THE ENE REACTION OF SINGLET OXYGEN: KINETIC AND PRODUCT EVIDENCE IN SUPPORT OF A PEREPOXIDE INTERMEDIATE

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Abstract-The ene reaction of singlet oxygen (¹O₂) was examined using time-resolved techniques and by an intramolecular trapping reaction. The Eyring activation parameters reveal that the rate of the ene reaction of ${}^{1}O_{2}$ with simple olefins is controlled by ΔS^{*} . A description of the reaction co-ordinate accommodating our findings and the results of others is presented.

The investigation of short-lived reactive intermediates has become a topic of considerable interest in chemistry. The objective of research of this type is to define the structure and properties of these species so that their role in observed chemical transformations can be clearly defined. The very nature of short-lived intermediates makes their investigation difficult. This is manifest in two important ways. First, it is not possible to isolate these intermediates in the classical sense. Thus, all of the desired information on structure and reactivity must be won indirectly. Secondly, the probe used to test the character of the intermediate may change the nature of the probed species. The shortlifetime is a consequence of a low barrier for reaction. Subtle changes in structure, for example, may have a pronounced effect on reactivity through a small and unexpected change in the reaction barrier.

The ene reaction of singlet oxygen $({}^{1}O_{2}, {}^{1}\Delta_{a})$ with olefins, Eq. (1), has been intensively studied for the past 20 years.¹ Part of the fascination with this reaction is a consequence of its utility in synthesis,² its implied involvement in biochemical processes³ and the key role it plays in the initiation of numerous photodegradation sequences.⁴ A second part derives from the early suggestion that a short-lived intermediate perepoxide plays a critical part in these reactions.⁵ The unusual structure of this intermediate piqued interest in a search for evidence of its existence. This search has employed the entire panoply of experimental and theoretical tools available to modern science.



In this report we describe our experiments on the ene reaction of ¹O₂. These fall into two categories : the first is an investigation of the activation parameters for this reaction; the second concerns the intramolecular trapping of the proposed perepoxide intermediate. Finally, we attempt to weave our findings into the fabric of other experimental and theoretical analyses of this reaction.



Perepoxide

Zwitterion

RESULTS

Temperature dependence of the reaction of ${}^{1}O_{2}$ with olefins

The rate of reaction of ${}^{1}O_{2}$ with olefins is conveniently studied by monitoring the time dependence of the intensity of its IR phosphorescence. We recently described⁶ the techniques and apparatus for the generation and detection of ${}^{1}O_{2}$ in this way. We have used these procedures to measure the rate constants for reaction of a series of olefins with 1O2.7

Irradiation of an O2-saturated carbon disulphide solution of tetraphenylporphyrin (TPP) with the output of a frequency doubled, Q-switched, Nd-YAG laser (532 nm, 20 ns, ca 15 mJ) generates ¹O₂ according to the scheme outlined in Eq. (2). The lifetime of ${}^{1}O_{2}$ under these conditions at room temperature is 3.4 ms as

$$\mathbf{TPP} \xrightarrow{\mathbf{h}\nu} \mathbf{TPP^{*1}} \xrightarrow{\mathbf{isc}} \mathbf{TPP^{*3}} \xrightarrow{\mathbf{3O_2}} \mathbf{1O_2} + \mathbf{TPP} \qquad (2)$$

indicated by the power-independent,^{6,8} first-order decay of the phosphorescence monitored at ca 1270 nm (Fig. 1).

Cyclopentene, for example, reacts with ¹O₂ to give an allylic hydroperoxide. When ¹O₂ is generated according to Eq. (2) in carbon disulphide containing 7.5×10^{-2} M cyclopentene, the lifetime of ${}^{1}O_{2}$ is shorter than it is in the absence of the olefin. As the cyclopentene concentration is increased, the measured lifetime of ${}^{1}O_{2}(\tau_{1z})$ is further shortened. These results are also displayed in Fig. 1.



