257. Effect of Substituents, Solvent, and Temperature on the Reactivity of the Zwitterionic Peroxides Arising from the Photo-Oxygenation of 2-(Methoxymethylidene)- and 2-(Phenoxymethylidene)adamantane

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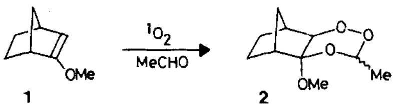
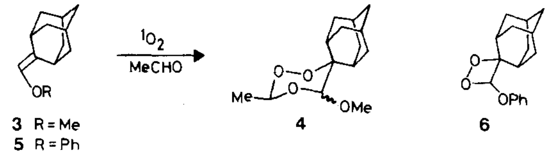
Summary

The photo-oxygenation of 2-(methoxymethylidene)adamantane (**3**) creates a zwitterionic peroxide which may be captured by acetaldehyde to give the corresponding pair of diastereoisomeric tricyclo[3.3.1.1^{3,7}]decane-2-spiro-6′-(3′-methyl-5′-methoxy-1′,2′,4′-trioxanes) (**4**). Ease of capture depends strongly on solvent polarity and temperature. When these are low, yields of trioxane are high ($\sim 80\%$). Conversely, 1,2-dioxetane formation is favoured at high temperature and solvent polarity. 2-(Phenoxymethylidene)adamantane (**5**), on photo-oxygenation, only gives the corresponding 1,2-dioxetane, even in the presence of acetaldehyde. From a *Hammett* study of the photo-oxygenation of the enol ether **5** and its *p*-methoxy, *p*-methyl, *p*-chloro and *m*-chloro derivatives **9**, **11**, **13**, and **15**), a good linear relation was found between substituent constants and oxygenation rates which yielded reaction constants (ρ) of 2.59, −2.40, −1.09, and −0.90 in benzene, AcOEt, CH_2Cl_2, and MeOH, respectively. This data attests to the formation of a zwitterionic peroxide which enjoys stabilization from its own substituents and by competing solvation and further explains the predominance of dioxetane to the detriment of trioxane formation.

Introduction. – Electron-rich olefins, on photo-oxygenation, have a propensity to form 1,2-dioxetanes [1]. Although singlet oxygen can add to the double bond in one step [2], a variety of two-step alternatives are possible. Radicals, charge-transfer complexes [3], and polar peroxidic species [4] have been invoked, all of which are supposed to cyclize subsequently to 1,2-dioxetane. Evidence in support of zwitterionic peroxides or perepoxides has been obtained in the past from experiments which exploit skeletal rearrangement [5] or trapping by alcohols [6] and sulfoxides [7]. We recently demonstrated that aldehydes, but not ketones, can also intercept certain zwitterionic peroxides to furnish 1,2,4-trioxanes [8]. Yields were variable and seemed to depend on the nature of the olefin. Enol ethers provide an illustration. Rose bengal-sensitized photo-oxygenation of 2-methoxy-2-norbornene (**1**) in acetaldehyde gave the *cis*-fused *exo*-1,2,4-trioxanes **2** in 13% yield. Similar photo-oxygenation of 2-(methoxymethylidene)adamantane (**3**) was more efficient giving the epimeric methyl derivatives **4** of the spirocyclic 1,2,4-trioxane (53% yield). Surprisingly, 2-(phenoxymethylidene)-

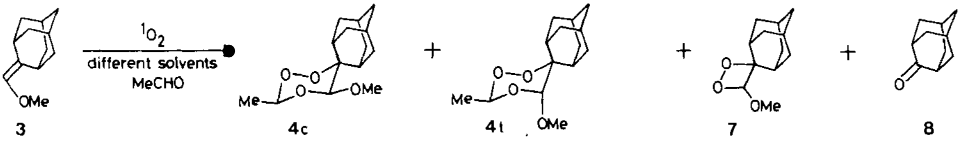




adamantane (**5**) afforded only the 1,2-dioxetane **6**, no trioxane being detected [9]. In the latter case, one wonders, if in fact, a zwitterionic species is involved at all. Clearly, further study of this new reaction is desirable. In particular, the factors affecting the efficiency of trapping need to be elucidated.

We now present our findings on the photo-oxygenation of 2-(methoxymethylidene)adamantane (**3**) with acetaldehyde in solvents of different polarity and at different temperatures. We also report on the rates of photo-oxygenation of 2-(phenoxymethylidene)adamantane (**5**) and several of its *p*- and *m*-substituted derivatives in solvents of different polarity.

