# Oxidation of secondary alcohols and ethers by dimethyldioxirane

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Abstract: The oxidation of several series of secondary alcohols 2–9, ethers 10–17, and related derivatives 18 and 19, by dimethyldioxirane, 1, in acetone at 25°C produced the corresponding ketones in good to excellent yields for all but two cases. (The exceptions: oxidation of 1-methoxy-2-methyl-1-phenylpropane (48%) and 1-methoxy-2,2-dimethyl-1-phenylpropane (24%).) The oxidation of the secondary alcohols was found to yield  $k_2$  values that were roughly 10-fold greater than those of the corresponding methyl ethers. The rate constant for oxidation of a silyl ether was slightly lower than that for the corresponding methyl ether while that for the ester derivative was roughly half the value. For oxidation of alcohols and methyl ethers, the  $k_2$  values became smaller as the R" series (Me, Et, *n*Pr, iPr, and *t*Bu) increased in steric bulk ( $\rho^* = 1.7$ ; r = 0.998 and  $\rho^* = 3.2$ ; r = 0.95, respectively). The Hammett study for the oxidation of the methyl ethers of  $\alpha$ -methyl-*p*-benzyl alcohols (10, 20–25) yielded a  $\rho$  value of -0.74. The activation parameters for oxidation of the parent compound of the ether series (1-methoxy-1-phenylethane) were  $\Delta H^{\ddagger} = 14.8 \pm 0.5 \text{ kcal/mol}$ ,  $\Delta S^{\ddagger} = -21.9 \text{ eu}$ ,  $\Delta G^{\ddagger} = 21.3 \text{ kcal/mol}$ ,  $k_2 (25°C) = 1.6 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ . The mechanistic aspects of the oxidation are discussed in relation to two mechanistic extremes: (*a*) direct insertion of the oxygen atom into the C —H bond and (*b*) direct abstraction of the H by dimethyldioxirane to yield a caged-radical pair, with subsequent coupling to hemi-ketal intermediates that fragment to yield acetone, alcohol or water, and ketone as the final products.

Key words: dimethyldioxirane, oxidation.

Résumé : L'oxydation de plusieurs séries d'alcools secondaires (2-9), d'éthers (10-17) et de dérivés apparentés (18 et 19), par le diméthyldioxirane (1) dans l'acétone, à 25°C, conduit aux cétones correspondantes avec des rendements allant de bons à excellents (à l'exception des deux cas suivants : 1-méthoxy-2-méthyl-1-phénylpropane (48%) et 1méthoxy-1-phénylpropane (24%)). On a observé que les valeurs de  $k_2$  des alcools secondaires sont environ 10 fois plus élevées que celles des éthers méthyliques correspondants. La constante de vitesse d'oxydation d'un éther silylé est légèrement inférieure à celle de l'éther méthylique correspondant alors que celle du dérivé ester est approximativement égale à la moitié de la valeur. Pour l'oxydation des alcools et des éthers méthyliques, les valeurs de  $k_2$  deviennent de plus en plus faibles avec une augmentation de l'empêchement stérique (Me, Et, *n*Pr, iPr, *t*-Bu) de la série R'' ( $\rho^* = 1.7$ ; r = 0.998 et  $\rho^* = 3.2$ ; r = 0.95 respectivement). Une étude de Hammett pour l'oxydation des éthers méthyliques des alcools benzyliques 10 et 20–25 conduit à une valeur de  $\rho$  de –0,74. Les paramètres d'activation pour l'oxydation du produit parent de la série des éthers (1-méthoxy-1-phényléthane) sont:  $\Delta H = 14.8 \pm 0.5$  kcal/mol,  $\Delta S = 21.9$  ue;  $\Delta G =$ 21,3 kcal/mol et  $k_2$  (25°C) = 1,6 × 10<sup>-3</sup> M<sup>-1</sup> s<sup>-1</sup>. On discute des aspects mécanistiques de l'oxydation en relation avec deux mécanismes extrêmes : (a) insertion directe de l'atome d'oxygène dans la liaison C-H et (b) enlèvement direct de l'hydrogène par le diméthyldioxirane, conduisant à une paire de radicaux en cage, suivie d'un couplage subséquent formant des intermédiaires hémicétals qui se fragmentent ensuite pour donner de l'acétone, de l'alcool ou de l'eau et la cétone comme produits finals.

