On the Reaction of Aminoxyls with Dioxiranes☆

Anna Dinoi[a], Ruggero Curci*[a], Patricia Carloni[b], Elisabetta Damiani[b], Pierluigi Stipa[b], and Lucedio Greci*[b]

Centro C.N.R. "M.I.S.O.", Dipartimento Chimica, Università di Bari[a],
via Amendola 173, I-70126 Bari, Italy

Dipartimento di Scienze dei Materiali e della Terra, Università di Ancona[b],
via Brecce Bianche, I-60131 Ancona, Italy

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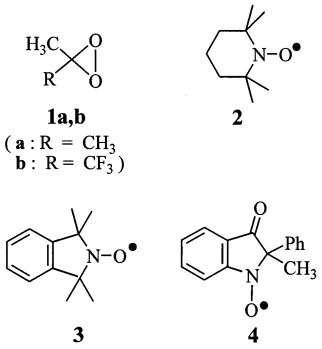
In the reactions of dimethyldioxirane (**1a**) and methyl(trifluoromethyl)dioxirane (**1b**) with 2,2,6,6-tetramethylpiperidinyl-1-oxyl (**2**) (TEMPO) in acetone, the corresponding methoxyamine 1-methoxy-2,2,6,6-tetramethylpiperidine (**5**) is produced in ≥98% yield, both in air and under N_2, and in the absence or presence of a hydrocarbon (adamantane). Kinetic experiments show that aminoxyl **2** triggers the radical decomposition of the dioxirane, in addition to scavenging methyl radicals derived therefrom. The reactions of an aminoxyl less prone to oxidation, namely 1,2-dihydro-2-methyl-2-phenyl-3*H*-indol-3-one-1-oxyl (**4**), with dioxiranes **1a** and **1b** in acetone have also been studied. In these cases, not only is the corresponding methoxyamine **8a** produced (yield 12−16%), but quinoneimine-*N*-oxides **10** (yield 12−21%) and **11** (yield 18−19%) are also formed. Furthermore, significant amounts (8−14%) of the amine **9** (the product of deoxygenation of **4**) can be isolated. These observations provide useful information concerning the free-radical mechanism that follows the initial attack by the aminoxyl at the dioxirane.

Introduction

Dioxiranes[1] have become well established as remarkable oxidants, capable of highly selective oxidations, including epoxidations and electrophilic *O*-insertion into non-activated alkane C−H bonds[1]. The latter transformation[1][2e] represents the highlight of dioxirane chemistry, since it allows the selective oxyfunctionalization of cyclic, polycyclic, and open-chain hydrocarbons[2e] with an efficiency matching that of cytochrome P-450 enzymes[3]. Because of its relevance, the mechanism of alkane oxidation by dioxiranes has recently become a matter of much debate[4][5][6][7], and thus reagents and conditions that may trigger the radical decomposition of dioxiranes (hence their radical reactivity)[5][8][9] have come under close scrutiny. In this context, Minisci et al. reported on an attempt to use the aminoxyl TEMPO (**2**) as a trapping agent for radicals purportedly formed during the oxidation of alkanes with dimethyldioxirane (**1a**, DMD)[4b]. They also suggested that TEMPO might induce the homolytic decomposition of the dioxirane. Indeed, in a previous communication it was reported by Adam, Bottle, and Mello[10] that photolysis of methyl(trifluoromethyl)dioxirane (**1b**, TFD) in the presence of 2,2,5,5-tetramethylisoindolin-2-oxyl (**3**, TMIO) produces methyl and trifluoromethyl radicals, which are trapped by the radical scavenger.

We now report our observations concerning the reactions of dimethyldioxirane (**1a**) and its trifluoro analogue **1b** with two representative aminoxyls having varied characteristics, namely TEMPO (**2**) and 1,2-dihydro-2-methyl-2-phenyl-3*H*-indol-3-one-1-oxyl (**4**, MPIO). We found that these radical species react readily with dioxiranes and promote their radical decomposition.



1a,b (**a**: R = CH_3; **b**: R = CF_3) **2** **3** **4**

Results and Discussion

Isolated dioxiranes generated in solution were employed as reagents in reactions with aminoxyls **2** and **4**. Solutions of 0.06−0.10 M dimethyldioxirane (**1a**)[2a] and 0.8−1.0 M methyl(trifluoromethyl)dioxirane (**1b**)[2d] in the parent ketones were prepared using procedures and equipment, and observing precautions, described in detail in previous reports.

