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# Photolysis of Dioxiranes in the Presence of a Nitroxide Radical Scavenger: The Intermediacy of Radical Anion and Diyl Species in the Production and Trapping of Methyl and Trifluoromethyl Radicals

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Electron transfer between dioxiranes **1** and nitroxide **2** affords the dioxirane radical anion–oxoammonium cation pair, which generates methyl radicals that are trapped by the nitroxide.

Dimethyldioxirane **1a** and its more reactive analogue methyl(trifluoromethyl)dioxirane **1b** have played an increasingly important role in synthetic chemistry as powerful yet selective oxidants.[1] Herein we give the first report of the reaction of dioxiranes **1** with a nitroxide to produce methyl radicals which were readily trapped by the radical scavenger. Photolysis of **1b** in the presence of a nitroxide, on the other hand, involved a completely different mechanism with trifluoromethyl radicals also being generated.

Recently[2] we have investigated the photochemical reaction

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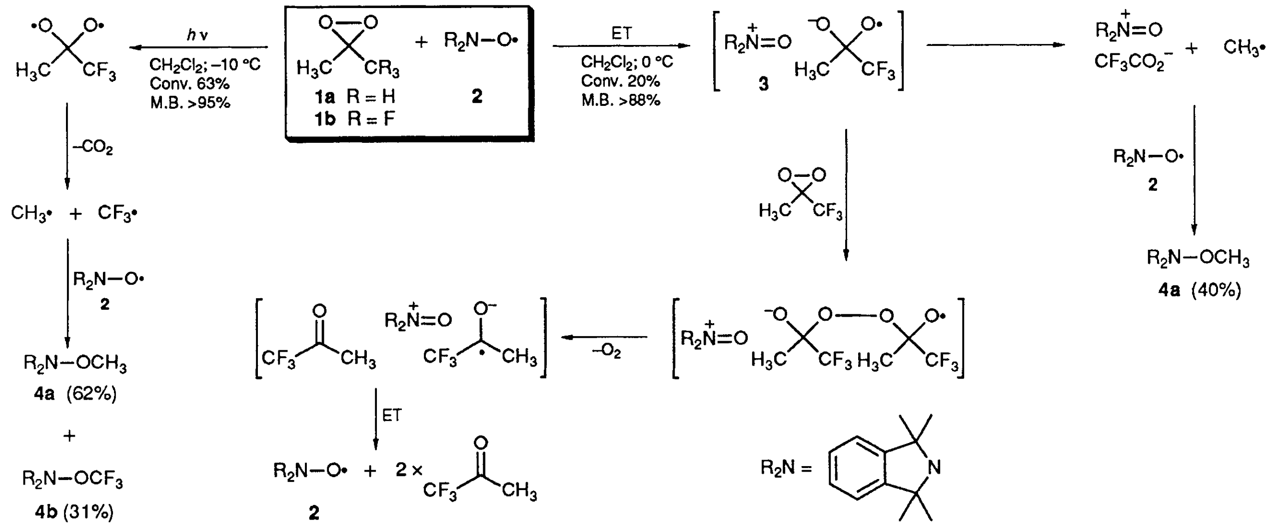

**Scheme 1** ET = electron transfer; M.B. = mass balance

pathways of dioxiranes **1b** and have proposed that a radical chain process is involved whereby methyl and trifluoromethyl radicals give rise to methyl and trifluoromethyl acetates derived from addition to the dioxirane. In support of this result we now provide experimental evidence that when the photolysis of the dioxirane **1b** is conducted in the presence of a radical trap, namely 1,1,3,3-tetramethyl-1,3-dihydroisoindolin-2-yloxyl **2**,[3] the adducts **4a** and **4b** are produced with suppression of the usual radical derived ester products.

After 30 min irradiation with $\lambda > 300$ nm[†] of the red solution formed on mixing of the dioxirane **1b** (3.0 ml, 0.34 mol dm$^{-3}$ in $CH_2Cl_2$, 1.0 mmol) and the nitroxide **2** (0.190 g, 1.00 mmol) in $CH_2Cl_2$ (5 ml) at −10 °C, no dioxirane remained (by 200 MHz $^1H$ NMR at −10 °C). Column chromatography (silica gel, 0.032–0.063 mm) followed by preparative GLC gave, for a 63% conversion of the nitroxide, the adducts **4a** (62%) and **4b** (31%) with a mass balance (based on the nitroxide) of over 95%. The methyl adduct **4a** had the same spectral characteristics ($^1H$ and $^{13}C$ NMR) and melting point as the known[4] authentic material. The trifluoromethyl adduct **4b** is a stable, low-melting, white, crystalline solid (needles from the preparative GLC, m.p. 72.5–73 °C)[‡] which was robust enough to give the expected molecular ion of *m/z* 259 in its electron impact (70 eV) mass spectrum. This is the first example of the trapping of the highly reactive trifluoromethyl radical by a nitroxide.

