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NEW CHEMISTRY OF ZWITTERIONIC PEROXIDES ARISING BY PHOTOOXYGENATION OF ENOL ETHERS[1]†

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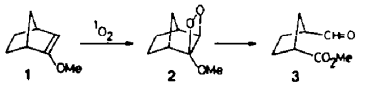
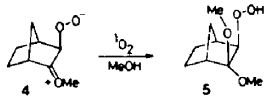
Abstract—The rose bengal-sensitized photooxygenation of 2-methoxynorborn-2-ene (**1**) in acetaldehyde gave *cis*-1-carboxaldehyde-3-carbomethoxycyclopentane (31%) and the *cis* and *trans*-Me derivatives of the *cis*-fused *exo*-1,2,4-trioxanes arising by addition of a molecule of oxygen and acetaldehyde to **1** at C3 and C2 respectively (13%). Similar photooxygenation of 2-(methoxymethylidene)adamantane in the presence of acetaldehyde, propionaldehyde and pivalaldehyde gave adamantanone (31–42%), and the *cis* and *trans* tricyclo[3.3.1.1^{3,7}]decane-2-spiro-6′-[3-alkyl-5-methoxy-1,2,4-trioxanes] in yields of 32–53%. Trioxane formation under similar conditions was experienced for 1,1-di-t-butyl-2-methoxyethene and 2-(methylmercaptomethylidene)adamantane. The results are discussed in terms of an intermediate zwitterionic peroxide which can either close directly to a 1,2-dioxetane or, if aldehyde is present, condense across the CO function giving the 1,2,4-trioxane.

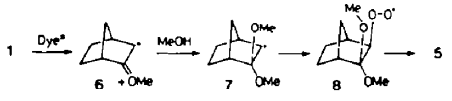
Those electron-rich olefins which are unable to form hydroperoxides invariably react with singlet oxygen to give 1,2 dioxetanes.[2] Although the addition of a molecule of oxygen to the double bond is operationally simple, the course actually followed may be more complex. The reaction could occur by a one-step [2 + 2] cyclo-addition[3] or by a variety of two-step processes. Speculation about the nature of possible intermediates runs the gamut from charge-transfer complexes[4] to radicals,[5,6] and zwitterions.[6] A good illustration of the mechanistic possibilities is provided by 2-methoxynorbornene (**1**) which is an ideal substrate as $^1O_2$ cannot generate a hydroperoxide because the required allylic shift is geometrically impossible.[7] Moreover, as methylene blue-sensitized photooxygenation in aprotic solvents reveals, only the *exo* 1,2-dioxetane (**2**) is formed initially. Subsequently, cleavage affords *cis*-1-carboxaldehyde-3-carbomethoxycyclopentane (**3**).



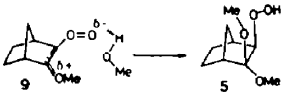
We originally contended that the dioxetane **2** was produced in two steps, the first being the attachment of $^1O_2$ to the *exo*-face of the double bond of **1** to create the zwitterionic peroxide (**4**) which in a second step normally closes to dioxetane **2**. Evidence for this contention was provided by carrying out the MB-sensitized photooxygenation in methanol. The fact that sizable quantities of *exo*-hydroperoxy dimethylacetal (**5**) were obtained together with other products derived from dioxetane **2**, which itself was inert to methanol under the experimental conditions, pointed ineluctably, in our opinion, to an ionic species such as **4**.



However, alternative mechanisms have been proposed which purport to be equally compatible with the formation of the solvent-incorporated product **5**. It has been suggested[5] that 2-methoxynorbornene (**1**) could transfer an electron to an excited molecule of methylene blue to give the radical cation **6**, which on successive addition of methanol and oxygen evolves *via* **7** and **8** to the final product **5**.



Yet another suggestion,[4] but more firmly based on the rate and activation parameters determined for **1** in different solvents, is that $^1O_2$ reacts rapidly and reversibly to give an exciplex (**9**) which benefits from H-bonding when methanol is used as solvent. Such a solvated complex then further reacts to give dioxetane **2** and the acetal **5**.