Mots clés : diméthyldioxirane, oxydation.

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### Introduction

Dimethyldioxirane, **1**, has become an extremely versatile reagent for the fast, mild oxidation of a great variety of organic substrates (for reviews, see ref. 1) since the initial report of its isolation and characterization (2, 3). Although

considerably less reactive than methyl(trifluoromethyl)dioxirane (4), dimethyldioxirane is often the reagent of choice because of its facile, inexpensive preparation. For example, dimethyldioxirane has been shown to be useful (1) for olefin epoxidation, heteroatom oxidation, and oxidation of C—H bonds of saturated hydrocarbons, phenyl-substituted hydro-

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A memorial to Professor P.D. Bartlett. Your teaching continues to inspire!

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|                       | R′ | R″          | Ζ                 | $k_2 (M^{-1} s^{-1})^a$          | % Yield <sup>b</sup> | Relative reactivity |
|-----------------------|----|-------------|-------------------|----------------------------------|----------------------|---------------------|
| Alcohol               |    |             |                   |                                  |                      |                     |
| <b>2</b> <sup>c</sup> | Ph | Me          | Н                 | $(2.24\pm0.06) \times 10^{-2}$   | 98                   | ≅1.00               |
| 3                     | Ph | Et          | Н                 | $(1.48\pm0.03) \times 10^{-2}$   | 92                   | 0.66                |
| 4                     | Ph | nPr         | Н                 | $(1.45\pm0.03) \times 10^{-2}$   | 92                   | 0.65                |
| 5                     | Ph | iPr         | Н                 | $(1.02\pm0.02) \times 10^{-2}$   | 90                   | 0.46                |
| 6                     | Ph | <i>t</i> Bu | Н                 | $(6.9\pm0.1) \times 10^{-3}$     | 90                   | 0.31                |
| 7                     | Ph | Ph          | Н                 | $(8.9\pm0.1) \times 10^{-3}$     | 96                   | 0.40                |
| 8                     | Ph | Cyclopropyl | Н                 | $(1.97\pm0.03) \times 10^{-2}$   | 92                   | 0.88                |
| 9                     | Bz | Me          | Н                 | $(7.1\pm0.1) \times 10^{-3}$     | 85                   | 0.32                |
| Ethers                |    |             |                   |                                  |                      |                     |
| 10                    | Ph | Me          | Me                | $(1.63\pm0.03) \times 10^{-3}$   | 90                   | 0.073               |
| 11                    | Ph | Et          | Me                | $1.03\pm0.02 \times 10^{-3}$     | 81                   | 0.046               |
| 12                    | Ph | nPr         | Me                | $(7.6\pm0.1) \times 10^{-4}$     | 86                   | 0.034               |
| 13                    | Ph | iPr         | Me                | $(2.76\pm0.03) \times 10^{-4}$   | 48                   | 0.012               |
| 14                    | Ph | <i>t</i> Bu | Me                | $(2.23\pm0.03) \times 10^{-4}$   | 24                   | 0.010               |
| 15                    | Ph | Ph          | Me                | $(1.79\pm0.04) \times 10^{-3}$   | 84                   | 0.080               |
| 16                    | Ph | Cyclopropyl | Me                | $(1.52\pm0.03) \times 10^{-3}$   | 88                   | 0.068               |
| 17                    | Bz | Me          | Me                | $(8.4\pm0.1)$ × 10 <sup>-4</sup> | 80                   | 0.038               |
| Miscellaneous         |    |             |                   |                                  |                      |                     |
| 18                    | Ph | Me          | SiMe <sub>3</sub> | $(1.48\pm0.03) \times 10^{-3}$   | 95                   | 0.066               |
| 19                    | Ph | Me          | Ac                | $(9.2\pm0.1) \times 10^{-4}$     | 96                   | 0.041               |

Table 1. Second-order rate constants and product (ketone) yields for the oxidation of secondary alcohols, ethers, and related compounds by dimethyldioxirane in acetone at  $25^{\circ}$ C.