Reaction of TEMPO with Dimethyldioxirane

We found that either with the solution exposed to air or in solvent purged with N_2, dimethyldioxirane (**1a**) undergoes a rapid reaction with the aminoxyl TEMPO (**2**) in acetone at 20°C, *even in the absence of an alkane substrate*. In fact, under conditions analogous to those adopted by Minisci et al.[4b] (except that adamantane was omitted), the reaction affords the corresponding methoxyamine **5**[11] in high yield, accompanied by only trace amounts of the acetonoxy derivative **6**[12] (Eq. 1).

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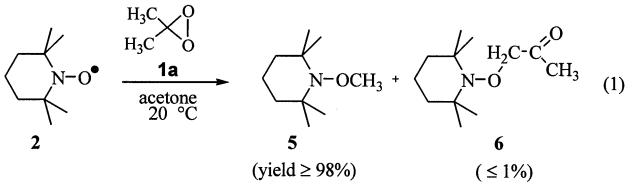


The identities of products **5** and **6** were confirmed by comparison (GC/MS, ^{1}H NMR) with authentic samples and/or with literature data[11][12]. Products derived from decomposition of dioxirane **1a**, i.e. methyl acetate[8a] $CH_3C(:O)OCH_3$ and acetyloxyacetone[9] $CH_3C(:O)O-CH_2C(:O)CH_3$ ($\leq$ 1%) were also detected. Representative data and reaction conditions are collected in Table 1 and Figure 1.

if alkane oxidation were to proceed via the formation of radical pairs and out-of-cage diffusion[4b] occurs (Chart 1).

Furthermore, the data in Table 1 illustrate that, both in air and under an inert atmosphere (nitrogen), the outcome of the reaction is unaffected by the presence of adamantane; indeed, the latter remains essentially unchanged. In all cases, the yield of methoxyamine **5** is practically quantitative, which is at variance with a report of a lower *yield* (ca. 60%)[4b].

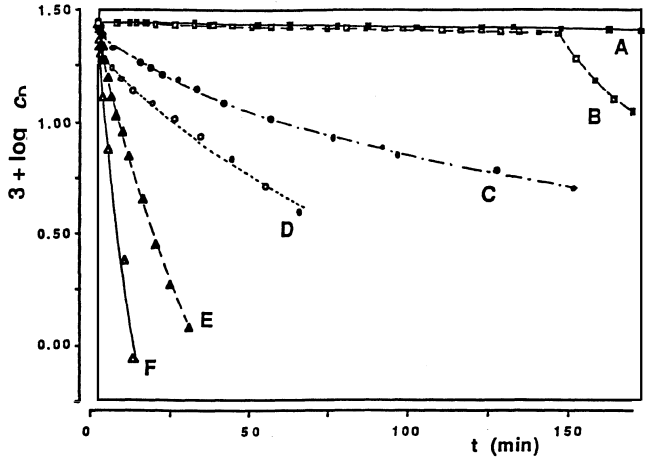
It is worthy of note that, both in air and under an inert (N_2) atmosphere, dioxirane decomposition induced by TEMPO becomes much faster than non-radical hydrocarbon hydroxylation[2e][5a]. For instance, under similar conditions, a second-order constant $k_2 = 0.31 \cdot 10^{-2}$ M^{-1}s^{-1} and an initial rate $R_o = 0.8 \cdot 10^{-5}$ M s^{-1} were estimated[5a]

Table 1. Reaction of TEMPO (**2**) with dimethyldioxirane (**1a**) in acetone at 20°C, in the absence and presence of adamantane (AdH)

Entry#	10^2•[DMD]$_o$ (M)	10^2•[TEMPO]$_o$ (M)	10^2•[AdH]$_o$ (M)	Atmosphere	Reactn. time (min)	TEMPO conv. (%)[a]	10^5•R_o (M s^{-1})[b]
1	2.93	0.55	–	air	240	98	2.66
2	2.93	0.55	–	N_2	120	98	7.45
3	2.80	2.94	–	air	50	70	4.55
4	2.80	2.93	–	N_2	20	78	16.5
5	2.84	14.0	–	air	20	18	13.6
6	2.90	2.80	2.80	air	50	63[c]	4.71
7	2.90	2.80	2.80	N_2	20	82[c]	16.5