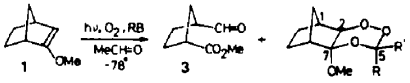
A significant difference between the two mechanisms is the role played by methanol. In the first, it behaves as a nucleophile, in the second as an acid in protonating the developing peroxide function. In any event, the methanol-mediated reaction constitutes a special case.

† Dedicated to Dr. Arnold Brossi on the occasion of his 60th birthday.

Consequently, we decided to investigate further the reaction of $^1O_2$ with enol ethers by resorting to other structural types and by using various aldehydes as solvent with the idea that the nature of the intermediate involved would be revealed. Aldehydes should be capable of eliciting the nucleophilic or radical character of peroxidic intermediates, whatever they are.

RESULTS

Rose bengal sensitized photooxygenation of 2-methoxynorbornene (**1**) in acetaldehyde at −78° gave the expected cleavage product **3** (31% yield), but also two isomeric *exo*-1,2,4-trioxanes (**10** and **11**) in a ratio of 2:3 in 13% yield.

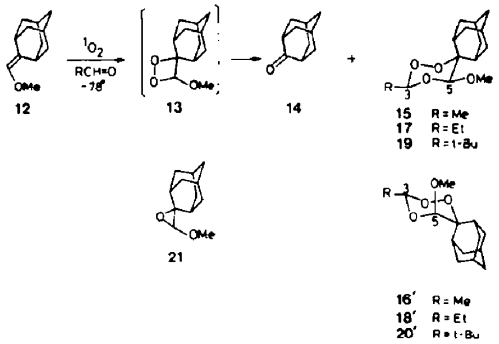


1 3

10 R=H, R'=Me
11 R=Me, R'=H

Similar photooxygenation of 2-(methoxymethylidene)adamantane (**12**) gave adamantanone (**14**) (31% yield), presumably *via* cleavage of the dioxetane **13**, together with a pair of *cis* and *trans* trioxanes **15** and **16**′ formed in 30 and 23% yield respectively.

Essentially, the same result was obtained with propionaldehyde and pivalaldehyde in tetrahydrofuran. Adamantanone (**14**) was formed in both cases in 42 and 36% yield respectively. More importantly, the corresponding *cis* and *trans*-3-ethyl- and 3-t-butyl-1,2,4-trioxanes (**17**, **18**′ and **19**, **20**′) were obtained in yields of 31, 14, 10 and 12% respectively. The experiment with pivalaldehyde was also marked by the formation of the epoxide **21**.



12 13 14

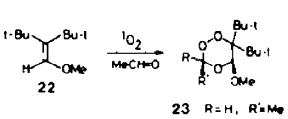
15 R=Me
17 R=Et
19 R=t-Bu

21

16′ R=Me
18′ R=Et
20′ R=t-Bu

Control experiments established that sensitizer was necessary for trioxane formation and that the 1,2-dioxetane derived from the enol ether **12**, *viz* **13**, did not itself react under the conditions of photooxygenation, but simply decomposed by scission to adamantanone.

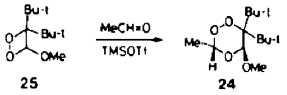
An acyclic structural analogue of **12** was next chosen. Photooxygenation of 1,1-di-t-butyl-2-methoxyethene (**22**) in the presence of acetaldehyde gave a mixture of *cis* and *trans*-3-methyl-1,2,4-trioxanes (**23** and **24**) in 31% yield.



22

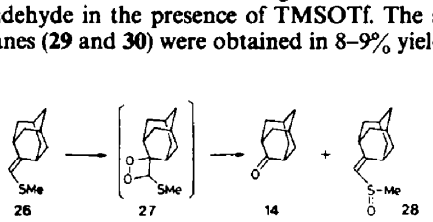
23 R=H, R'=Me
24 R=Me, R'=H

Although the above control experiment showed that 1,2-dioxetane **13** was inert towards acetaldehyde, the addition of trimethylsilyl trifluoromethanesulfonate (TMSOTf) as catalyst brought about an almost quantitative production of the corresponding *cis* and *trans* trioxanes (**15** and **16**) (58 and 38% yields respectively). Similarly, the dioxetane obtained from **22**, namely **25**, on TMSOTf catalysis gave a 64% yield of a single Me derivative, presumably **24**, identical to the major diastereoisomer obtained by photooxygenation of **22**.