<sup>a</sup>Obtained under pseudo-first-order conditions; errors are the standard deviations between duplicate experiments.

<sup>b</sup>NMR yield (±4%) from reactions with at least a 3 to 1 ratio of dioxirane to substrate.

<sup>c</sup>Reference 5*f*.

carbons, aldehydes, and alcohols (5). In addition, there have been several reports on the use of 1 for the removal of benzyl protecting groups of alcohols (6) as well as the oxidation of other ethers, acetals, and orthoesters (7). Similar conversions have been carried out with methyl(trifluoromethyl)dioxirane (8). An earlier study (5e) of the reaction of 1 with benzaldehydes to produce benzoic acids indicated that the formal CH insertion process involved radical intermediates. Recently, a mechanistic study (5f) on the reaction of substituted  $\alpha$ -methylbenzyl alcohols with dimethyldioxirane yielded results that could be interpreted as consistent with a direct reaction to yield caged-radical pairs. CH insertion studies on more difficult-to-oxidize positions by dioxiranes have been interpreted (8) to be consistent with a concerted insertion process. We report here a study of the oxidation of a series of secondary alcohols, the corresponding ethers, and related compounds by dimethyldioxirane in acetone.

#### Results

The reaction of excess dimethyldioxirane, **1**, with secondary alcohols (1-phenylethan-1-ol, **2**; 1-phenylpropan-1-ol, **3**; 1-phenylbutan-1-ol, **4**; 1-phenyl-2-methylpropan-1-ol, **5**; 1-phenyl-2,2-dimethylpropan-1-ol, **6**; benzhydrol, **7**;  $\alpha$ cyclopropylbenzyl alcohol, **8**; 1-phenyl-2-propanol, **9**), corresponding methyl ethers, **10–17**, and related compounds (1trimethylsilyloxy-1-phenylethane, **18**; 1-acetoxy-1-phenylethane, **19**; 1-(*p*-anisyl)-1-methoxyethane, **20**; 1-(*p*-tolyl)-1-methoxyethane, **21**; 1(*p*-fluorophenyl)-1-methoxyethane, **22**; 1-(*p*chlorophenyl)-1-methoxyethane, **23**; 1-(*p*-bromophenyl)-1methoxyethane, **24**; 1-(*p*-trifluoromethylphenyl)-1-methoxyethane, **25**) produced the corresponding ketones in good to excellent yields in most cases (reaction [1]). Generally, under similar conditions the yields of ketones were higher from the oxidation of alcohols **2–9** than from that of the methyl ethers **10–17**.

In most cases, at least a threefold excess of 1 was necessary to achieve efficient conversion. For all but the slowest oxidation reactions, use of an inert  $(N_2)$  atmosphere resulted in product yields within experimental error of those obtained when open to the atmosphere. Low yields of ketones were obtained in two cases, the dimethyldioxirane oxidation of 1-methoxy-2-methyl-1-phenylpropane, 13, and 1-methoxy-2,2-dimethyl-1-phenylpropane, 14 (48% and 24%, respectively). The products (ketones) were isolated and identified by comparison of NMR and GC–MS data with those of authentic samples. The product yields are listed in Table 1.

Kinetic studies of the oxidation of 2-19 were carried out in acetone at 25°C by UV techniques. Excellent linear correlations were obtained under pseudo-first-order conditions with either the dioxirane or the substrate in at least a 10-fold



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**Table 2.** Effect of temperature and added solvents on the second-order rate constants for oxidation of 1-methoxy-1-phenylethane (10) by dimethyldioxirane.