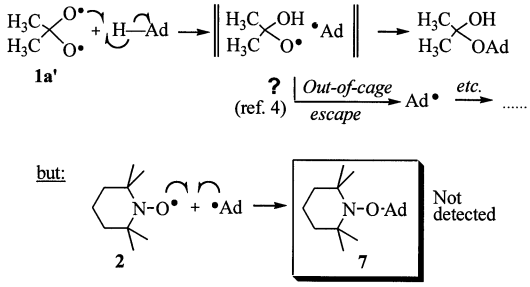
[a] In all cases, the yield of methoxyamine **5** was ≥98%, as based on the amount of TEMPO consumed; conversions were determined (±2%) by GC or GC/MS. – [b] Initial rates, estimated from the slopes of plots of dioxirane concentration vs. time over the initial 10–20% of the reaction; the data reported are averages (±5%) from duplicate runs. – [c] Trace amounts of 1-adamantanol were also detected (cf. refs.[4][5a]).

Figure 1. Decrease of dioxirane **1a** concentration (c_D) with time from ca 0.03 M initial concentration in acetone at 20.0°C: **A**: in air, in the absence of TEMPO; **B**: solvent purged with dry N_2, in the absence of TEMPO; **C**: in air, in the presence of 0.005 M TEMPO; **D**: solvent purged with dry N_2, in the presence of 0.005 M TEMPO; **E**: in air, in the presence of equimolar TEMPO; **F**: solvent purged with dry N_2, in the presence of equimolar TEMPO



When reactions of TEMPO with the dioxirane were performed in the presence of an equimolar amount of adamantane (e.g. entries 6 and 7), comparison with GC and GC/MS data of authentic adamanthoxyamine **7**[13] allowed us to establish that the latter is *not* formed in any detectable amount. However, this trapping product would be expected

Chart 1

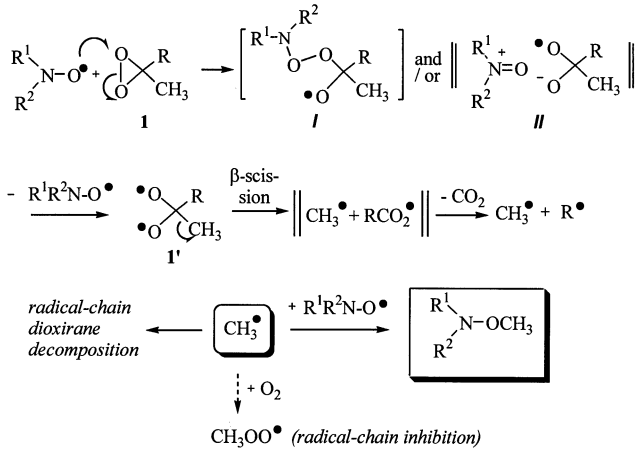


for the hydroxylation of adamantane (AdH) by dioxirane **1a** in air, in contrast to the much faster rates of entries 1, 3, and 5 (Table 1). The data in Table 1 and the kinetics of dioxirane consumption with time depicted in Figure 1 indicate that TEMPO, even at a molar ratio ca. 1:6 with respect to the dioxirane, is quite effective in causing peroxide decomposition. On the basis of R_o values collected for the reaction in air (entries 1, 3, and 5), from a plot of log R_o vs. log/[TEMPO]$_o$, a fractional kinetic order of about 0.5 for the aminoxyl can be estimated.

A further observation is that, in agreement with previous literature[1][8a], i.e. similar to other radical species such as $O_2^{\bullet-}$[8a], the aminoxyls *themselves induce* the radical decomposition of the peroxide, in addition to trapping radical species derived therefrom. Consistent with this view, both in air and under N_2, the rates are found to depend markedly

upon the aminoxyl concentration, as shown in Table 1 (entries 1−5) and Figure 1.