Fig. 1. Effect of cyclopentene concentration on the lifetime of ${}^{1}O_{2}$ in CS₂ at room temperature.



Fig. 2. Dependence of the ${}^{1}O_{2}$ lifetime $(1/k_{obs})$ on temperature and concentration of cyclopentene in CS₂.

The bimolecular rate constant for the quenching $(k_q;$ the sum of both physical and chemical processes) of ${}^{1}O_2$ by cyclopentene is obtained by analysis of the effect cyclopentene concentration has on k_q according to Eq. (3) where k_o is the rate constant for decay of ${}^{1}O_2$ in the absence of the olefin. These data are plotted in Fig. 2

$$\frac{1}{\tau_{1O_2}} = k_o + k_q \text{ [cyclopentene]}$$
(3)

and give a bimolecular rate constant equal to 5.8×10^4 M⁻¹ s⁻¹ at 25° (Table 1).

The rate constant for the chemical reaction (k_r) of ${}^{1}O_2$ with cyclopentene in methanol solution has been reported previously to be 8.7×10^4 M⁻¹ s^{-1.9} Our findings show that k_q and k_r are approximately equal for this and for other olefins. This observation leads to the conclusion that physical quenching of ${}^{1}O_2$ by cyclopentene does not contribute significantly to k_q . A similar conclusion, based on related observations, has been noted recently for 2-methyl-2-pentene.¹⁰ It, thus, appears that for simple olefins physical quenching of ${}^{1}O_2$ is unimportant and we consider k_q to be equivalent to k_r .

The temperature dependence of k_q is easily obtained by procedures similar to those described above. Plots of the observed ${}^{1}O_{2}$ lifetime in carbon disulphide containing cyclopentene at various temperatures are shown in Fig. 2. It is apparent that k_q decreases as the temperature decreases. Analysis of this behaviour for cyclopentene (and other olefins) according to the Eyring formalism gives the activation parameters ΔH^{\ddagger} and ΔS^{\ddagger} and is shown in Fig. 3. These results are summarized in Table 1 for carbon disulphide and (for some olefins) perdeuterioacetone solutions.



Fig. 3. Eyring plots of quenching rate constants for several olefins: (△) trans-2-butene; (□) isobutylene; (○) cis-2-butene; (▽) trimethylethylene; (●) tetramethylethylene.

Olefin	Solvent	ΔH [‡] * (kcal/mol)	ΔS ^{‡ b} (e.u.)	$\frac{\Delta S_{norm}^{\ddagger}}{(e.u.)}$	$(M^{-1}s^{-1})$
 ><	CS ₂	0.5	- 23	- 30	2.2 × 10 ⁷
, -<	CS ₂	0.7	- 30	-31°	7.2 × 10 ⁵
\sim	(CD ₃) ₂ CO	1.1	-27	- 28°	$1.3 imes 10^6$
	CS ₂	1.6	- 32	-35	4.8 × 10 ⁴
	CS ₂	2.0	- 31	- 34	3.9 × 10 ⁴
\bigcirc	CS ₂	1.2	- 32	-35	5.8 × 10 ⁴
<u> </u>	CS ₂	0.3	- 42	-45	7.2 × 10 ³
ل	CS ₂	0.4	- 39	-42	7.7 × 10 ³
<u>)</u> =α+	CS ₂	0	-43	- 46	4.0×10^{3}
◯ =œ,	CS ₂	-0.1	- 42	45	5.2×10^3
◯ =∞,	(CD ₃) ₂ CO	-0.2	-42	- 45	6.1 × 10 ³

Table 1. Reaction of ¹O₂ with various olefins

• The reproducibility of independent runs for ΔH^{\ddagger} is estimated to be ± 0.8 kcal/mol and for ΔS^{\ddagger} 1.0 e.u.

^bCalculated for 25° from the measured activation parameters.

^c In the normalization of ΔS^{3} for this compound only two 'equivalent' sites were assumed since reaction occurs primarily from the more 'crowded' side in essentially equal amounts.

