropene within 15 minutes at room temperature [7].

EXPERIMENTAL

I.r., ¹H (at 60.00 MHz) and ¹⁹F n.m.r. (at 56.46 MHz with trifluoroacetic acid as external reference; positive chemical shifts are to low field of the reference), and mass spectra were obtained with a Perkin-Elmer spectrophotometer model 21, a Perkin-Elmer R10 instrument, and an A.E.I. MS/2H spectrometer (electron beam energy 70 eV), respectively.

Preparation of trifluoromethyl (2,3-dimethylbut-3-en-2-yl) nitroxide

Silver(II) oxide (0.50 g, 4.0 mmol) was added slowly to N-trifluoromethyl-N-2,3-dimethylbut-3-en-2-ylhydroxylamine (1.83 g, 10.0 mmol), contained in a 25 ml flask, when, after a short induction period, a vigorous exothermic reaction took place. Further silver(II) oxide (1.50 g, 12 mmol) was

added, then the volatile product was dried (molecular sieve) to give trifluoromethyl (2,3-dimethylbut-3-en-2-yl) nitroxide (nc) (1.51 g, 8.3 mmol, 83%) (Found: C, 46.2; H, 6.3; N, 7.6. $C_7H_{11}F_3NO$ requires C, 46.2; H, 6.1; N, 7.7%), as a deep red liquid with λ_{max} . ca. 500 and 227 nm (ϵ 2040 in hexane), which decomposed slowly at room temperature.

WARNING On one occasion when the silver residues were warmed in vacuo, a small explosion occurred.

Preparation of trifluoromethyl (2,3-dimethylbut-2-yl) nitroxide

In a similar manner, oxidation of N-trifluoromethyl-N-2,3-dimethylbut-2-ylhydroxylamine (4.58 g, 25 mmol) gave trifluoromethyl (2,3-dimethylbut-2-yl) nitroxide (nc) (3.42 g, 18.6 mmol, 75%) (Found: C, 45.9; H, 7.3; N, 7.9. $C_7H_{13}F_3NO$ requires C, 45.7; H, 7.1; N, 7.9%), as a deep red liquid with λ_{max} . 506 and 232 nm (ϵ 1800 in hexane), which decomposed slowly at room temperature.

Oxidation of the hydroxylamine with lead tetra-acetate at room temperature gave trifluoronitrosomethane (38%), identified by i.r. spectroscopy.

Reactions of trifluoromethyl (2,3-dimethylbut-3-en-2-yl) nitroxide

(a) With benzaldehyde

Dropwise addition of the nitroxide (0.92 g, 5.0 mmol) to benzaldehyde (2.66 g, 25 mmol) at room temperature resulted in an exothermic reaction, complete after 3 h, when removal of material volatile at room temperature (2.81 g), comprising benzaldehyde (90%) and N-trifluoromethyl-N-2,3-dimethylbut-3-en-2-ylhydroxylamine (I) (10%), left a residue, which was distilled to give O-benzoyl-N-trifluoromethyl-N-2,3-dimethylbut-3-en-2-ylhydroxylamine (nc) (0.59 g, 2.1 mmol, 82%) (Found: C, 58.6; H, 5.7; N, 5.0. $C_{14}H_{16}F_3NO_2$ requires C, 58.5; H, 5.6; N, 4.9%), b.p. 150 °C at 0.1 mmHg, with δ_F 15.2 p.p.m. and δ_H 7.4-8.0 (C_6H_5), and 4.83 and 4.97 ($=CH_2$), 2.0 ($=CCH_3$), and 1.4 p.p.m. (2 x CH_3).

(b) With benzoin

The nitroxide (0.583 g, 3.2 mmol) and benzoin (0.344 g, 1.62 mmol) in methylene chloride (10 cm³), refluxed for 7 h, gave after removal of the solvent, a fraction (0.30 g) volatile at room temperature, shown by i.r. spectroscopy and g.l.c. to be mainly hydroxylamine (I), together with decomposition products, and a residue (0.36 g) of benzil and benzoin in approximately equal amounts (i.r.).