Results. – Photo-oxygenation of **3** in the presence of acetaldehyde at constant temperature (**u** 78°) in 8 different solvents gave 4 products, the pair of diastereoisomeric trioxanes **4**, the dioxetane **7**, and 2-adamantanone (**8**). The reaction was efficient in that overall yields of 90% were consistently obtained. The relative amounts of the 4 products were readily ascertained by HPLC using cyclododecanone as standard. Good separation, even for the pair of diastereomers **4c** and **4t**, was obtained. Resolution was sharp, permitting unambiguous integration of the constituent peaks (*Fig. 1*).



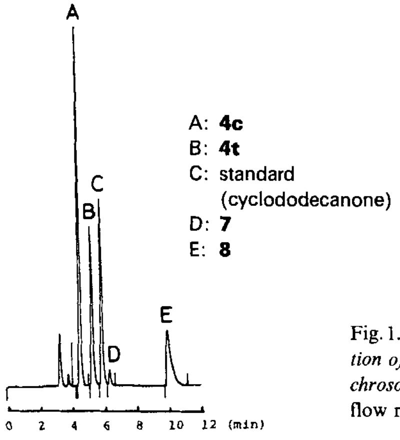


Fig. 1. *HPLC analysis of the mixture obtained from the photo-oxygenation of* **3** *and acetaldehyde in THF at –31°C.* Column: *Merck Lichrosorb Si 60 (5)* 250 mm × 4.0 mm; solvent: 3% THF in isooctane; flow rate: 0.9 ml/min; detection: refractive index (*Waters R401*).

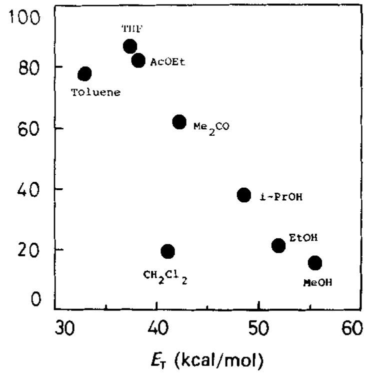


Fig. 2. *Relative yields of 1,2,4-trioxanes* **4c**/**4t** *obtained from the photo-sensitized oxygenation of* **3** *at −78°C in different solvents*

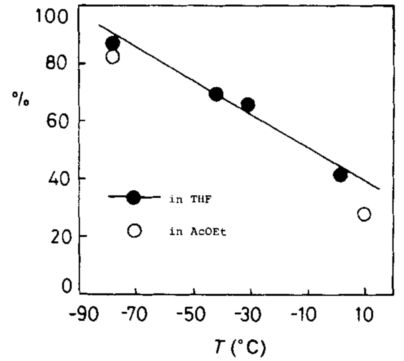


Fig. 3. *Yields of 1,2,4-trioxanes* **4c**/**4t** *obtained from the photo-sensitized oxygenation of* **3** *at different temperatures*

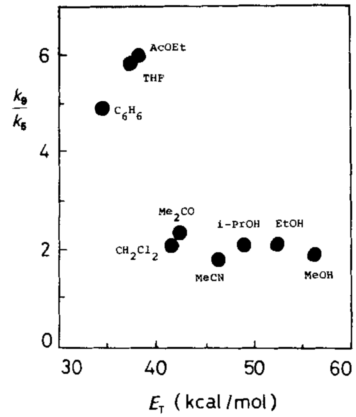


Fig. 4. *Relative rates of the photo-oxygenation of enol ethers* **9** *and* **5** *in different solvents*

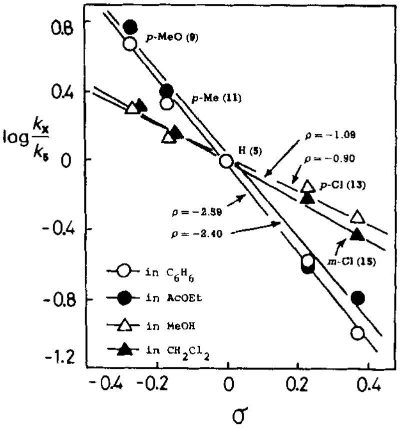


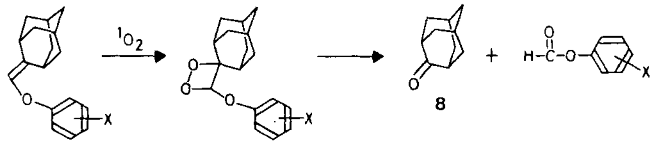
Fig. 5. Hammett *plot of the logarithms of the relative rates of photo-oxygenation of 2-(aryloxymethylidene)adamantanes in different solvents.* X = **5**, **9**, **11**, **13**, and **15**.