It is immediately apparent from Table 1 that the variation of k_q for all of the olefins examined appears to be a response to a change in ΔS^{\ddagger} rather than ΔH^{\ddagger} . Similar results were noted earlier for the reaction of ${}^{1}O_{2}$ in toluene with furans and indoles 11 and, more recently, for enol ethers. 12 In all cases, these findings reveal important information about the structure of the transition state for reaction of ${}^{1}O_{2}$ with these unsaturated reagents. In the Discussion we analyse the significance of these findings to the mechanism of the ene reaction.

Reaction of ${}^{1}O_{2}$ with enol esters

One approach for the development of evidence to support the involvement of a short-lived reactive intermediate is to divert it toward a predictable path with an intra- or intermolecular trapping agent. This approach has been used, for example to support the existence of a zwitterionic intermediate in the reaction of ${}^{1}O_{2}$ with some norbornenyl ethers in methyl alcohol solution. 13 We have examined the reaction of ${}^{1}O_{2}$ with some enol esters. The findings from investigation of the effect of solvent on the kinetics of these reactions and on the nature of the products support the involvement of an intermediate with some characteristics expected of a perepoxide. 14

Irradiation of an O_2 -saturated $(CD_3)_2CO$ solution of the enol ester, 1, containing methylene blue (MB) as sensitizer at room temperature or at -78° with visible light leads to its rapid consumption and the appearance of a single product in 95% yield as evidenced by changes in the ¹H-NMR spectrum of the reaction solution. The photo-oxidation product, isolated from the reaction mixture by chromatography on silica gel at -50° , is identified as the peroxy ester, 2. dependent reaction of ${}^{1}O_{2}$ with enol ethers has been reported previously by Asveld and Kellogg.¹⁵ In the present case, the dioxetane is not sufficiently stable to permit isolation in pure form. However, lowtemperature chromatography provides a solution of 3 containing, as the only impurity, 10% adamantanone. The spectral, thermal and chemiluminescent properties of 3 permit its certain identification. Under these photooxidation conditions enol ester 1 may also give a low yield (*ca* 3%) of an unisolated methanol addition product detected spectroscopically after reaction in CH₃OD.

Photo-oxidation of the enol ester, 4, in acetone gives one product, in 95% yield, identified as the hydroperoxide, 5. This ene reaction product could not be isolated, but its spectral properties and reduction by NaBH₄ to 1-(hydroxymethyl)cyclohexene confirm its structure. Similar results are obtained in CD_3OD except that the initial ene product is unstable in this solvent.

The rate constant for quenching of ${}^{1}O_{2}$ by these enol esters can be easily determined by monitoring the decay of the IR phosphorescence characteristic of ${}^{1}O_{2}$ at different olefin concentrations, as described above. The results of this study are presented in Table 2. We note that the measured rate constants do not reflect the dramatic change in product composition attending solvent or structure change but instead are nearly constant. To confirm that the ${}^{1}O_{2}$ quenching process and the product-forming reaction are the same, we photo-oxygenated a mixture of the enolesters 1 and 4 to low conversion in (CD₃)₂CO and obtained the anticipated mixture of the oxygenation products 2 and 5 in appropriate yields.

The reaction of ${}^{1}O_{2}$ with substituted enols has been

The reaction takes quite a different course when it is carried out in CD_3OD . Instead of the exclusive formation of 2, the major product, formed in 70% yield, is identified as dioxetane (3). A related solvent-

studied previously. Pusset *et al.*¹⁶ report only ene and [4+2]-cycloaddition reactions from steroidal enol and dienol acetates. Silyl enol ethers react with ¹O₂ to give competing ene and silicon migration products.^{17,18}



Table 2. Rate constants for reaction of the enol esters 1 and 4 in	l
CD_3OD and $(CD_3)_2CO$ with 1O_2 at room temperature	