(c) With cumene

Dropwise addition of the nitroxide (0.92 g, 5.0 mmol) to cumene (3.00 g, 25 mmol) at room temperature resulted in almost complete reaction in 3 h. The hydroxylamine (I) and excess of cumene were removed in vacuo after 9 h, and the residue was distilled to give O- α,α -dimethylbenzyl-N-trifluoromethyl-N-2,3-dimethylbut-3-en-2-ylhydroxylamine (nc) (0.61 g, 2.0 mmol, 80%) (Found: C, 63.5; H, 7.2; N, 4.5. C₁₆H₂₂F₃NO requires C, 63.8; H, 7.3; N, 4.7%), as a pale yellow liquid b.p. 85 °C at 0.1 mmHg, with δ_F 16.6 p.p.m. and δ_H 7.3 (C₆H₅), 4.75 and 4.65 (=CH₂), 1.8 (CH₃C=), 1.7 [(CH₃)₂CO], and 1.3 and 1.1 p.p.m. [non-equivalent (CH₃)₂CN].

(d) With fluorene

The nitroxide (1.82 g, 10.0 mmol) and fluorene (0.83 g, 5.0 mmol) in methylene chloride (5 cm³), after 4 h at room temperature and removal of the solvent, gave a mixture of 2 components (t.l.c.) separated by chromatography (on activated alumina with benzene elution) into impure O-12-fluorenyl-N-trifluoromethyl-N-2,3-dimethylbut-3-en-2-ylhydroxylamine (Found: C, 72.1; H, 5.8; N, 3.6. Calc. for C₂₀H₂₀F₃NO: C, 69.1; H, 5.7; N, 4.0%), with δ_F 16.8 p.p.m. and δ_H 7.4 (aromatic H), 5.7 (CHO), 4.9 (=CH₂), 1.9 (CH₃C=), and 1.2 p.p.m. [(CH₃)₂C], as a colourless, viscous, liquid, and fluorenone (0.08 g, 0.44 mmol), together with a fraction volatile at room temperature comprising mainly hydroxylamine (I) (0.65 g, 3.55 mmol) and its decomposition products.

(e) With tetrafluoroethylene

The nitroxide (0.45 g, 2.47 mmol) and tetrafluoroethylene (0.15 g, 1.5 mmol) sealed in a Pyrex ampoule (5 cm³), gave after 5 days at room temperature recovered tetrafluoroethylene (0.025 g, 0.25 mmol) and 6,6,7,7-tetrafluoro-4,9-bistrifluoromethyl-2,3,3,10,10,11-hexamethyl-5,8-dioxa-4,9-diazadodeca-1,11-diene (nc) (0.56 g, 1.20 mmol, 97%) (Found: C, 41.7; H, 4.9; N, 5.9; F, 40.9. C₁₆H₂₂F₁₀N₂O₂ requires C, 41.4; H, 4.7; N, 6.0; F, 40.9%), as a colourless viscous liquid with δ_F 15.0 (CF₃, triplet, 12 Hz) and -11.4 p.p.m. (CF₂) and δ_H 4.95 and 4.85 (=CH₂), 1.9 (CH₃C=), and 1.4 p.p.m. (CH₃CN).

(f) With hexafluoropropene

The nitroxide (0.91 g, 5.0 mmol) and hexafluoropropene (1.39 g, 9.25 mmol), sealed in a Rotaflo tapped ampoule (50 cm³), gave after 4 days at room temperature and removal of unreacted hexafluoropropene, a pale yellow, viscous residue (1.28 g), comprising mainly one component (90%) by g.l.c. Distillation (at 150 °C/<1 mmHg) yielded impure 6,7,7-trifluoro-4,6,9-tristrifluoromethyl-2,3,3,10,10,11-hexamethyl-5,8-dioxa-4,9-diazadodeca-1,11-diene with δ_F 12 (CF₃N), 5 and 3 (CF₃C), -5 (CF₂), and -53 p.p.m. (CF), and δ_H 4.9 (=CH₂), 1.8 and 1.7 (CH₃C=), and 1.4 and 1.3 (CH₃CN).

(g) With hydroquinol

The nitroxide in benzene solution was rapidly reduced at room temperature by hydroquinol.

(h) With trimethylsilane

The nitroxide (0.45 g, 2.46 mmol) and trimethylsilane (1.46 g, 19.7 mmol), sealed in a 100 cm³ tube at room temperature, gave after 2 days and removal of unreacted silane, a mixture (0.36 g) of hydroxylamine (I) (1.16 mmol) and O-trimethylsilyl-N-trifluoromethyl-N-2,3-dimethylbut-3-en-2-ylhydroxylamine (0.58 mmol), identified by n.m.r. spectroscopy with δ_F 13.9 p.p.m. and δ_H 4.9 (=CH₂), 1.9 (CH₃C=), 1.4 (CH₃CN), and 0.3 p.p.m. (CH₃Si), which readily decomposed.