All products were the consequence of the intermediacy of singlet oxygen as evidenced by the customary tests [10]. Addition of small amounts of 1,4-diazabicyclo[2.2.2]octane (DABCO) to the reaction mixture caused a small decrease in the yield of products, but left the ratio of **4c**/**4t** essentially unchanged (namely 2.4 compared to 2.2 without DABCO). The addition of 2,6-di(*t*-butyl)-*p*-cresol, a typical radical scavenger [11], was without effect on yield or ratio. Significant variations in product composition were observed for solvents of different polarity *(Fig. 2)*. Once again, the ratio of diastereoisomeric trioxanes remained invariant.

Temperature also had a marked effect on trioxane formation. Photo-oxygenation of **3** in tetrahydrofurane (THF) and AcOEt gave a well-defined trend for the yield of trioxanes **4** relative to the other products formed *(Fig. 3)*.

A second set of photo-oxygenations was carried out with 2-(phenoxymethylidene)-adamantane (**5**) and its *p*-methoxy (**9**), *p*-methyl (**11**), *p*-chloro (**13**), and *m*-chloro (**15**) derivatives. In all cases, the corresponding 1,2-dioxetanes (**6**, **10**, **12**, **14**, and **16**) or their cleavage products were formed. Comparison of the rate of photo-oxygenation of **9** with that of the parent compound **5** revealed significant divergences in solvents of different polarity *(Fig. 4)*.

Further confirmation of the effect of the aryl substituent and its dependence on solvent polarity was provided by determining the relative rates of pairs of 2-(aryloxymethylidene)adamantanes using **5** as reference. The plot of the logarithms of the relative rates against the *Hammett* σ values determined in 4 solvents produced 4 good straight lines *(Fig. 5)*. The derived reaction constants (ρ) were found to be −2.59 ($r = 0.997$) and −2.40 ($r = 0.994$) for the non-polar solvents benzene and AcOEt, while values of −0.90 ($r = 0.995$) and −1.09 ($r = 0.996$) characterized the polar solvents MeOH and CH_2Cl_2 respectively.



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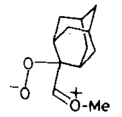
5 X = H
9 X = *p*-MeO
11 X = *p*-Me
13 X = *p*-Cl
15 X = *m*-Cl

6 X = H
10 X = *p*-MeO
12 X = *p*-Me
14 X = *p*-Cl
16 X = *m*-Cl

Discussion. – It is immediately seen that trioxane formation from **1** depends critically on the choice of solvent *(Fig. 2)*. Yields of trioxanes **4** were high (80%) in solvents of low polarity as exemplified by toluene, THF and AcOEt, although CH_2Cl_2 was an exception¹). In contrast, yields of trioxane were low with countervailing high yields of dioxetane and adamantanone in solvents of high polarity, typified by the alcohols. A suitable explanation is found in terms of a polar intermediate such as the zwitterionic peroxide **17** or the perepoxide **18**. Any real distinction between these species will be difficult to make. Nevertheless, the essential feature is that the positive charge is stabilized as an oxonium cation while the negative charge remains localized on the distal oxygen substituent. Consequently, both species, although electrically neutral, are expected to be nucleophilic. Solvents which dissipate these charges by whatever means, by hydrogen bonding for example, will render **17** unreactive towards a potential external electrophile such as acetaldehyde. Consequently, collapse of the opposing charges by monomolecular closure to dioxetane will prevail.

This result finds an apt parallel in the dye-sensitized photo-oxygenation of an enol ester where intramolecular trapping of an intermediate polar peroxide occurred only in acetone, but not in MeOH [11].



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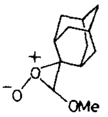

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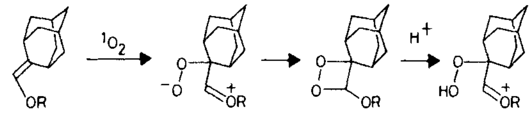
¹) The E_T values in *Fig. 2* refer to the pure solvents. No correction was made for the presence of acetaldehyde in solution as its E_T value is not known. However, assuming it to be similar to that of acetone, a disproportionately greater influence should be operative in solvents of low polarity than in those of high polarity.