Enol ester	Solvent	$\frac{10^{-4} k_{e}}{(s^{-1} M^{-1})}$
1	(CD ₃) ₂ CO	3.4
1	CD ₃ OD	2.1
4	(CD ₃) ₂ CO	7.5
4	CD ₃ OD	4.8
-	CD30D	4.0

Similarly, silylketene acetals add ${}^{1}O_{2}$ to give both silylperoxy esters and 1,2-dioxetanes, perhaps through a common zwitterionic intermediate.¹⁹ Enol ethers have been intensively studied^{13,20} and shown to give reaction-condition-dependent yields of ene, dioxetane and solvent incorporation products with ${}^{1}O_{2}$. Recently, an intermolecular version of this trapping reaction with an electrophilic carbonyl group has been reported.²¹

The novel migration product obtained from ${}^{1}O_{2}$ oxygenation of the enol ester, 1, in $(CD_{3})_{2}CO$ implicates a dipolar state on this reaction surface. The observation that the rates of reaction of these enol esters are relatively insensitive to structural and solvent change but that the products formed are dramatically dependent on these parameters tends to eliminate a concerted reaction path. Instead, a sequence proceeding through a solvent-independent transition state, essentially common to the enol esters 1 and 4, to a dipolar intermediate whose fate depends on the solvent and availability of allylic hydrogens is implicated. These concepts are presented more fully in the Discussion.

DISCUSSION

This section is divided into three parts. In the first part, we interpret the results of the investigation of the activation parameters for the ene reaction, in the second, the acyl shift reaction is discussed and in the final part, our findings are related to those of others in an attempt to obtain a consistent picture of the reaction co-ordinate for ${}^{1}O_{2}$ with an olefin.

An entropy-controlled process determines the ene reaction rate

The data in Table 1 show that the rate of quenching of ${}^{1}O_{2}$ depends on the structure of the olefin. Of the compounds we studied, 2,3-dimethyl-2-butene reacts with the greatest rate constant $-2.2 \times 10^{7} \text{ M}^{-1} \text{ s}^{-1}$ at 25°. This value is *ca* 1000 times less than the diffusion limit. Therefore, there must be many non-productive encounters between the reactants for each encounter that leads to consumption of ${}^{1}O_{2}$. These encounters may involve reversible formation of an exciplex, but this cannot be the rate-limiting step.

The activation parameters (ΔH^{\ddagger} and ΔS^{\ddagger}) listed in Table 1 reveal a pattern that provides some insight to the structure of the transition state. For the olefins we examined, the values of ΔH^{\ddagger} are quite small and, in most cases, do not differ significantly from each other or from zero. Thus, while there may be differences among the activation energies for the olefins, these differences are masked by a larger dependence on the activation entropy. Interpretation of the effect of olefin structure on ΔS^{\dagger} requires normalization for the destruction of external rotational symmetry, when it exists, in the starting olefin.²² For example, tetramethylethylene has three two-fold rotation axes, which are not likely to be preserved at the transition state. In comparison, trimethylethylene does not lose any such symmetry when it reacts. Similarly, ΔS^{\dagger} must be adjusted statistically for the number of apparently equivalent reactive sites;[†] four for tetramethylethylene, two for *cis*-2-butene, etc. These normalized activation entropies ($\Delta S_{norm}^{\dagger}$) are listed in Table 1.

The ΔS_{norm}^2 values appear to fall clearly into two groups. One group exhibits ΔS_{norm}^2 of ca - 32 e.u. and the second group ca - 45 e.u. There is a simple structural feature that seems to determine which of these two groups the olefin belongs to. Those olefins that have two hydrogen-bearing alkyl substituents in a *cis* relationship (*cis* olefins) fall into the first group. The olefins that do not exhibit this structural feature (non-*cis* olefins) fall into the second. This finding indicates that the transition state for the ene reaction is 'more organized' or, perhaps, further along the reaction co-ordinate for the non-*cis* olefins than it is for the *cis* olefins. This finding has some important implications for the description of the reaction co-ordinates that are discussed later.