| $k_2 \ (\mathrm{M}^{-1} \ \mathrm{s}^{-1})$ | Temperature ±0.3°C | Solvent   |
|---|--------------------|---|
| $(1.37\pm0.03) \times 10^{-3}$              | 20.0°C             | Acetone   |
| $(1.63\pm0.03) \times 10^{-3}$              | 25.0°C             | Acetone   |
| $(2.59\pm0.03) \times 10^{-3}$              | 30.0°C             | Acetone   |
| $(4.65\pm0.05) \times 10^{-3}$              | 35.0°C             | Acetone   |
| $(5.74\pm0.06) \times 10^{-3}$              | 40.0°C             | Acetone   |
| $(1.05\pm0.01) \times 10^{-2}$              | 45.0°C             | Acetone   |
| $(2.44\pm0.03) \times 10^{-3}$              | 25.0°C             | H <sub>2</sub> O-acetone (1.0:5.5 by vol)                 |
| $(1.73\pm0.03) \times 10^{-3}$              | 25.0°C             | CH <sub>2</sub> Cl <sub>2</sub> -acetone (1.0:1.0 by vol) |
| $(1.82\pm0.02)$ × 10 <sup>-3</sup>          | 25.0°C             | CHCl <sub>3</sub> -acetone (1.0:1.0 by vol)               |

**Table 3.** Product yields (ketone) and second-order rate constants for the oxidation of 1-methoxy-1-arylethanes (secondary *p*-substituted benzyl methyl ethers) by dimethyldioxirane in acetone at  $25^{\circ}$ C.

| Compound | <i>p</i> -Х     | % Yield <sup>a</sup> | $k_2 \ (M^{-1} \ s^{-1})^{b}$    |
|----------|-----------------|----------------------|----------------------------------|
| 20       | MeO             | 98 (98)              | $(3.10\pm0.05) \times 10^{-3}$   |
| 21       | Me              | 84 (94)              | $(2.22\pm0.05) \times 10^{-3}$   |
| 10       | Η               | 83 (90)              | $(1.63 \pm 0.03) \times 10^{-3}$ |
| 22       | F               | 76 (89)              | $(1.31\pm0.03) \times 10^{-3}$   |
| 23       | Cl              | 78 (82)              | $(1.21\pm0.03) \times 10^{-3}$   |
| 24       | Br              | 74 (80)              | $(1.11\pm0.03) \times 10^{-3}$   |
| 25       | CF <sub>3</sub> | 61 (62)              | $(7.2\pm0.1) \times 10^{-4}$     |

<sup>*a*</sup> $\pm$ 4% under N<sub>2</sub> (O<sub>2</sub>); 3 to 1 ratio of dioxirane to substrate.

<sup>b</sup>Pseudo-first-order conditions with 10-fold excess of dioxirane.

excess. Either approach yielded  $k_2$  values within experimental error  $(\pm 5\%)$  as expected for this second-order reaction. For convenience, most experiments were carried out with a 10-fold excess of dioxirane. Reproducibility between duplicate runs was excellent (generally 1–2%). In general, the  $k_2$ values for oxidation of the alcohol series were at least 10fold greater than those for the corresponding methyl ether series. The  $k_2$  values for 13 and 14, the only compounds for which the product yields were poor, were the lowest in the entire set of data. Formal replacement of the methyl ether in 10 by either the trimethylsilyl ether (18) or the acetate (19) yielded  $k_2$  values that were slightly lower with excellent product yields. Formal replacement of the phenyl group in compounds 2 and 10 by a benzyl group (9 and 17) produced  $k_2$  values that were three- and twofold slower, respectively. Oxidation of both the alcohol and methyl ether series showed the same general trend: as the alkyl group in the  $\alpha$ position ( $\mathbb{R}''$ , Table 1) becomes bulkier, the  $k_2$  value becomes smaller (Me > Et > nPr > iPr > tBu). An excellent correlation (r = 0.998) was obtained for a plot of log  $k_2$  vs.  $\sigma^*$  with a Taft  $\rho^*$  value of 1.7 for compounds 2–6. The corresponding methyl ether series, 10-14, showed a marginal correlation (r = 0.95) with a  $\rho^*$  of 3.2. The  $k_2$  value for R''= cyclopropyl in both series is only slightly lower than for R =methyl, and higher than for R'' = ethyl. A minor discrepancy between the two series is for R'' = phenyl:  $k_2$  for 7 falls between 5 ( $\mathbf{R}'' = i\mathbf{Pr}$ ) and 6 ( $\mathbf{R}'' = t\mathbf{Bu}$ ); and  $k_2$  for 15 is slightly faster than that for 10 (R'' = Me). The kinetic data (secondorder rate constants  $k_2$ ) are summarized in Table 1.