Equally important is the effect of temperature on the fate of the polar species **17** or **18** *(Fig. 3)*. Even in non-polar solvents such as THF and AcOEt, high temperatures diminish their life-time, favouring their closure to dioxetane. Low temperatures preserve them, so that incorporation of acetaldehyde to give trioxane stands a chance. Such effects have already been noted in the photo-oxygenation of indoles which underwent almost exclusively oxidative cleavage of the C(2),C(3) bond at room temperature *via* an intermediate dioxetane. It was only at –78° that trapping by alcohols and amino groups of the intermediate zwitterionic peroxide became the dominant reaction course [12].

Compared to its 2-methoxymethylidene analogue **3**, the behaviour of 2-(phenoxymethylidene)adamantane (**5**) is, at first glance, puzzling. They both share the same capability to form 1,2-dioxetanes on photo-oxygenation (**7** and **6**). It therefore seems reasonable to suppose that analogously charged peroxidic species are involved, *e.g.* **17** and **19**. However, **17** possesses the special property of being trapped by aldehyde, whereas **19** escapes scot-free by closing to dioxetane **6**. This same pattern is repeated by the behaviour of the corresponding β-hydroperoxy cations **20** and **21** derived from dioxetanes **7** and **6** by protonation [13]. The methoxonium ion **20** reacts readily with aldehydes to give the trioxanes. In comparison, the phenoxonium ion **21** is more sluggish. It combines only with the more electrophilic aldehydes.



3 R = Me
5 R = Ph

17 R = Me
19 R = Ph

7 R = Me
6 R = Ph

20 R = Me
21 R = Ph

Despite the lack of outright chemical trapping, unmistakable signs for the existence of the phenoxonium ion **19** are provided by the kinetic data on the derivatives of 2-(phenoxymethylidene)adamantane (**5**). Substantial variations of the relative rates of photo-oxygenation of **5** *vs.* its p-methoxy derivative **9** are seen in solvents of varying polarity *(Fig. 4)*. In polar solvents, *e.g.* the alcohols, the effect of the p-methoxy group is almost inoperative ($k_9/k_5 \approx 2$). In non-polar, aprotic solvents such as benzene, the p-methoxy group exerts its effect more fully ($k_9/k_5 \approx 6$). This behaviour is in keeping with previous reports on the enhancement of the rate of dioxetane formation by polar solvents [14].

The present result is best explained in terms of a zwitterionic peroxide like **19**. Stabilization by solvation of the cationic centre will compete with that provided by a substituent on the phenyl ring. In strongly polar solvents, the p-methoxy substituent on **19** is not needed for stabilization; the solvent does it instead. In other words, singlet oxygen on reacting with **9** in MeOH displays about the same electrophilicity as it does towards the parent **5**. However, in benzene, singlet oxygen appears to be more electrophilic towards **9** than it is to **5**.

The *Hammett* plot reveals these aforementioned effects to better advantage *(Fig. 5)*. Two different pairs of linear correlations characterize the relative rates in the 2 polar and 2 non-polar solvents respectively. The negative reaction constants certainly confirm the electrophilicity of singlet oxygen, but the significantly different sets of values, *viz.* -2.5 and -1.0, should not be construed as evidence for the operation of 2 different reaction mechanisms. The difference is simply a reflection of the predominance of substituent effects in non-polar solvents and their attenuation when solvation takes over in polar solvents such as CH_2Cl_2 and alcohols. This latter result has special relevance to a *Hammett* study of the photo-oxygenation of mono- and disubstituted furanes determined in one solvent, namely CH_2Cl_2 [15]. The mechanistic conclusions derived therefrom could well be modified if the study were extended to other solvents, in particular less polar ones which would allow the role of substituents to assume greater importance.

Lastly, we return to the chemical difference between 2-(methoxymethylidene)- (**3**) and 2-(phenoxymethylidene)adamantane (**5**). The reason why **3** gives trioxane and **5** does not must reside in the much greater stability and attendant charge delocalization of the zwitterionic peroxide **19** over **17**, even at low temperature.