The strong-red colour of the product mixtures is characteristic[5] of the oxoammonium ion **3**, the one-electron oxidation product of the nitroxide. The red coloration arose immediately upon treatment of the dioxirane **1b** (1.5 ml, 0.34 mol dm$^{-3}$ in $CH_2Cl_2$, 0.50 mmol) with the nitroxide **2** (0.111 g, 0.584 mmol) in $CH_2Cl_2$ (2 ml). After 2 h at 0 °C, work-up of the reaction mixture and column chromatography (silica gel, 0.032–0.063 mm) also afforded for a 20% conversion of the nitroxide, without the need for photolysis, the methyl adduct **4a** (40%) in a mass balance of 88%; only traces of the trifluoromethyl adduct **4b** were detected by reversed phase HPLC. Similar results were obtained for the dioxirane **1a**, in that **4a** was detected upon treatment of a solution of the nitroxide with **1a**, albeit to a much smaller extent and the red colour of the oxoammonium salt **3** was not observed. Photolysis of this solution produced a *ca.* twofold increase, depending on the temperature and the irradiation time, in the amount of **4a**.

Furthermore, the reaction mixture of **1b** and the nitroxide also contained appreciable amounts of trifluoroacetone[§] (up to *ca.* three times the amount of **4a** depending on the reaction conditions), the usual oxygen transfer product of the dioxirane **1b**, which is not formed in its photolytic decomposition.[2] A blank reaction of the nitroxide in trifluoroacetone did not produce the adducts **4** (with or without photolysis), as determined by reversed phase HPLC.

The oxoammonium ion **3** was generated independently[4] by the action of $Cl_2$ on a solution of the nitroxide in acetonitrile. When **3** was treated with sodium acetate or sodium trifluoroacetate (with or without photolysis) the adducts **4a,b** were not produced. These results rule out the possibility that the adducts **4a,b** are derived from the oxoammonium acetate through ionic reactions.

It appears that the radical anion, derived from electron transfer to the dioxirane **1b**, plays a key role in the production of **4a** but not **4b**. The lower mass balance for the non-photolytic reaction no doubt reflects the amount of the material converted to the oxoammonium salt. Notably, the trifluoromethyl adduct **4b** was not produced unless the reaction mixture was irradiated. Nitroxides are known to undergo photolytically induced electron transfer reactions to produce oxoammonium salts;[6] however, with the dioxirane **1b** the electron transfer process occurs thermally, without the necessity of irradiation. The nitroxide **2** has a spectral window at the wavelength of the light used in the photolysis ($\lambda > 300$ nm), where its absorption is very low ($\varepsilon < 8$), and thus the electron transfer process between dioxirane and electronically excited nitroxide should be negligible. Besides, such photoinduced electron transfer would only increase the production of the dioxirane radical anion–oxoammonium cation pair and thus produce more **4a**.

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[†] From a Pyrex-filtered mercury high-pressure arc lamp or at $300 < \lambda < 350$ nm in a Rayonet photochemical reactor.

[‡] $^1H$ NMR ($CDCl_3$): δ 1.4 (s, 6H, 2 × $CH_3$), 1.5 (s, 6H, 2 × $CH_3$), 7.0 (m, 2H, ArH) and 7.2 (m, 2H, ArH); $^{13}C$ NMR ($CDCl_3$): δ 25.5 ($CH_3$), 29.1 ($CH_3$), 69.0 (C-1,3), 121.6 (C-4,7), 122.8 (q, $J_{CF}$ 255 Hz, $CF_3$), 127.1 (C-5,6), 143.2 (C-3a,7a); $^{19}F$ NMR ($CFCl_3$): δ −61.1 ($CF_3$).

[§] The $^1H$ NMR (200 MHz) spectrum of the reaction mixture at −10 °C showed a signal at δ 2.25 and the $^{13}C$ NMR (63 MHz) spectrum exhibited signals at δ 24.6, 115.9 (q, *J* 291 Hz) and 189.3 (q, *J* 35.9 Hz) attributable to this species. The addition of authentic trifluoroacetone resulted in the intensification of these signals.

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We propose that the photolysis affects the dioxirane directly, by inducing both methyl and trifluoromethyl cleavage, in accord with our previous results.[2] In the photolysis, the electron transfer process represents a colourful yet minor side process. In the absence of light, the dioxirane radical anion (produced by electron transfer between **1b** and **2**) predominantly generates methyl radicals. Moreover the relatively large amounts of the trifluoroacetone may arise from the reaction of the dioxirane radical anion with further dioxirane **1b**, followed by loss of dioxygen (Scheme 1). Electron back transfer from the ketyl radical anion to the oxoammonium ion produces the ketone and regenerates the nitroxide. We conclude that the production of methyl and trifluoromethyl radicals arises from the photolysis of the dioxirane directly and that the electron transfer reaction of the dioxirane **1** with the nitroxide **2** gives rise to methyl radicals.

The results presented here support our proposal that a (σ,π)-type dioxyl diradical leads to the formation of methyl and trifluoromethyl radicals by β-alkyl scission. Nevertheless, the non-photolytic production of methyl radicals from dioxiranes, as detected by nitroxide trapping, represents an unusual reaction pathway for these species. Not only is this electron transfer process mechanistically important, but is also significant for synthetic purposes, especially in view of the preparation of nitroxides from secondary amines by oxidation with dioxiranes.[7] It is therefore recommended that dimethyldioxirane **1a** should be used for such oxidations.

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