The oxidation reaction of 1-methoxy-1-phenylethane (10) and *p*-substituted analogs 20-25 by dimethyldioxirane was

chosen for futher characterization. Unlike epoxidation reactions (5e) with 1, the ether oxidations did not show large changes in rate upon addition of water to the solvent. This result is similar to that found (5f) for the dimethyldioxirane oxidation of  $\alpha$ -methylbenzyl alcohols. Rate accelerations that correlated with the hydrogen bond donor capacity of the medium have been noted (5c) for the reaction of 1 with *cis*-1,2-dimethylcyclohexane. Additional solvent effect studies including some intramolecular hydrogen-bonding effects have been described (5g). The rate constants for the oxidation of 10 were determined at 5° intervals from 20° to 45°C (see Table 2). The activation parameters determined by the Arrhenius method were found to be  $\Delta H^{\ddagger} = 14.8 \pm 0.5 \text{ kcal/mol}; \Delta S^{\ddagger} = -21.9 \text{ e.u.}; \Delta G^{\ddagger} = 21.3 \text{ kcal/mol}; k_2 (25^{\circ}\text{C}) = 1.63 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ . In addition, the oxidation of *p*substituted analogs of 10 showed that electron-donating groups increased the rate of oxidation while electron-withdrawing groups decreased it. A Hammett plot of the second-order rate constants at 25°C for oxidation of 10 and 20-25 by 1 showed an excellent LFER against  $\sigma_p$  constants with a  $\rho$ value of  $-0.74 \pm 0.03$ . These data are shown in Table 3.

#### Discussion

The oxidations of secondary alcohols and hydrocarbons by 1 and methyl(trifluoro-methyl)dioxirane have been interpreted (1, 5a-d, 8) in terms of direct reaction without involvement of a chain process. Recently, Ingold and coworkers (9) have shown, based on radical rearrangement arguments, that the oxidation of 2-cyclopropylpropane by 1 is not a free-radical chain process. Historically, the AIBN catalyzed  $O_2$  oxidation of benzyl methyl ether was found (10*a*) to be faster than that of benzyl alcohol. The direct reaction of 1 with secondary methyl ethers also shows different characteristics from those of free-radical chain processes. The results clearly show that the oxidation of secondary alcohols by 1 is at least 10-fold faster than that of the corresponding methyl ethers and related derivatives. The Hammett p value of -0.74 for oxidation of methyl ethers 10 and 20-25 by 1 is essentially equivalent to that of -0.7, as was obtained (5f: note, the  $\rho$  value reported was off by 2.303; correct value is -0.7) for the oxidation of alcohol 2 derivatives. Free-radical reactions on benzyl ethers, hydrogen atom abstraction by alkyl peroxy radicals on benzyl phenyl ether (5, 9a), or by benzoyloxy radicals on dibenzyl ether (5, 10b), were found to show  $\rho$  values of -0 and -0.65, respectively. The direct reaction of *p*-nitroperbenzoic acid with substituted benzyl Scheme 1.