Scheme 1



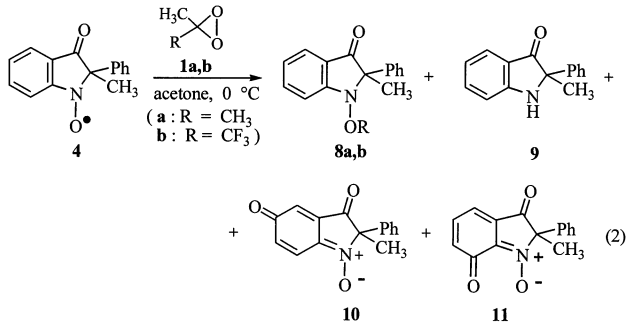
As outlined in Scheme 1, by analogy with the reaction of TEMPO with acyl peroxides[14], one might envisage an S_H2-type attack by the aminoxyl at the dioxirane O−O bond, yielding the very labile covalent adduct ***I***. Concurrent with, or alternatively to this, an outer-sphere electron-transfer might give rise to the caged pair ***II*** containing the oxoammonium cation[15]; the fact that the characteristic intense red color[14a][15] of the oxoammonium species is not observed could be due to fast in-cage back electron transfer, thereby leading to generation of the crucial bis(oxy)methylene biradical **1′** (Scheme 1). It is worthy of note that, at variance with findings concerning the reaction of acyl peroxides with TEMPO[14], in our case no products derived from oxidative degradation[14a] of the nitroxide were detected. Then, due to β-scission of the bis(oxyl) diradical **1′** to yield methyl radicals, radical-chain dioxirane decomposition would ensue, as shown in Scheme 1. The inhibition of radical decomposition of dioxirane by dissolved oxygen gas has been reported[4][5a], and is well understood[8a] in terms of the trapping of diffusing methyl radicals. On the other hand, formation of the methoxyamine by the alternative trapping of the reactive $CH_3^•$ by TEMPO should occur at a rate of ca. 10^8 M s^{-1} [16].

Reaction of TEMPO with Methyl(trifluoromethyl)dioxirane

The reaction of TEMPO with the trifluoromethyl analogue (**1b**) gave similar results as those described above, but proceeded at a remarkably faster rate. Typically, with initial TFD (**1b**) and TEMPO concentrations both of ca. 0.1 M in acetone at 0°C, 55% conversion of the aminoxyl was achieved within just 20 min. and methoxyamine **5** was obtained in high yield (≥96% by GC). In accordance with the *non-photolytic* (i.e. thermal) reactivity of dioxirane **1b** towards TMIO[10], formation of the $CF_3^•$ trapping product (i.e. the trifluoro analogue of **5**) was not detected to any appreciable amount; this might be due to the much faster generation of $CH_3^•$ compared to $CF_3^•$ following β-cleavage of bis(oxy)methylene biradical **1′**[17].

Reaction of MPIO with Dimethyldioxirane and Methyl(trifluoromethyl)dioxirane

It is of interest to compare the reactivity of dioxiranes towards TEMPO (**2**) with that towards 1,2-dihydro-2-methyl-2-phenyl-3*H*-indol-3-one-1-oxyl (**4**). In fact, the former should be more prone to oxidation, considering the different anodic potentials [E_{pa} = +0.62 and +1.10 V vs. SCE (in DMF/water, 6:4) for TEMPO[18][19] and MPIO[19], respectively]. This difference is sufficient to make other reaction pathways available. The outcome of the reactions of aminoxyl **4** (MPIO) with dioxiranes **1a** and **1b** in acetone is shown in Eq. 2.



Representative product distributions are presented in Table 2. Compounds **8a**[20], **9**[21], **10**[20], and **11**[22] could be isolated by semi-preparative TLC; they were identified by their spectral characteristics and/or by comparison with authentic samples.

In accord with the aforementioned higher oxidation potential of MPIO compared to that of TEMPO, we found that a moderate excess of DMD (**1a**) was necessary in order to achieve high aminoxyl conversion; this might be ascribed to dioxirane chain decomposition competing with methyl radical trapping by the aminoxyl **4** (cf. Scheme 1). However, the formation of indoxyl **9** (the deoxygenation product of **4**) and of quinoneimine *N*-oxides **10** and **11** suggests that other reaction pathways also become viable with this aminoxyl. The latter products are clearly derived from oxidation of the aromatic ring in aminoxyl **4**, for which several pathways might be envisaged. One possibility involves the process depicted in Scheme 2.

The dioxirane radical anion/oxoammoniun cation pair might arise by an inner-sphere ET, following the formation of the initial labile adduct ***I*** (Scheme 1)[23]. Then, oxyfunctionalization at the aromatic ring of **4** might occur largely by an in-cage process, for instance as depicted in Scheme 2 (R = CH_3)[24]. Here, labile intermediates such as **12** and **13** could be formed following attack at the aromatic ring; indeed, it is well documented[25] that oxoammonium ions (arising from oxidation of aromatic nitroxides such as MPIO) sustain nucleophilic attack at conjugated positions of their benzene ring[26]. Then, in line with the general reactivity of dioxiranes towards aminoxyls outlined in Scheme 1, in the reactions of MPIO (**4**) with dioxirane **1a** and **1b**, formation of the trapping product methoxyamine **8a** is still prominent (cf. Eq. 2 and Table 2).