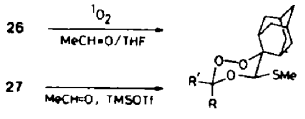


25 24

The sulfur analogue of **12**, on photooxygenation is expected to give an unstable dioxetane **27**. In fact, 2-(methylmercaptomethylidene)adamantane **26** in CH_2Cl_2 at −78° gave only adamantanone **14** and the sulfoxide **28** in 58 and 33% yield. Repetition of the experiment, but in CH_2Cl_2 and acetaldehyde, gave mainly **14**. However, replacing CH_2Cl_2 by THF brought about a tiny, but significant change. Adamantanone was still overwhelmingly formed, but the *cis* and *trans*-3-methylmercaptotrioxanes (**29** and **30**) were also detected in 4% yield. The validity of this result was confirmed by generating the unstable dioxetane **27** at −78° and allowing it to condense with acetaldehyde in the presence of TMSOTf. The same trioxanes (**29** and **30**) were obtained in 8–9% yield.



26 27 14 28

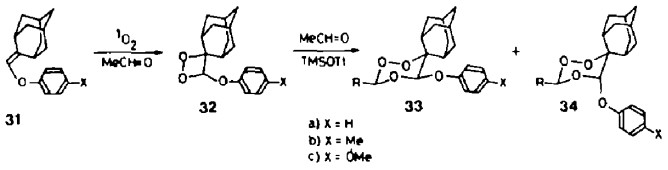


29 R=H, R'=Me
30 R=Me, R'=H

Lastly, a series of 2-(phenoxymethylidene)adamantanes bearing *p*-Me and OMe substituents including the parent (**31**) was submitted to photooxygenation in the presence of acetaldehyde. In no case was trioxane formed, but only the corresponding dioxetanes **32**. However, as we have reported elsewhere,[7] the latter on catalysis with TMSOTf condensed with acetaldehyde to give the 3-phenoxy-1,2,4-trioxanes (**33** and **34**).

DISCUSSION

The first conclusion which can be drawn about the course of the photooxygenation of 2-methoxynorbornene (**1**) is that the creation of the radical cation **6**, although possible when MB is used as sensitizer,[5] is improbable for the anionic sensitizer rose bengal.[9] Moreover, the incorporation of triplet oxygen and acetaldehyde by **6** to give trioxanes **10** and **11** is equally

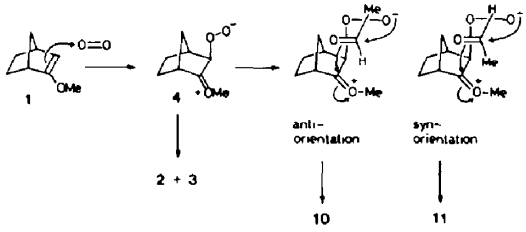


improbable. In a general way, if radicals were involved, they would be expected to engender acyl radicals by abstraction of a H-atom from the aldehyde function.[10] We believe that the intermediacy of a zwitterionic peroxide **4** formed by attack of $^1O_2$ on the *exo* face of **1** best explains the products. Closure of **4** to dioxetane **2** followed by cleavage to **3** is the normal event.

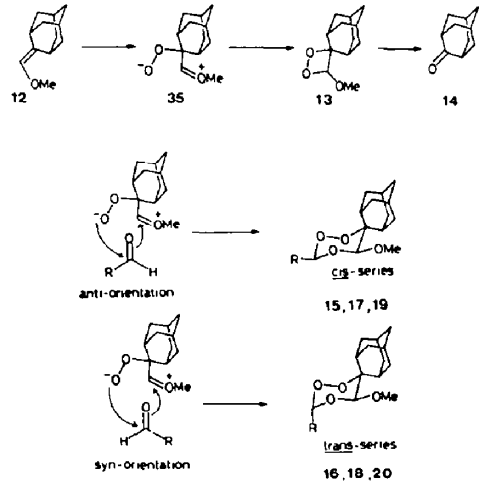
However, acetaldehyde, when present, can participate to make the 6-membered trioxane ring in two ways. Adoption of an *anti* orientation with respect to the OMe substituent leads to **10**, whereas the *syn*-orientation gives **11**. The newly-created ring is fused *cis* and *exo* to the norbornane skeleton. The actual shape of the 1,2,4-trioxane ring can only be surmized, but it probably adopts a boat conformation. Nonetheless, the configuration of the C5 substituent in **10** and **11** is secure.