methyl ethers was found (11*a*) to show a  $\rho^+$  value of -0.9. The differences in activation parameters for oxidation of the secondary methyl ethers by 1 vs. those of the secondary alcohols (5f) are roughly an increase of 3 kcal/mol in  $\Delta H^{\ddagger}$  and a decrease in  $\Delta S^{\ddagger}$  (less negative). A  $\Delta S^{\ddagger}$  of approximately – 15 eu has been estimated (8) for the oxidation of cyclohexanol by methyl(trifluoromethyl)dioxirane. The relative reactivity as a function of R" within the alcohol and methyl ether series shows similar trends. Plots of log  $k_2$  vs.  $\sigma^*$  constants give reasonable correlations with the greater sensitivity found in the ether series. The sign of the  $\rho^*$  is opposite that of the Hammett  $\rho$  value and opposite that found (11b) for  $\rho^*$  for the reaction of *p*-nitroperbenzoic acid with substituted alkenes. The  $\rho^*$  of reaction [1] presumably is strongly influenced by steric effects. The data showed a poor correlation with the Taft steric parameter  $(E_S)$ . The lower reactivity of methyl ether series coupled with the larger range of relative reactivity could be viewed as a steric effect. Alternatively, it could be argued that the alcohols undergo faster oxidation by 1 due to hydrogen bonding with 1 and (or) the solvent. Our deuterium isotope effect study (5f) for the oxidation of 2 with dimethyldioxirane has shown a  $k_{OH}/k_{OD}$ value of 1.09. This value could represent a large secondary effect or perhaps an extremely small primary effect, indicative of a hydrogen bond between the alcohol OH and the dioxirane in the transition state.

The reaction of dimethyldioxirane with secondary alcohols, ethers, and related derivatives can be viewed in terms of two mechanistic extremes: (a) a direct insertion process and (b) a caged-radical process (Scheme 1). The direct insertion process has been postulated (1, 8) to involve an "oxenoid" atom insertion into the side of the C-H bond via a multicentered transition state. Our previous study (5f) of the oxidation of  $\alpha$ -methylbenzyl alcohols by 1 was interpreted in terms of a caged-radical process in which direct reaction of 1 and the substrate yields a singlet pair of radicals that are not solvent separated. For the caged-radical process to be valid, combination of the radicals must be faster than both rearrangement of the carbon-based radical and escape from the cage. In addition, for the oxidation of methyl ethers (Z = Me), the caged-radical process must yield a hemiketal, which would be expected to rapidly fragment to the final products. The concerted process has been favored (8) as the simplest explanation due, in part, to the lack of detection of (hemiketal) intermediates for secondary alcohol and hydrocarbon oxidation. At present, the data do not clearly distinguish between these two possibilities. Note that for secondary ether oxidation, hemiketal intermediates must be formed regardless of pathway. The two mechanisms are not necessarily mutually exclusive. The trajectory of approach of the dioxirane to the C—H bond remains to be elucidated.

In conclusion, the oxidation of secondary alcohols, methyl ethers, and related derivatives with excess dimethyldioxirane generally produces high yields of ketones. Reaction times are convenient if a 10-fold excess of dioxirane is employed. The differences in reactivity with each series and between different series of compounds show the method to be of synthetic utility.

## **Experimental**

#### A. General

Infrared spectra were recorded on a Perkin–Elmer system 2000 FT-IR spectrophotometer. All <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained in chloroform- $d_1$  at 30°C on a Varian 300 MHz spectrometer. The GS–MS data were obtained on a Shimadzu GC-17A gas chromatograph coupled to a Shimadzu QP-5000 mass spectrometer.

