Journal of Fluorine Chemistry, 17 (1981) 561–564
© Elsevier Sequoia S.A., Lausanne – Printed in the Netherlands
Received: October 27, 1980

Nitroxide Chemistry. Part XIX. Reaction of Bistrifluoromethyl Nitroxide with Diphenylketene and Related Compounds (Ph_2CHCOX, X = OH, Cl, NH_2)

RONALD E. BANKS,* ROBERT N. HASZELDINE and MICHAEL B. MURRAY

Department of Chemistry, The University of Manchester
Institute of Science and Technology, Manchester M60 1QD
(Great Britain)

SUMMARY

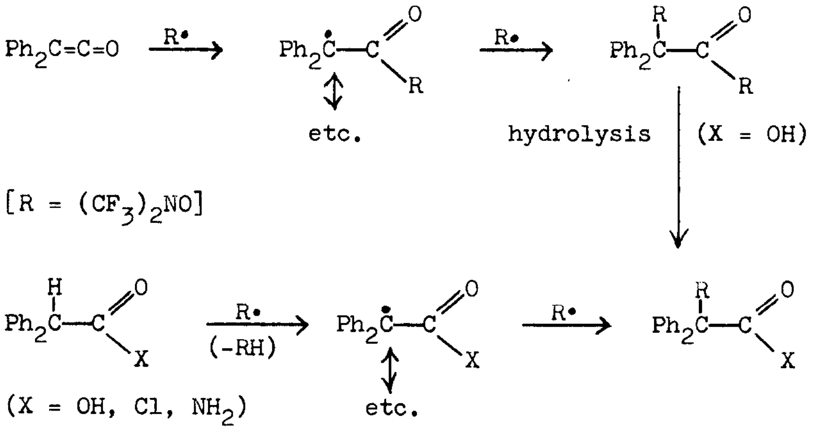
The following reactions have been accomplished: $2(CF_3)_2NO\cdot + Ph_2C{=}C{=}O \longrightarrow Ph_2C[ON(CF_3)_2]CO_2N(CF_3)_2 \longrightarrow$ (on hydrolysis) $Ph_2C[ON(CF_3)_2]CO_2H$; $2(CF_3)_2NO\cdot + Ph_2CHCOX \longrightarrow (CF_3)_2NOH + Ph_2C[ON(CF_3)_2]COX$ (X = OH, Cl, NH_2).

INTRODUCTION

The paucity of studies involving free-radical attack on ketenes recorded in the recent 'Patai' review of cumulene chemistry [1] prompts us to disclose that nearly a decade ago we found that bistrifluoromethyl nitroxide combines smoothly with diphenylketene in carbon tetrachloride at sub-zero temperatures to yield the 2:1 adduct $Ph_2C[ON(CF_3)_2]C(O)ON(CF_3)_2$ quantitatively. The structure of this new compound was established by elemental analysis, spectroscopic methods, and hydrolysis to provide the 'parent' acid $Ph_2C[ON(CF_3)_2]CO_2H$, a product which is best obtained by treating diphenylacetic acid with bistrifluoromethyl nitroxide (see the Scheme). Abstraction of benzylic hydrogen by the nitroxide [2] from diphenylacetyl chloride and diphenylacetamide produces the corresponding α-(bistrifluoromethylamino-oxy) derivatives quantitatively.

---

*To whom enquiries should be addressed.



Scheme

EXPERIMENTAL

N.m.r. Spectroscopy

Spectra were obtained using Perkin-Elmer R10 and R20A instruments operating at 60 (^1H) or 56.46 (^{19}F) MHz; chemical shifts (p.p.m.) were determined relative to external trifluoroacetic acid (δ_F) or benzene (δ_H), absorptions downfield from reference spikes being assigned positive values.

Reaction of Bistrifluoromethyl Nitroxide with Diphenylketene

The nitroxide (1.73 g, 10.3 mmol) was condensed, *in vacuo*, into a cold (-196 °C) Pyrex ampoule (200 cm^3) containing diphenylketene (1.00 g, 5.15 mmol) and carbon tetrachloride (25 cm^3). The ampoule was sealed (4 mm PTFE-glass Rotaflo valve) and removed from the cooling bath so that it could warm slowly to room temperature; while it was still quite cold (*ca.* -10 °C), the purple colour associated with bistrifluoromethyl nitroxide suddenly disappeared. Removal of carbon tetrachloride from the product at reduced pressure provided (bistrifluoromethylamino-oxy)(bistrifluoromethylamino-oxycarbonyl)diphenylmethane (nc) (2.73 g, 5.15 mmol, 100%) (Found: C, 41.9; H, 2.2. $C_{18}H_{10}F_{12}N_2O_3$ requires C, 40.8;

H, 1.9%), b.p. 95 °C at ca. 2 mmHg, $\lambda_{max.}$ (film) 5.48 μm (C=O str.), δ_F (ca. 15% w/v in CCl_4) +11.2 (s) and +12.45 (s) (rel.int. 1:1), δ_H (same soln.) +0.92 (s), and m/e 530 ($M^{+\cdot}$, <1), 362 {$Ph_2C[ON(CF_3)_2]CO^+$, 45}, 334 {$Ph_2C[ON(CF_3)_2]^+$, 14}, 194 ($Ph_2CCO^{+\cdot}$, 57), 182 ($Ph_2CO^{+\cdot}$, 36), 166 ($Ph_2C^{+\cdot}$, 29), 105 ($PhCO^+$, 76), 77 (Ph^+, 53), and 69 (CF_3^+, 100%).