Rearrangement of enol esters requires a dipolar intermediate

The reaction of ${}^{1}O_{2}$ with the enol esters we have investigated gives three different types of products. The identity of the major product in each case depends on the details of the structure of the ester and on the reaction solvent.

Oxygenation of the ester, 1, in acetone solution gives the novel acyl-shifted product, 2. This rearrangement is best understood as originating from an intermediate containing a nucleophilic oxygen atom. Several intermediates of this type have been considered to play critical roles in the reactions of ${}^{1}O_{2}$. Here we consider two possibilities—the closed perepoxide, 6, and the zwitterions, 7 or 8. Either of these could easily account for the observed acyl-shift of 1.



When the oxygenation of 1 is carried out in methanol solution the major product is the dioxetane, 3, not the perester, 2. Critically, the rate constant for reaction of ${}^{1}O_{2}$ with 1 does not differ significantly in methanol from its value in acetone. This finding requires that the product-determining step in the reaction must not be the same as the rate-determining step. This conclusion in turn requires the intervention of a reactive

[†] The number of equivalent sites is dependent on the actual mechanism of the reaction. We have chosen the most general case with each methyl group as apparently equivalent. However, the mechanism we suggest below indicates that two *cis* groups can be counted as one site. The conclusions are independent of the counting scheme.

intermediate. Structures 6, 7, or 8 satisfy this criterion.

It is clear that the enolester, 1, does not have an allylic hydrogen atom that is suitable for participation in the ene reaction. However, the enol ester, 4, does have this feature and the ene reaction is the dominant reaction, in this case, for either acetone or methanol solvent. It is important to recognize that the rate constant for reaction of 4 with ${}^{1}O_{2}$ (Table 2) is independent of solvent and only a factor of about two larger than that of enol ester 1. We take this as evidence indicating that the rate-determining step is the same for reaction of ${}^{1}O_{2}$ with either 1 or 4 and that the different chemical consequence is a result of the partitioning of the intermediate. In this regard we note that the perepoxide, 6, can proceed to the three classes of products but that the alternative open zwitterions 7 and 8 cannot give directly the acyl-shifted and ene products, respectively and in our view are, therefore, less likely candidates. When an appropriate allylic hydrogen is available, the intermediate follows a path to the ene product regardless of solvent. Lacking an appropriate hydrogen, cyclization to the dioxetane predominates in methanol, where intermolecular hydrogen bonding satisfies part of the negative charge of the intermediate. In acetone, where external hydrogen bonds are unavailable, stronger interaction with the carbonyl group leads exclusively to the acyl-shifted product.

The ¹O₂-olefin reaction co-ordinate

There have been numerous computational and experimental attempts to define the reaction coordinate for ${}^{1}O_{2}$ and an olefin. Many of these are presented in other papers in this 'Symposium-in-Print'. Here we briefly review some of the salient points and then consider a reaction co-ordinate consistent with our findings and with the results of others.

The computational investigation of the ${}^{1}O_{2}$ reaction co-ordinate has followed a tortuous course. In an early attempt, Inagaki and Fukui²³ used the semiempirical SCF CNDO/2 method and the CI-perturbation procedure to identify a perepoxide as a 'quasi'intermediate on the potential energy surface for the addition of ¹O₂ to ethylene. Similarly, Dewar and Thiel²⁴ identified a perepoxide on this surface using MINDO/3. Later Harding and Goddard²⁵ employed extended basis set GVB-CI calculations to conclude that a biradical species is ca 8 kcal below a perepoxide and that the latter is not a permissible intermediate. Yamaguchi et al.²⁶ conclude that both ab initio calculations with the STO-3G basis set and the semiempirical MINDO/3 calculations at the unrestricted Hartree-Fock level predict that 1,4-diradicals are more stable than perepoxides. However, the most recent and highest level calculation reported by Hotokka et al.27 using the CASSCF-CCI method shows that formation of the perepoxide intermediate has a lower activation energy than does the biradical pathway. With this report the computational investigation has come full circle.