Conclusions. – The present findings reveal that the addition of singlet oxygen to an enol ether creates a dipolar intermediate, conveniently depicted as a zwitterionic peroxide. Factors which stabilize it, such as polar, protic solvents and electron-donating substituents, render the peroxide less capturable by an aldehyde and facilitate its closure to a 1,2-dioxetane. On the other hand, non-polar solvents, low temperature, and electron-withdrawing substituents will prevent dispersion of charge and therefore enhance reactivity towards aldehydes favouring trioxane formation. Knowledge of these factors could be useful for designing experiments with other electron-rich mono-enes and dienes to give reactive peroxides and subsequently variously substituted trioxanes. Consequently, better access should be possible to this little known class of heterocycles which has assumed importance in view of the anti-malarial activity of a naturally occurring member, Qinghaosu [16].

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Experimental Part

General. All solvents used were of analytical quality *(Merck)*. Rose bengal (RB), methylene blue (MB), and *meso*-tetraphenylporphine (TPP) were obtained from *Fluka* and *EGA*, respectively, and used as received. HPLC analyses were determined on a *Waters M-45* instrument equipped with a *R401* differential refractometer and a *Hewlett-Packard 3380S* integrator. GLC analyses were performed on a *Hewlett-Packard 5880A* series instrument using a a glass-capillary column (0.2 mm × 12.5 m; liquid phase: cross-linked dimethyl silicone). Physical constants and spectra were determined as follows. Melting points (m.p.): *Reichert* hot-stage microscope (uncorrected). ^{1}H- and ^{13}C-NMR spectra (chemical shifts in ppm relative to internal TMS (= 0 ppm), coupling constants J in Hz): *Varian XL-100* or *Bruker WH 360* spectrometers. Mass spectra: *CH-4 MAT* instrument. Elemental analyses were carried out by Drs. *H.* and *K. Eder*, Service de Microchimie, Institut de Chimie Pharmaceutique, University of Geneva.

Preparation of Enol Ethers. 2-*(Methoxymethylidene)adamantane (= 2-(methoxymethylidene)tricyclo[3.3.1.1^{3,7}]decane)* (**3**) [17] was obtained by the *Horner-Wittig* reaction [18], and the *2-(aryloxymethylidene)adamantanes (= 2-(aryloxymethylidene)tricyclo[3.3.1.1^{3,7}]decanes)* **5**, **9**, **11**, **13**, and **15** were prepared from 2-adamantanone and the appropriate α-aryloxyacetic acid [19] [13]. *2-[(3-Chlorophenoxy)methylidene]adamantane* (**15**): Yield 61% (based on 2-adamantanone), m.p. 43–44° (recrystallized from hexane). ^{1}H-NMR (360 MHz, $CDCl_3$): 7.20 (*dd*, J = 8, 8, 1H); 6.97 (*m*, 2H); 6.88 (*m*, 1H); 6.15 (*s*, 1H); 3.06 (br. *s*, 1H); 2.44 (br. *s*, 1H); 2.1–1.75 (*m*, 12H). MS: 276 (35, $M^+ + 2$), 274 (100, M^+), 240 (4), 219 (5), 217 (11), 193 (7), 147 (41), 119 (18), 105 (39), 91 (69).

Preparation of 1,2-Dioxetanes. The known 1,2-dioxetanes **6**, **10**, **12**, and **14** were prepared by photo-oxygenation of the appropriate 2-(aryloxymethylidene)adamantanes [13] [20].

Tricyclo[3.3.1.1^{3,7}]decane-2-spiro-3'-(4'-methoxy-1',2'-dioxetane)[2] (**7**). A solution of **3** (210 mg, 1.18 mmol) and MB (5 mg) in MeOH (10 ml) was irradiated with a 500-W high-pressure Na lamp for 1 h at −78° while O_2 was passed. The progress of the reaction was followed by TLC (silica gel). On completion of the reaction, the solvent was evaporated. Chromatography of the residue (*Florisil*, pentane/CH_2Cl_2) gave **7** (157 mg, 63%) as a pale yellow solid, m.p. 62–63.5° (recrystallized from hexane at −78°). ^{1}H-NMR (100 MHz, $CDCl_3$): 5.24 (*s*, 1H); 3.47 (*s*, 3H); 2.8–2.4 (*m*, 2H); 2.1–1.4 (*m*, 12H). Anal. calc. for $C_{12}H_{18}O_3$ (210.27): C 68.55, H 8.63; found: C 68.42, H 8.74.