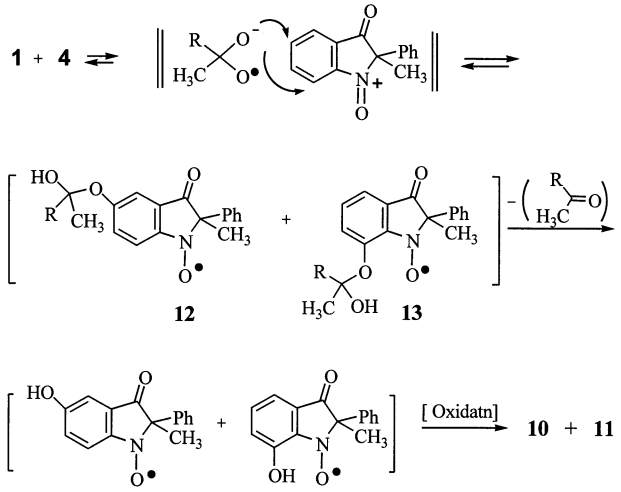
As in the case of TEMPO (see above), the corresponding labile trifluoromethoxyamine (from $CF_3^•$ trapping) could

Table 2. Product distribution from the reaction of indolinoneoxyl (**4**) with dioxiranes in acetone at 0°C

Dioxirane	(D/A) ratio [a]	Reactn. time (h)	Conv.[b] (%)	Products (% yield) [c] alkoxyamine	amine	quinoneimine *N*-oxide
DMD (**1a**)	3	3	80	**8a** (16)	**9** (8.5)	**10** (12), **11** (18)
TFD (**1b**)	1	0.5	75	**8a** (12)	**9** (14)	**10** (21), **11** (19)[d]

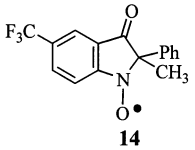
[a] Ratio of initial dioxirane and aminoxyl concentrations; initial concentrations of dioxiranes **1a** and **1b** were in the ranges 0.02−0.04 and 0.20−0.40 M, respectively. − [b] Degree of aminoxyl conversion, as determined from substrate recovery (semi-preparative TLC). − [c] Yield of product isolated (±3%), based on the amount of aminoxyl reacted. − [d] Other products also detected (see text).

Scheme 2



not be detected. However, in one case, a trace amount of a by-product was isolated, the EPR spectrum of which was consistent with that simulated for the 5-trifluoromethyl trapping product **14** (Figure 2); it exhibited many similarities [e.g. a_F ca. 3.9 (3 F) G] with EPR spectral data recorded for analogous 2,2-diphenylindolinone-1-oxyls in which a CF_3 substituent is attached at the aromatic nucleus[22]. Further work is in order to confirm this parallel.

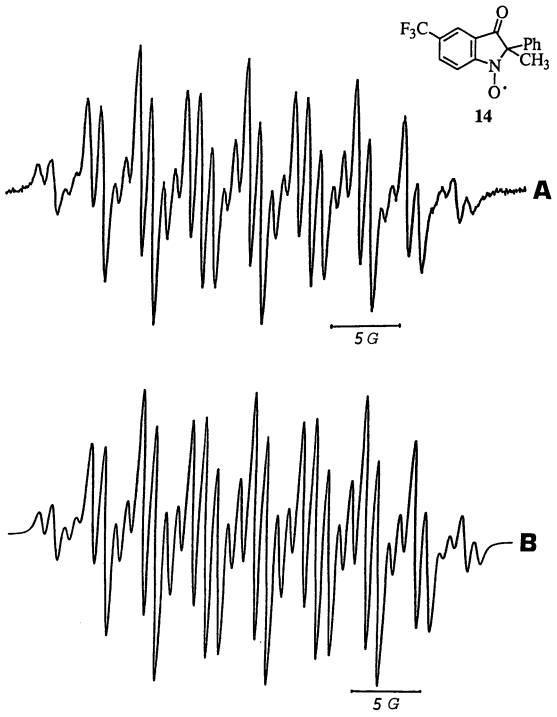
One conspicuous difference between the reactivity towards dioxiranes of TEMPO (or TMIO) and that of MPIO is that the latter aminoxyl yields significant amounts of the corresponding indoxyl **9** (Eq. 2, Table 2). This product is derived from deoxygenation of the parent aminoxyl **4**. By analogy to the reported[27][28] deoxygenation of electron-rich *N*-oxides by dioxiranes, this finding can most simply be explained by invoking fragmentation of the initially formed labile adduct ***I′*** (cf. Scheme 1) according to the pattern outlined in Eq. 3.