The attempts to define the ${}^{1}O_{2}$ -olefin reaction coordinate experimentally also have been marked with some controversy. There are several findings that bear directly on the analysis of the results described above.

Schulte-Elte et al.²⁸ and later Orfanopoulos et al.²⁹ discovered that ${}^{1}O_{2}$ prefers to react with tri-substituted olefins on the more crowded side (syn addition). This is clearly evident in our analysis of the activation parameters where the *cis* olefin group shows a much less negative ΔS^{\ddagger} than does the non-*cis* olefin group. From this relationship we conclude that the ratedetermining step for the ene reaction must involve some degree of bonding to one or both (if two are available) of the allylic hydrogens. A similar conclusion has been reached from different data by Frimer *et al.*³⁰

Grdina et al.³¹ have carried out an extensive investigation of the reaction of ${}^{1}O_{2}$ with isotopicallylabelled 2,3-dimethyl-2-butene. They interpreted the results to support a reactive intermediate with "structural requirements not dissimilar to those of the perepoxide". They conclude that, "were it not for the... compelling calculations of Goddard and Harding" that the actual perepoxide would be supported. The more recent calculations²⁷ make those of Harding and Goddard²⁵ less compelling.

Jefford and co-workers have argued against the perepoxide intermediate and for an open zwitterion.³² However, at least part of the argument used to explain the syn-addition with this model is no longer valid since our results require the side-selection to occur during the rate-limiting step and this is not consistent with the open zwitterion model.

Our findings and the results described above allow a reasonably detailed description of the reaction coordinate. The first identifiable step in the sequence is the reversible formation of an exciplex or encounter complex. The geometry of this complex is not known. The rate-limiting step in the ene reaction is the conversion of this complex to a perepoxide. For simple alkenes, this step is irreversible in that it always (or nearly always) leads to consumption of ${}^{1}O_{2}$ and the olefin. The bonding in the perepoxide is complex and evidently involves the allylic hydrogen anti-bonding orbitals, as suggested by Inagaki and Fukui²³ and by Stephenson.³³ The conversion of the exciplex to the perepoxide is the entropy-controlled process revealed by our analysis of the temperature dependence of these reactions.

The fate of the perepoxide depends on the details of structure of the olefin and the reaction conditions. This is revealed by our investigation of the enol esters and other studies described briefly above. In polar, hydrogen-bonding solvents (methanol for example), the perepoxide can be converted to, or at least react as if it were, an open zwitterion. The data indicate that it is the partitioning of the intermediate that controls the product distribution, not the initial irreversible reaction of ${}^{1}O_{2}$ and the olefin.

EXPERIMENTAL

General.¹H-NMR spectra were obtained either on a Varian EM 390 spectrometer operating at 90 MHz or a Varian HR 220 spectrometer operating at 220 MHz in the Fourier transform mode. All IR spectra were obtained either on a Perkin-Elmer Model 237B grating IR spectrophotometer or on a Nicolet Model 7003 Fourier transform IR spectrophotometer. Elemental analyses were performed by Analysis Laboratories, Department of Chemistry, University of Illinois, Urbana, Illinois, U.S.A.

Photo-oxygenations were performed using a 250 W, 24 V Sylvania tungsten-halogen projector lamp. The output was filtered at 490 nm using a Corning 3-70 filter. NMR tubes were used as the photo-oxygenation vessels. O_2 was passed through a drying tube of anhydrous CaSO₄ and molecular sieves, bubbled through the photo-oxygenation solution in the NMR tube via a Teflon needle and passed out through a bubbler filled with mineral oil. The outside of the upper portion of the NMR tube was cooled with dry ice to prevent solvent evaporation. The lifetime measurements were performed as previously described.⁶