Treatment of (bistrifluoromethylamino-oxy)(bistrifluoromethylamino-oxycarbonyl)diphenylmethane (1.00 g) with hot (90 °C) 2M-sodium hydroxide (20 cm^3) in a mechanically-shaken Pyrex ampoule (50 cm^3) for 6 h, followed by extraction (CCl_4) of the product to remove unchanged starting material (0.65 g), acidification (H_2SO_4) of the aqueous layer and further extraction (CCl_4), provided α-(bistrifluoromethylamino-oxy)diphenylacetic acid (0.24 g), identified by comparison of its i.r. and n.m.r. spectra with those of a sample prepared as described below.

Reaction of Bistrifluoromethyl Nitroxide with Diphenylacetic Acid and Some of Its Derivatives

(a) With diphenylacetic acid

Bistrifluoromethyl nitroxide (1.60 g, 9.52 mmol) was condensed, in vacuo, into a cold (-196 °C) Pyrex ampoule (200 cm^3) containing diphenylacetic acid (1.00 g, 4.72 mmol) and carbon tetrachloride (25 cm^3). The tube was sealed (Rotaflo valve) and stored at room temperature until only a faint purple colour [traces of unreacted $(CF_3)_2NO\cdot$] remained (15 h). Volatile material [$(CF_3)_2NOH$ (0.78 g, 4.62 mmol), CCl_4, and $(CF_3)_2NO\cdot$ (traces)] was removed from the ampoule, in vacuo, leaving a residue which was recrystallised from petroleum ether (b.p. 30-40 °C) to provide α-(bistrifluoromethylamino-oxy)diphenylacetic acid (nc) (1.77 g, 4.67 mmol, 99%) (Found: C, 49.7; H, 2.8; F, 29.4; N, 3.6%. $C_{16}H_{11}F_6NO_3$ requires C, 50.6; H, 2.9; F, 30.0; N, 3.7%), m.p. 106 °C, $\lambda_{max.}$ (20% soln. in CCl_4) 3.25 vbr. (O-H str.) and 5.81 (C=O str.) μm, δ_F (20% soln. in CCl_4) + 12.88, δ_H (same soln.) +0.77 (C_6H_5) and +4.55 br. (OH), and m/e 334 [$M^{+\cdot}$ - $\cdot CO_2H$, 10 (top mass peak)], 182 ($Ph_2CO^{+\cdot}$, 42), 166 ($Ph_2C^{+\cdot}$, 2), 105 ($PhCO^+$, 100), 69 (CF_3^+, 36%).

(b) With diphenylacetyl chloride

Experiment (a) above was repeated, using 1.48 g (8.81 mmol) of the nitroxide and 1.00 g (4.34 mmol) of the acyl chloride, to give (after 15 h at 20 °C) α-(bistrifluoromethylamino-oxy)diphenylacetyl chloride (nc) (1.70 g, 4.28 mmol, 99%) (Found: C, 49.2; H, 2.8. $C_{16}H_{10}ClF_6NO_2$ requires C, 48.4; H, 2.5%), m.p. 46 °C, b.p. 110 °C at 764 mmHg (Siwoloboff), $\lambda_{\underline{max.}}$ (film) 5.63 µm (C=0 str.), δ_F (10% soln. in CCl_4) $\underline{+12.80}$, and δ_H (same soln.) +0.85.

(c) With diphenylacetamide

Experiment (a) was repeated exactly, except that diphenylacetamide (1.00 g, 4.74 mmol) was used instead of the parent acid. A waxy solid left in the reaction vessel after volatile material had been pumped away was found to be α-(bistrifluoromethylamino-oxy)diphenylacetamide (nc) (1.80 g, 4.76 mmol, 100%) (Found: C, 50.5; H, 3.5; N, 7.2. $C_{16}H_{12}F_6N_2O_2$ requires C, 50.8; H, 3.2; N, 7.4%), m.p. 109 °C, $\lambda_{\underline{max.}}$ (20% soln. in CCl_4) 2.86, 3.19 br. (N-H str.), and $\underline{5.89}$ (C=0 str.), and δ_F (same soln.) +13.2.

REFERENCES

1 'The Chemistry of Ketenes, Allenes and Related Compounds' (Parts 1 and 2), ed. S. Patai, Wiley:Chichester, 1980.

2 This is a well-established type of reaction for the nitroxide [R.E. Banks, D.R. Choudhury, and R.N. Haszeldine, J.C.S. Perkin Trans. I (1973) 1092].