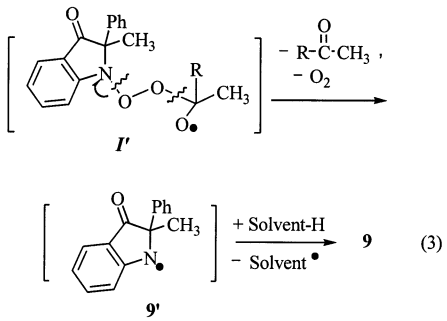


The reason for this pathway becoming practicable in the reaction of MPIO with dioxiranes might have its origin in the extra resonance stabilization available to the aminyl radical intermediate **9′**[29].

Taken as a whole, the aforementioned observations indicate that the reactivity of dioxiranes toward aminoxyls might present several facets and mechanistic features that are arduous to unravel. However, besides the mechanistic details, the results reported herein show conclusively that aminoxyls readily undergo *direct* reaction with dioxiranes and *trigger the radical decomposition* of these powerful oxidants. Thus, it can be concluded that aminoxyls are not suitable traps for radical intermediates formed in the course of DMD oxidations.

Figure 2. Experimental (**A**) and simulated (**B**) EPR spectrum of 5-(trifluoromethyl)-1,2-dihydro-2-methyl-2-phenyl-3*H*-indol-3-one-1-oxyl (**14**) ($CHCl_3$): a_N 8.85 (1 N), a_F 3.93 (3 F), $a_{H\text{-}7}$ 2.83 (1 H), $a_{H\text{-}4,6}$ 1.00 (2 H), $a_{H(CH3)}$ 0.19 G (3 H)





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Experimental Section

Instrumentation: M.p.: Electrothermal melting point apparatus. Melting points are not corrected. − FT-IR: Nicolet 20SX. − ^{1}H NMR: Varian Gemini 200 or Varian XL 200 (200 MHz). Spectra were referenced to residual isotopic impurity $CHCl_3$ (δ = 7.24) of the solvent $CDCl_3$ and/or to TMS. − MS: Carlo Erba QMD 1000 GLC/MS spectrometer with a direct probe apparatus (EI, 70 eV). − EPR: Varian E4 spectrometer. Hyperfine coupling constants are given in Gauss. − GC: Perkin-Elmer 8420 capillary gas chromatograph with FID and VOCOL fused silica capillary column (3.0 mm film thickness, 60 m × 0.53 mm ID). − GC/MS: Hewlett-Packard model 5890 gas chromatograph with Hewlett-Packard model 5970 mass selective detector (EI, 70 eV) and cross-linked methylsilicone capillary column (HP1, 0.33 mm film thickness, 25 m × 0.22 mm ID).

Materials: High purity commercial solvents (Fluka) dichloromethane, acetone, cyclohexane, ethyl acetate, and 1,1,1-trifluoro-2-propanone (TFP) (b.p. 22°C) were further purified by standard methods, stored over 5-Å molecular sieves at 2−5°C, and routinely redistilled prior to use. For semi-preparative TLC, silica gel plates (0.25 mm layer thickness, 60 Å medium pore diameter) (Fluka) were employed. High purity commercial 2,2,6,6-tetramethylpiperidinyl-1-oxyl (**2**, TEMPO) (Fluka) was further purified by sublimation (m.p. 38−39°C). The synthesis and spectral characteristics of 1,2-dihydro-2-methyl-2-phenyl-3*H*-indol-3-one-1-oxyl (**4**, MPIO) (m.p. 167°C) have been reported elsewhere[30]. Previously described protocols were employed in order to obtain dioxiranes **1a** and **1b** as solutions in the parent ketones[1][2]. We used the "Curox" triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (a gift from Peroxid-Chemie GmbH, Munich, Germany) as a source of potassium peroxymonosulfate, which was employed in the synthesis of the dioxiranes.