All solvents were either spectral or HPLC grade (Aldrich). Dimethyldioxirane (1) was prepared and isolated by a modified version (12) of the general method developed by Murray and Teyaraman (3*a*). The redistilled acetone solution ( $\leq 0.1$ M) of 1 was stored at  $-20^{\circ}$ C with little or no decomposition after several weeks (over MgSO<sub>4</sub>). Initial dioxirane concentration was determined by NMR techniques (integration of thioanisole and oxidation product signals) for reaction of the stock solution with a known quantity of thioanisole. The value was within experimental error (±5%) of that determined by monitoring the change in absorbance at 330 nm before and after reaction with excess 2,3-dimethyl-2-butene (added neat via syringe) and dividing by the  $\varepsilon$  value of 12.9. All the final products (ketones) and alcohols 2, 3, 6, 7, and 9 were commercially available (Aldrich) and were used without further purification. Alcohols 4, 5, and 8 were prepared from the corresponding ketones (Aldrich) by conventional NaBH<sub>4</sub> reduction and were purified by vacuum distillation. Methyl ethers 10-17 and 20-25 were prepared in ~65% yields by a two-step procedure: first, the parent ketones of alcohols 2–9 were converted to their corresponding dimethyl ketals (13) by treatment with methyl orthoformate in methanol (HCl catalyst); after purification by vacuum distillation the dimethyl ketals were converted to the corresponding methyl ethers (14a) by treatment with AlCl<sub>3</sub> in ethyl ether, followed by LiAlH<sub>4</sub>; the methyl ethers were purified by vacuum distillation. The boiling points of the methyl ethers were in good agreement with literature values (14). Silyl ether **18** and acetate **19** were prepared from alcohol **2** by standard silylation ( $Me_3SiCl-Et_3N$ ) and acylation ( $Ac_2O$ ) procedures, and were purified by vacuum distillation. All compounds were characterized by physical and spectral (<sup>1</sup>H NMR, IR, and GC-MS) data.

#### **B.** Kinetic studies

Kinetic experiments were performed using a Shimadzu UV-3101PC UV-VIS-NIR scanning spectrometer. The cell temperature (25°C unless specified) was maintained via a constant temperature circulating bath ( $\pm 0.3^{\circ}$ C) and was checked before and after each kinetics run using a YSI model 425C telethermometer with a number 423 probe. The following is a general, representative procedure for the kinetics studies: dimethyldioxirane solutions (1.000 mL, 10 equiv.) of known concentration (≤0.100 M) in dried acetone were placed in a 1 cm UV cell at the desired temperature. After temperature equilibration, 1.0 equiv. of the substrate in 0.100 mL acetone was added via syringe and the solution was rapidly mixed by bubbling air via disposable pipet. The reaction was monitored by measuring the change in absorbance at 380 nm vs. time (pseudo-first-order conditions). The  $\varepsilon$  value at 380 nm for 1 is  $4.51 \pm 0.03$ . The value of the relative absorbance was determined by subtraction of the final value from the instantaneous value as a function of time. The pseudo-firstorder rate constants  $(k_{obs})$  were calculated by plotting the ln (relative absorbance) versus time and were linear for at least two half-lives. The second-order rate constants  $(k_2)$  were calculated by dividing the pseudo-first-order rate constant  $(k_{obs})$  by the initial concentration of dimethyldioxirane. Reproducibility between runs was generally better than 5% of the  $k_2$  value. Correlation coefficients were excellent for all experiments. Several experiments were repeated under pseudo-first-order conditions with the substrate in 10-fold excess. The rate constants were found to be essentially identical (within experimental error) to those determined with 1 in excess, confirming the validity of the approach.

#### **C. Product studies**

The products from the reaction of compounds 2–25 with 3 equiv. of isolated dimethyl-dioxirane at room temperature (~1.5 mmol of substrate) were analyzed after 6–24 h by GC–MS. The GC–MS data showed the ketones to be formed in high yield in all cases except for oxidation of 13 and 14. The GC–MS data were in excellent agreement with those of authentic ketone samples. After removal of the solvent (acetone), the residue was taken up in CDCl<sub>3</sub> and then was analyzed by <sup>1</sup>H NMR spectroscopy. The <sup>1</sup>H NMR data were in agreement with those of authentic (commercial) ketone samples. For most cases (within experimental error), little or no reduction in final ketone yields was observed for reactions carried out under inert (N<sub>2</sub>) atmosphere. The percentage yields (±4%) were determined (with anisole as added internal standard) from the <sup>1</sup>H NMR spectral data.