Yields of trioxane diminish in passing from acetaldehyde to pivalaldehyde (Table 1), probably reflecting increasing hindrance in either of the two orientations. Of particular note is the occurrence of the epoxide **21** in the reaction with pivalaldehyde. Its origin probably stems from the action of triplet oxygen on the aldehyde to give the peracid which in turn epoxidizes **12**.[11]

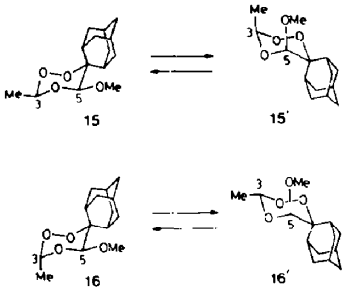
An interesting structural aspect which arises from the spirocyclic attachment of the adamantane moiety is the possibility of conformational inversion. For the *cis* series (**15**, **17** and **19**) the diequatorial conformation is adopted. It is known from NOE experiments with **15** that the C3 and C5 protons are contiguous. As a result, the diaxial conformation **15'**, which is sterically unreasonable anyway, is ruled out. However, two conformations, having non-bonded interactions of apparently similar magnitude, are possible for the *trans*



Similar mechanistic arguments also apply to 2-(methoxymethylidene)adamantane (**12**). Attack by $^1O_2$ on the exocyclic double bond generates the zwitterionic peroxide **35** which is free to incorporate an aldehyde molecule (RCH=O) in an *anti* or *syn* orientation thereby leading to two sets of 1,2,4-trioxanes in which the two single substituents are disposed *cis* and *trans* respectively. As before, closure of **35** to the 1,2-dioxetane **13** followed by scission to **14** constitutes the normal course.



isomer (**16'**, **18'** and **20'**). The C3 alkyl and the C5 OMe substituents have to choose which one of them will occupy an equatorial position (**16** vs **16'**). Once again, NOE experiments show that **16'** with the OMe substituent axial represents the preferred conformation.



However, at this juncture, it is well to realize that the foregoing configurational and conformational arguments are predicated on the assumption that the 1,2,4-trioxane ring exists rigidly in the chair conformation. In fact, few crystallographic structure determinations of this relatively unknown heterocycle have been reported so far.[12] Accordingly, an X-ray analysis was performed on a single crystal of the *trans*-3-t-butyl derivative **20'**. Fortunately, the assumption is experimentally justified; the trioxane exists as a chair and the OMe substituent does indeed occupy the axial position (Fig. 1).

Table 1. Yields[a] of products obtained from 2-(methoxymethylidene)adamantane (**12**)

Aldehyde	1,2,4-Trioxanes *cis*	1,2,4-Trioxanes *trans*	Adamantanone **14**	Epoxide **21**
MeCHO[b]	**15** 30%	**16** 23%	31%	—
EtCHO[b]	**17** 31	**18** 14	42	—
t-BuCHO[c]	**19** 10	**20** 12	36	12%

[a]Isolated by preparative TLC (silica gel) (see Exptl.).
[b]Neat.
[c]THF (10 ml), aldehyde (1 ml).