Reaction of TEMPO (**2**) *with Dimethyldioxirane* (**1a**): To a stirred solution of TEMPO (**2**) (0.060−0.32 M) in acetone (10 ml) kept at 20°C, a standardized solution of dioxirane **1a** (16 ml, 0.08 M, 0.64 mmol) in acetone was added in one portion. The reaction mixture was monitored by iodometry until the peroxide had been completely consumed. The reaction mixture was then analyzed by GC and/or GC/MS in order to determine the substrate conversion and product yields (Table 1). After addition of a small amount of 1,2-diphenylhydrazine (in order to quench any unreacted TEMPO by converting it into the corresponding hydroxylamine), and removal of the solvent in vacuo, the identities of the products were confirmed by ^{1}H-NMR analysis.

1-Methoxy-2,2,6,6-tetramethylpiperidine (**5**)[11]: b.p. 60°C (8 Torr). − ^{1}H NMR ($CDCl_3$): δ = 3.60 (s, 3 H), 1.44 (m, 6 H), 1.15 (s, 6 H), 1.09 (s, 6 H). − MS (70 eV); *m/z* (%): 171 (6) [M^+], 157 (10), 156 (100) [$M^+ - CH_3$], 125 (5), 109 (20), 100 (12), 97 (10), 88 (36), 87 (10), 83 (11), 69 (44), 58 (14), 56 (44), 55 (57), 43 (16), 42 (56), 41 (93), 40 (10), 39 (36).

1-Acetonoxy-2,2,6,6-tetramethylpiperidine (**6**)[12]: Oil; ^{1}H NMR ($CDCl_3$): δ = 4.40 (s, 2 H), 2.17 (s, 3 H). − MS (70 eV); *m/z* (%): 213 (7) [M^+], 198 (52) [$M^+ - CH_3$], 156 (29) [$M^+ - 57$], 126 (19), 123 (12), 109 (10), 83 (42), 82 (10), 81 (10), 70 (18), 69 (50), 58 (33), 56 (64), 55 (100), 43 (54), 42 (35), 41 (59), 39 (16).

Kinetic Measurements: Runs were performed by following the decrease of dioxirane concentration (by iodometry) with time, according to previously described analytical techniques[2e][5]. The following is representative of the simple procedure adopted in these experiments: at zero time an aliquot of a thermostatted (20.00 ± 0.05°C) solution of TEMPO (**2**) (0.15 mmol) in acetone (10 ml) was added in one portion to a 0.08 M dimethyldioxirane (**1a**) solution in acetone (16 ml, 0.64 mmol) (also thermostatted). Aliquots (0.2 ml) of the reaction solution were then withdrawn at timed intervals, quenched with excess KI/EtOH, and the liberated I_2 was determined by iodometry. Runs were performed under various conditions, keeping the ratio of initial dioxirane **1a** and TEMPO (**2**) concentrations in the range 0.1−5. Initial rates R_o (M s^{-1}) were estimated from the slopes of plots of dioxirane concentration *vs.* time, based on the initial 10−20% of the reaction. In each case, at least two independent runs were performed and the R_o values averaged (estimated error ≤ ±5%) (Table 1).

Reaction of MPIO (**4**) *with Dimethyldioxirane* (**1a**): To a stirred solution of MPIO (**4**) (190 mg, 0.8 mmol) in CH_2Cl_2 (5 ml) kept at 0°C, a standardized solution of dioxirane **1a** (3 ml, 0.08 M, 0.240 mmol) in acetone was added in three portions. According to TLC analysis, after 3 h total substrate conversion had not been achieved. Removal of the solvent in vacuo and semi-preparative TLC (cyclohexane/ethyl acetate, 8:2) resulted in partial recovery of the starting material (37 mg, 0.156 mmol) and isolation of the reaction products (individual yields are reported in Table 2). Compounds **8a**[20], **9**[21], **10**[20], and **11**[22] were identified by comparison of their spectral characteristics with those of authentic samples obtained independently and/or literature data. Very small amounts of the following labile intermediates (see Results and Discussion) could be detected and quickly isolated by TLC; the labile nature of radical intermediates **12a** and **13a** prevented their further purification by crystallization or by common chromatographic techniques:

5-(2-Hydroxy-2-propyloxy)-1,2-dihydro-2-methyl-2-phenyl-3H-indol-3-one-1-oxyl (**12a**): IR (KBr): $\tilde{\nu}$ = 3358, 1719, 1607 cm^{-1}. − MS (70 eV); *m/z* (%): 311 (5) [$M^+ - 1$], 281 (7), 222 (58), 77 (100). − EPR (C_6H_6): a_N 9.18 (1 N), $a_{H\text{-}7}$ 2.83 (1 H), $a_{H\text{-}4,6}$ 1.00 G (2 H)[31].