(i) With nitric oxide

The nitroxide and nitric oxide (1:1) gave a brown compound at low temperatures, which decomposed to the reactants on warming in vacuo to room temperature.

(j) Miscellaneous reductions

Qualitative observations were made that the nitroxide was rapidly reduced by thiophenol, diphenyldisulphide being formed, by a solution of 2,4-dinitrophenylhydrazine in methylene chloride, with evolution of nitrogen, by ethane thiol, by triphenylphosphine, and by the amines, pyrrole, piperidine, diethylamine, and triethylamine.

Reactions of trifluoromethyl (2,3-dimethylbut-2-yl) nitroxide

(a) Thermolysis

The nitroxide (0.24 g, 1.3 mmol), after 24 h at 50 °C, had almost completely decomposed, yielding a red-brown oil. The volatile products comprised carbonyl fluoride, silicon tetrafluoride, and a fraction condensing at -23 °C (0.083 g), which contained the hydroxylamine (II) (ca. 0.23 mmol, 18%) and at least 10 other components (by g.l.c.) which were not identified. Many were formed by decomposition of the hydroxylamine (II) itself. A brown involatile residue remained.

(b) With mercury

The nitroxide reacted upon shaking with mercury at room temperature during 20 min, but no organic product could be identified.

(c) With tetrafluoroethylene

The nitroxide (0.42 g, 2.3 mmol) and tetrafluoroethylene (0.59 g, 5.9 mmol), sealed in vacuo in a 100 cm³ tube, gave after three days (reaction was nearly complete after 1 day) and removal of unreacted tetrafluoroethylene, a viscous oil, extracted with carbon tetrachloride and distilled to give 6,6,7,7-tetrafluoro-4,9-bistrifluoromethyl-2,3,3,10,10,11-

hexamethyl-5,8-dioxa-4,9-diazadodecane (nc) (0.40 g, 0.86 mmol, 75%) (Found: C, 41.2; H, 5.9; N, 5.8; F, 40.6. $C_{16}H_{26}F_{10}N_2O_2$ requires C, 41.0; H, 5.6; N, 6.0; F, 40.6%) as a colourless liquid, b.p. 60 °C at 0.1 mmHg with δ_F 16.7 (CF_3) and -10.6 p.p.m. (CF_2) and δ_H 2.1 (CH), 1.2 (CH_3CN) and 1.0 (CH_3CC).

(d) With hexafluoropropene

The nitroxide (0.266 g, 1.44 mmol) and hexafluoropropene (0.200 g, 1.35 mmol), after 14 days at room temperature and removal of unreacted olefin, gave a viscous oil, flash distilled in vacuo to give 6,7,7-trifluoro-4,6,9-tris-trifluoromethyl-2,3,3,10,10,11-hexamethyl-5,8-dioxa-4,9-diazadodecane (nc) (0.265 g, 0.51 mmol, 71%) (Found: C, 39.6; H, 5.2; N, 5.5. $C_{17}H_{26}F_{12}N_2O_2$ requires C, 39.4; H, 5.0; N, 5.4%) as a colourless liquid with δ_F 17 (CF_3N), 3 and 4 (CF_3C), -4 (CF_2), and -48 (CF), and δ_H 2.1, 1.3, and 1.0 p.p.m. The ^{19}F n.m.r. spectrum indicated it to be a mixture of at least 2 isomers.

(e) With toluene

The nitroxide (0.75 g, 4.1 mmol) and toluene (4.21 g, 52.5 mmol), sealed in a 10 cm³ tube and heated at 48 °C for 20 h, gave small amounts of crystals (inorganic, SiF_6^{2-} by i.r.) and unreacted toluene, hydroxylamine (II) (by i.r. and g.l.c.), and a fraction, b.p. 50 °C at 0.1 mmHg (0.07 g) which g.l.c. (Apiezon L, 81-150 °C) indicated to be 94% Q-benzyl-N-trifluoromethyl-N-2,3-dimethylbut-2-ylhydroxylamine (0.27 mmol, 13%) (Found: C, 58.9; H, 7.7; N, 5.1. Calc. for $C_{14}H_{20}F_3NO$: C, 61.1; H, 7.3; N, 4.9%) containing toluene and hydroxylamine (II), which was identified by n.m.r. spectroscopy with δ_F 16.6 p.p.m. and δ_H 7.2 (C_6H_5), 4.7 (CH_2), 2.0 (CH), 1.1 (CH_3CN), and 0.9 (CH_3CC)

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