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#### References

- (a) R. Curci. In Advances in oxygenated processes. Vol. 2. Edited by A.L. Baumstark. JAI Press, Greenwich, Conn. 1990;
  (b) R.W. Murray. Chem. Rev. 89, 1187 (1989);
  (c) W. Adam, L.P. Hadjiarapoglou, R. Curci, and R. Mello. In Organic peroxides. Edited by W. Ando. Wiley and Sons, Chichester, England. 1992. Chap. 4.
- (a) J.O. Edwards, R.H. Pater, R. Curci, and F.D. Fusca. Photochem. Photobiol. **30**, 63 (1979); (b) R. Curci, M. Fiorentino, L. Froisi, J.O. Edwards, and R.H. Pater. J. Org. Chem. **45**, 4758 (1980).
- (a) R.W. Murray and R. Teyaraman. J. Org. Chem. 50, 2847 (1985); (b) R.W. Murray, R. Jeyaraman, and L. Mohan. Tetrahedron Lett. 27, 2335 (1986).
- R. Mello, M. Fiorentino, O. Sciacovelli, and R. Curci. J. Org. Chem. 53, 3890 (1988).
- (a) R.W. Murray, R. Jeyaraman, and R. Mohan. J. Am. Chem. Soc. 108, 2470 (1986); (b) R. Mello, M. Fiorentino, C. Fusco, and R. Curci. J. Am. Chem. Soc. 111, 6749 (1989); (c) R.W. Murray and Gu. Daquan. J. Chem. Soc. Perkin Trans. 2, 451 (1994); (d) D. Kuck, A. Schuster, C. Fusco, M. Fiorentino, and R. Curci. J. Am. Chem. Soc. 116, 2375 (1994); (e) A.L. Baumstark, M. Beeson, and P.C. Vasquez. Tetrahedron Lett. 30, 5567 (1989); (f) A.L. Baumstark and F. Kovac. Tetrahedron Lett. 35, 8751 (1994); (g) R.W. Murray and H. Gu. J. Phys. Org. Chem. 2, 751 (1996).
- (a) R. Csuk and P. Dörr. Tetrahedron, **50**, 9983 (1994); (b) B.A. Marples, J.P. Muxworthy, and K.H. Baggaley. Synlett, 646 (1992).
- (a) R. Curci, L. D'Accolti, M. Fiorentino, C. Fusco, W. Adam, M.E. Gonzalez-Nunez, and R. Mello. Tetrahedron Lett. 33, 4225 (1992); (b) A. Messegues, M. Fener, F. Sanchez-Baeza, and J. Casas. Tetrahedron Lett. 35, 2981 (1994).
- (a) R. Curci, M. Fiorentino, C. Fuseo, and R. Mello. *In* Dioxygen activation and homogenous catalytic oxidation. *Edited by* L.I. Simándi. Elsevier Science Publishers B.V., Amsterdam. 1991. pg. 147; (b) W. Adam and L.P. Hadjiarapoglou. Top. Curr. Chem. **164**, 45 (1993); (c) R. Curci, A. Dinoi, and M.F. Rubino. Pure Appl. Chem. **67**, 811 (1995).
- R. Vanni, S.J. Garden, J.T. Banks, and K.U. Ingold. Tetrahedron Lett. 7999 (1995).
- (a) G.A. Russell and R.C. Williamson, Jr. J. Org. Chem. 12, 2357 (1964); (b) R.L. Huang, H.H. Lee, and S.H. Ong. J. Chem. Soc. 3336 (1962).
- (*a*) H.J. Schneider, A. Ahlhelm, and W. Mueller. Chem. Ber. 3297 (1984); (*b*) H.J. Schneider and W. Mueller. J. Org. Chem. 50, 4609 (1985).
- (a) A.L. Baumstark and C.J. McCloskey. Tetrahedron Lett. 3311 (1987); (b) W. Adam, L. Hadjiarapoglou, and J. Bialas. Chem. Ber. **124**, 2377 (1991).
- 13. C.E. Kaslow and W.R. Lawton. J. Am. Chem. Soc. **72**, 1723 (1950).
- (a) E.L. Eliel, V.G. Badding, and M.N. Rerick. J. Am. Chem. Soc. 84, 2371 (1962); (b) M. Shi, Y. Okamoto, and S. Takamuku. J. Org. Chem. 55, 3821 (1990); (c) J.P. McCormick and D.L. Barton. J. Org. Chem. 45, 2566 (1980).