7-(2-Hydroxy-2-propyloxy)-1,2-dihydro-2-methyl-2-phenyl-3H-indol-3-one-1-oxyl (**13a**): IR (KBr): $\tilde{\nu}$ = 3414, 1721, 1606 cm^{-1}. − MS (70 eV); *m/z* (%): 311 (6) [$M^+ - 1$], 238 (100), 222 (18), 77 (89). − EPR (C_6H_6): a_N 9.03 (1 N), $a_{H\text{-}5}$ 3.20 (1 H), $a_{H\text{-}4,6}$ 1.00 (2 H), $a_{H\ (CH3)}$ 0.18 G (3 H)[31].

Reaction of MPIO (**4**) *with Methyl(trifluoromethyl)dioxirane* (**1b**): To a stirred solution of MPIO (**4**) (190 mg, 0.8 mmol) in CH_2Cl_2 (5 ml) kept at 0°C, a standardized solution of dioxirane **1b** (1 ml, 0.8 M, 0.8 mmol) in 1,1,1-trifluoropropanone was added in one portion. After 0.5 h, TLC analysis revealed that total conversion of the substrate had not been achieved. According to the procedure described above, some starting material (45 mg, 0.19 mmol) was recovered and compounds **8a**, **9**, **10**, and **11** were isolated in the yields shown in Table 2. A further reaction product was isolated as a deliquescent solid in trace amounts (< 5 mg), which gave: EPR ($CHCl_3$): a_N 8.85 (1 N), a_F 3.93 (3 F), $a_{H\text{-}7}$ 2.83 (1 H), $a_{H\text{-}4,6}$ 1.00 (2 H), $a_{H\ (CH3)}$ 0.19 G (3 H). This intermediate was tentatively identified as 5-(trifluoromethyl)-1,2-dihydro-2-methyl-2-phenyl-3*H*-indol-3-one-1-oxyl (**14**) by comparison with simulated EPR spectra (Figure 2).

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[23] It should be noted that in this case the intense red color of the aminoxyl **4** starting material would preclude direct observation of the rise of the red-colored oxoammonium species.

[24] Based on the available literature (refs.[8b][8c]), dioxirane radical anions freely diffusing out of the cage would be expected to react readily with the dioxirane, yielding the dimer $^{-}O-CR(CH_3)-O-O-CR(CH_3)-O^{\bullet}$, and hence $R(CH_3)C=O$ and superoxide $O_2^{-\bullet}$.

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[26] Actually, by carrying out the reaction of DMD with **4** at intermediate conversions (30−50%), two new aminoxyls could be isolated in tiny amounts (≤ 3%) by TLC, one having a greenish- and the other a reddish-brown color in solution; this is typical of indolinone-1-oxyls substituted with electron-donor groups at C-5 and at C-7, respectively[25]. The IR spectra of both compounds displayed an O−H absorption near 3400 cm^{-1} besides the expected carbonyl stretching (ca. 1720 cm^{-1}), and a band at ca. 1600 cm^{-1}, which is typical of the indoline framework[20][21]. Based on their MS m/z = 311 [$M^+ - 1$] peaks and fragmentation patterns (see Experimental Section), we tentatively assign to these intermediates the isomeric structures of adducts **12a** and **13a** (Scheme 2, **12** and **13**: R = CH_3). The EPR spectra are consistent with these assignments; in fact, besides yielding different a_N (1 N) and similar $a_{H\text{-}4,6}$ (2 H) values, one compound gives $a_{H\text{-}7}$ = 2.83 G and the other $a_{H\text{-}5}$ = 3.20 G, which is in agreement with isomeric **12a** and **13a**, respectively (see Experimental Section; *cf.* also C. Berti, M. Colonna, L. Greci, L. Marchetti, *Tetrahedron* **1977**, *33*, 3149−3154). It should be mentioned that, in the reaction of **4** with TFD (**1b**), the analogous adducts **12b** and/or **13b** (Scheme 2, **12** and **13**: R = CF_3) could not be detected; this might be ascribed to their faster consecutive conversion into quinoneimine *N*-oxides by TFD, an oxidant which is more powerful than DMD.

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[31] The original EPR spectrum is available on request by e-mail to: <Ruggero Curci> csmirc17@area.ba.cnr.it.

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