2-Adamantanecarboxaldehyde. To a dry flask containing 1.61 g (10.0 mmol) of 2-adamantanecarbonitrile and 11 ml of dry benzene was added, over a 30 min period, 10 ml of a soln of diisobutylaluminum hydride (1.0 M in hexane, 10 mmol). After stirring for an additional 10 min, 25 ml of 5% H₂SO₄ was added. After stirring for 30 min, the organic layer was removed and the aq layer was washed with 20 ml of ether. The combined organic solns were washed with water, followed by saturated NaHCO₃ and, finally, brine. The resulting organic soln was dried over MgSO₄, filtered and concentrated to give 1.48 g of crude 2-adamantanecarboxaldehyde. Sublimation (50°, 1 mm) yielded 1.22 g (74%) of 2-adamantanecarboxaldehyde: m.p. 125–127°; ¹H-NMR (CDCl₃) δ 1.55–2.00 (10H, m), 2.30 (5H, br s), 9.60 (1H, s); IR v^{mest} 1726, 2700, 2852 cm⁻¹. Calc for C₁₁H₁₆O: C, 80.42; H, 9.83%. Found: C, 80.25; H, 9.73%.

(Adamantylidene)methyl acetate (1). A 0.876 g quantity of a potassium hydride suspension (22.2% in mineral oil, 4.85 mmol) was added to a dry flask. The mineral oil was removed by washing with three 5 ml portions of pentane. A soln of 532 mg(3.24 mmol) of 2-adamantanecarboxaldehyde in 5 ml of dry DME was added to the stirring potassium hydride powder over 5 min. After stirring for 10 min, the milky white suspension was added to 2.30 ml (24.2 mmol) of acetic anhydride over 5 min. After stirring for 10 min, the reaction mixture was added to a flask containing 25 ml of hexane and 25 ml water. Solid NaHCO3 was added cautiously to the stirring mixture until a saturated soln was obtained. After stirring for 15 min the organic layer was separated and the aq layer extracted with three 10 ml portions of hexane. The organic solns were combined, washed with brine, dried over MgSO4, filtered and concentrated to yield crude 1 as a yellow oil. Kugelrohr distillation (200°, 3 mm) yielded 592 mg (88%) of 1 as a colourless oil: ¹H-NMR (CS₂) δ 1.55-2.08 (12H, m), 2.02 (3H, s), 2.31 (1H, br s), 2.94 (1H, br s), 6.76 (1H, s). Calc for C13H18O2: C, 75.68; H, 8.81%. Found: C, 75.95; H, 9.03%.

(Cyclohexylidene)methyl acetate (4). A 36.1 g quantity of a suspension of potassium hydride (22.2% in mineral oil, 0.20 mol) was added to a dry flask. The mineral oil was removed with three 50 ml portions of pentane and 100 ml of dry DME was added to the resulting potassium hydride powder. A soln of 15.0 g (0.134 mol) of cyclohexanecarboxaldehyde in 125 ml of DME was added to the stirring potassium hydride suspension over 30 min. After the mixture was stirred for 30 min, the resulting suspension was added to a dry flask containing 82.1 g (0.805 mol) of acetic anhydride over a 20 min period. After stirring for an additional 15 min, the reaction mixture was poured into a flask containing 500 ml of pentane and 250 ml of water. Solid NaHCO3 was added cautiously with stirring until a saturated soln was obtained. After stirring for 30 min the organic layer was separated and the aq layer extracted with two 100 ml portions of pentane. The combined organic solns were dried over MgSO4, filtered and concentrated to yield 21.2 g of crude 4. Distillation at 124-129° (70 mm) yielded 78.1 g (88%) of pure 4 as a colourless oil: 1H-NMR(CDCl₃) δ 1.31–1.71(6H, m), 1.90–2.07(2H, m), 2.13(3H, s), 2.16–2.37 (2H, m), 6.84 (1H, br s); IR $v_{max}^{CS_2}$ 1746, 1760 cm⁻¹. Calc for C9H14O2: C, 70.08; H, 9.17%. Found: C, 69.84; H, 9.25%.