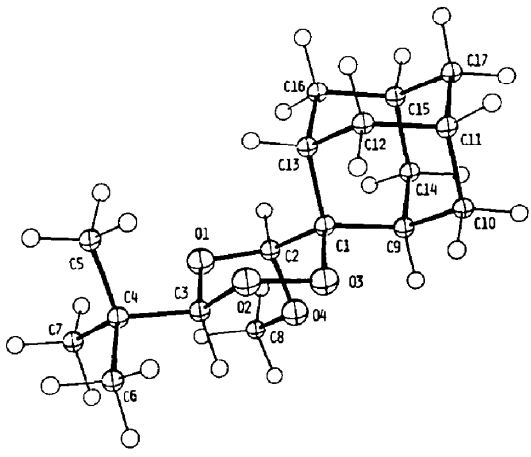


Fig. 1. Computer-generated perspective drawing of the structure of trioxane **20'**.

Comparison of the R_f values and the characteristic chemical shifts (Table 2) shows them to be consistent with the configurational assignments. This means that the *trans* isomers **16'** and **18'** have the same conformation as does **20'**. By the same token, the conformations of **17** and **19** are the same as that secured for **15**.

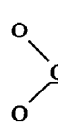
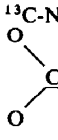
The acyclic analogue **22** behaves just like **12** and therefore deserves no further comment. On the other hand, the sulfur analogue **26** is unusual in being able to form that rare species, an S-substituted 1,2-dioxetane (**27**). Such dioxetanes are highly unstable as they decompose rapidly even at $-30°$. Their intermediacy is usually inferred from the scission products.[13] The present trapping experiment with acetaldehyde to give trioxanes **29** and **30** is grossly inefficient, but nonetheless it suffices to demonstrate that a precursive zwitterionic peroxide is implicated.

In summary, we believe that the foregoing examples of trioxane formation from the reaction of $^1O_2$ with different enol ethers in the presence of different aldehydes are all explicable in terms of a transient polar peroxidic species best formulated as a discrete zwitterionic peroxide. Products arising from radicals were not observed. The results parallel those obtained with 1,3-dimethylindole[14] and complement a recent case of intramolecular capture by a CO function of a zwitterionic peroxide formed from an enol ester.[15]

From the range of yields of trioxanes observed, which are never more than 53%, it is obvious that substituent and solvent effects are also critical in deciding whether the zwitterionic intermediate is capturable or not. We have found that ketones in general are not sufficiently electrophilic to condense with neutral zwitterionic peroxides such as **4** or **35**, however they readily react with β-hydroperoxy cations, giving the corresponding 1,2,4-trioxanes.[16] Moreover, despite their similarity, 2-(phenoxymethylidene)adamantanes (**31**), unlike their 2-OMe counterpart **12**, are totally inert towards acetaldehyde on photooxygenation. Clearly, subtle effects are operating. If zwitterionic peroxides do arise from **31**, they are insufficiently nucleophilic for reaction. On the other hand, the formal equivalents of these zwitterions, produced by the action of TMSOTf[8] or protic acids[17] on the corresponding 1,2-dioxetanes (**32**) react quite well with acetaldehyde, but not with acetone, to give 1,2,4-trioxanes.

A quantitative study of solvent and substituent effects on zwitterionic peroxide reactivity with respect to trioxane production is reported elsewhere.[17b]

Table 2. Characteristic R_f values and chemical shifts[a] of the *cis* and *trans*-1,2,4-trioxanes derived from **12**

Trioxanes C(3)R		R_f	^{1}H-NMR H—C—OMe	^{1}H-NMR H—C—R	^{13}C-NMR 	^{13}C-NMR 	^{13}C-NMR O—C—
cis **15**	Me	0.52[b]	4.53 (s)	5.42 (q)	106.8	99.9	83.8
trans **16'**	Me	0.45[b]	4.90 (s)	5.68 (q)	95.7	93.5	82.5
cis **17**	Et	0.42[c]	4.52 (s)	5.19 (t)	106.8	104.0	84.0
trans **18'**	Et	0.31[c]	4.92 (s)	5.49 (t)	97.4	95.7	82.7
cis **19**	t-Bu	0.62[c]	4.49 (s)	4.93 (s)	108.5	108.2	84.1
trans **20'**	t-Bu	0.42[c]	4.93 (s)	5.19 (s)	101.1	95.7	82.6

[a]δ values in $CDCl_3$.
[b]TLC, silica gel, CH_2Cl_2.
[c]TLC, silica gel, CH_2Cl_2 : hexane = 3:2.