*Tricyclo[3.3.1.1^{3,7}]decane-2-spiro-3'-[4'-(*m*-chlorophenoxy)-1',2'-dioxetane]* (**16**). A solution of **15** (150 mg, 0.546 mmol) and RB (15 mg) in THF (6 ml) was irradiated with a 500-W high-pressure Na lamp for 12 h at −50° while O_2 was passed. The progress of the reaction was monitored by TLC (silica gel). Column chromatography (silica gel) at r.t. (CH_2Cl_2/hexane 1:3) gave **16** (66 mg, 39%), m.p. 60–65° (recrystallized from pentane at −78°). ^{1}H-NMR (360 MHz, $CDCl_3$): 7.24 (*dd*, J = 8, 8, 1H); 7.08 (*ddd*, J = 8, 2.5, 1, 1H); 6.91 (*dd*, J = 2.5, 2.5, 1H); 6.75 (*ddd*, J = 8, 2.5, 1, 1H); 6.02 (*s*, 1H); 2.95 (br. *s*, 1H); 2.70 (br. *s*, 1H); 2.1–1.6 (*m*, 12H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): 107.5, 93.0 (*d*, and *s*, resp., 2 1,2-dioxetane C-atoms); the other C-atoms were difficult to assign owing to decomposition during measurement. Anal. calc. for $C_{17}H_{19}ClO_3$ (306.79): C 66.56, H 6.24, Cl 11.56; found: C 66.35, H 6.45, Cl 11.71.

Procedure for Photo-oxygenation of **3** *in the Presence of Acetaldehyde in Different Solvents.* A solution of **1** (1.9×10^{-2}M) in the solvent (5 ml) and acetaldehyde (1 ml), together with sensitizer, was irradiated with a 500-W high-pressure Na lamp for 1 h while O_2 was continuously passed at −78°. In general, RB (3×10^{-4}M) was used as sensitizer, except in CH_2Cl_2 and toluene when MB (1×10^{-3}M) and TPP (3×10^{-4}M) were used, respectively.

After evaporation of the solvent, an internal standard (dodecanone, *ca.* 40% equiv. to **1**) was added to the mixture, and the solution was passed through a short silica-gel column (*ca.* 3 cm) to remove sensitizer. Samples suitable for HPLC analysis were prepared by taking the dodecanone mixture and dissolving it in the HPLC solvent (0.5 ml) which was then filtered through a *Millex-SR* (0.5 μ) cartridge (anal. conditions, see *Fig. 1*). Yields of products were determined by comparing and calibrating peak areas with that of the internal standard. Authentic samples of the trioxanes **4c** and **4t** [8a] and dioxetane **7** were prepared independently and found to be stable under the abovementioned HPLC conditions.

Photo-oxygenation of **3** *in the Presence of Acetaldehyde at Different Temperatures.* The photo-oxygenation of **3** was carried out exactly as described above, except that at −78° it was performed under O_2 contained in a balloon.

Photo-oxygenation of **3** *in MeOH.* The RB-sensitized photo-oxygenation of **3** was carried out in MeOH at −78° as above in the absence of acetaldehyde. No MeOH addition product was formed as confirmed by HPLC. Instead, **7** (6%) and **8** (87%) were obtained.

Competitive Photo-oxygenations of 2-(Aryloxymethylidene)adamantanes. A solution of **5** and **9** (4.2×10^{-1}M) in the solvent (2 ml) with internal standard (tetradecane) at 10° was irradiated with a 500-W high-pressure Na lamp under O_2. Generally, MB (6×10^{-4}M) was used as sensitizer, except in benzene, THF, and AcOEt, when TPP (3×10^{-4}M) was employed. The progress of photo-oxygenation was monitored by GLC. The pseudo-first-order rate constant for the decrease of starting enol ethers was calculated by the linear regression method using at least 5 points. The *Hammett* study was done the same way using **5** as standard.

Control Experiments. Reaction of 2-(Aryloxymethylidene)adamantanes with Chemically Generated Singlet Oxygen. The thermal decomposition of 1,4-dimethyl-1,4-peroxy-1,4-dihydronaphthalene was used as a source of singlet oxygen [22]. Solutions of CH_2Cl_2 containing the enol ether **5**, **9**, **11**, **13**, or **15** (*ca.* 1.4×10^{-2}M) and endoperoxide (*ca.* 1.4×10^{-1}M) were stirred for 2 days at r.t. in the dark. GLC of the mixture showed *ca.* 25 to 70% conversion of the enol ethers to 2-adamantanone. The enol ethers were found to be stable under the same conditions in the absence of endoperoxide.

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[2] Although dioxetane **7** has been previously described, it was not isolated and purified [21].

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