Photo-oxygenation of (adamantylidene)methyl acetate (1) in acetone. To a 5 mm NMR tube were added 59 mg (0.28 mmol) of 1 and 0.40 ml of a soln of methylene blue in acetone-d₆ (saturated). The resulting soln of 1 was photo-oxygenated for 2 hr. The photo-oxygenation mixture was concentrated on a rotary evaporator and chromatographed on a column of silica gel at - 50° (eluted with 5% EtOAc in hexane) to yield crude 2. Recrystallization from pentane at - 50° gave pure 2 as white crystals: m.p. 42-43.5°; ¹H-NMR (CDCl₃) δ 1.59-1.92 (12H, m), 1.98 (3H, s), 2.26 (2H, br s), 9.36 (1H, s); IR v^(DCl₃)/_{max} 1793, 1767 cm⁻¹. Calc for C₁₃H₁₈O₄: C, 65.52; H, 7.63%. Found: C, 65.68; H, 7.63%. Peroxide titre 92% of theory; molecular weight (osmometry) 264 ± 26. Photo-oxygenation of 1 in CD₃OD. To a 5 mm NMR tube were added 38 mg (0.18 mmol) of 1 and 0.35 ml of a soln of methylene blue in CD₃OD (3.0×10^{-4} M). The resulting soln of 1 was photo-oxygenated for 30 min. The photooxygenation mixture was chromatographed on a column of silica gel at -50° (eluted with 10% isopropyl alcohol in hexane) without concentration. The chromatographic fractions containing the dioxetane, 3, were combined and added to 20 ml of CCl₄. This mixture was concentrated to ca 5ml on a rotary evaporator. An additional 35 ml of CCl₄ was added and the resulting mixture was concentrated to 1.0 ml, giving a soln of 3 contaminated with ca 10% adamantanone (by ¹H-NMR): NMR (CCl₄) δ 1.56–1.91 (12H, m), 2.18 (3H, s), 2.66 (2H, br s), 6.41 (1H, s).

Photo-oxygenation of (cyclohexylidene)methyl acetate (4) in $(CD_3)_2CO$. Enol acetate (4) [21.3 mg(0.138 mmol)] 0.40 ml of a soln of methylene blue in acetone-d₆ (saturated) and 4.9 mg (0.133 mmol) of p-dichlorobenzene (as an internal standard) were added to a 5 mm NMR tube. This soln of 4 was photo-oxygenated for 45 min. The ¹H-NMR of the resulting mixture was recorded and gave resonances characteristic of 5 (95%): NMR (acetone-d₆) δ 1.34–1.71 (4H, br s), 1.82–2.22 (4H, br s), 2.07 (3H, s), 5.93 (1H, m), 6.39 (1H, s).

Reduction of 5 with NaBH₄. Enol acctate (4) [54.7 mg (0.355 mmol)] was combined with 0.50 ml of a soln of methylene blue in an acetone- d_6 (saturated) in a 5 mm NMR tube and photooxygenated for 60 min. The resulting mixture was added dropwise to a stirring mixture of 0.50 g of NaBH₄, 5 ml of methanol and 5 drops of 6 M NaOH. A vigorous reaction resulted. After stirring for 15 min, 10 ml of 2 M HCl were cautiously added. After stirring for an additional 15 min, the reaction mixture was extracted with three 7.5 ml portions of ether. The combined ether extracts were washed with brine, dried over MgSO₄, filtered and concentrated on a rotary evaporator. The concentrated mixture consisted of an oil plus a white solid (presumably undesired boron salts). CCl₄ (10 ml) was added and the resulting suspension filtered. The resulting soln was reconcentrated. The concentrate and 8.1 mg (0.055 mmol) of p-dichlorobenzene (as an internal standard) were added to an NMR tube and the ¹H-NMR spectrum was recorded. The spectrum included resonances identical to those of authentic 1-(hydromethyl)cyclohexene (59%, based on the amount of 5 photo-oxygenated).

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