EXPERIMENTAL

General

TLC silica gel 60 F_{254} Merck. Preparative layer chromatography: silica gel 60 F_{254} (thickness 2 mm). Physical constants and spectra were determined as follows. Melting points (m.p.): Reichert hot-stage microscope (uncorrected). IR spectra: Perkin–Elmer 681 spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra (chemical shifts in ppm relative to internal TMS (=0 ppm), coupling constants J in Hz): Bruker WH 360 and Varian XL-100 spectrometers. Mass spectra: CH-4 MAT and Finnigan GC/MS 4023 using the INCOS data system. Elemental analyses were carried out by Drs H. and K. Eder, Service de Microchimie, Institut de Chimie Pharmaceutique, University of Geneva.

Procedure for photooxygenation

The soln to be photooxygenated was placed in a vessel cooled by a dry ice–acetone bath. Irradiation was provided by a 500 W high-pressure sodium lamp while O_2 was passed through the soln. The progress of the reaction was monitored by TLC.

Preparation of starting materials

Compounds **12**,[18] **22**,[19] and **26**[20] were prepared by the Horner–Wittig reaction. Compounds **31**[17,21] were prepared by decarboxylation of the corresponding β-lactones.[21] Compound **1** was prepared from norbornanone.[22]

Photooxygenation of 2-methoxynorborn-2-ene (**1**) *in acetaldehyde at* $-78°$

A soln of **1** (750 mg, 6.05 mmol) in acetaldehyde (15 ml) containing rose bengal (RB) (30 mg) was photooxygenated for 3 hr. The solvent was evaporated and the residue was separated by chromatography over florisil. Elution with hexane–CH_2Cl_2 (2:1) gave **10** and **11**, whereas elution with CH_2Cl_2 afforded **3**.

Aldehyde ester **3** (228 mg, 31%). R_f = 0.13 (CH_2Cl_2, silica gel). IR (NaCl, neat): 2820 (m, CHO), 2720 (m, CHO), 1735 (vs, C=O), 1220 and 1170 (br. s, —O—). ^{1}H-NMR (100 MHz, $CDCl_3$): 1.8–2.1 (m, 4H), 2.15 (t, J = 8, 2H), 2.5–3.0 (m, 2H, 3.68 (s, 3H), 9.66 (d, J = 2, 1H).

cis *and* trans-1,2,4-*Trioxanes* (**11**) *and* (**10**). (158 mg, 13%, b.p. 43°/0.03 mm Hg. R_f = 0.47 (CH_2Cl_2, silica gel). ^{1}H-NMR (360 MHz, $CDCl_3$): 1.25–1.7 (m), 1.31 (d, J = 5, Me, **11**), 1.43 (d, J = 5, Me, **10**), 2.05–2.25 (m), 2.43 (m), 3.28 (s, OMe, **11**), 3.31 (s, OMe, **10**), 3.93 (d, J = 2, H—C—O, **10**), 4.09 (d, J = 2, H—C—O, **11**), 5.34 (q, J = 5, H—C—Me, **10**), 5.62 (q, J = 5, H—C—Me, **11**). ^{13}C-NMR (90.6 MHz, $CDCl_3$): pair of characteristic peaks, 19.7 (q) and 19.9 (q), 21.1 (t) and 21.6 (t), 25.6 (t) and 26.2 (t), 35.1 (t) and 35.6 (t), 39.7 (d), 40.2 (d), 42.5 (d) and 43.5 (d), 49.8 (q) and 50.8 (q), 90.7 (d) and 91.0 (d), 96.1 (d) and 98.7 (d), 104.4 (s); overlapped. The structure and ratio of **10** and **11** was ascertained from the ^{1}H- and ^{13}C-NMR spectra. The zero coupling for protons at C1 and C2 confirms the *exo* orientation of the dioxa element. The similarity of the spectra indicates that **10** and **11** are epimeric at C5. Saturation of the resonance of the OMe group of the minor epimer **10** performed in a FID difference experiment at 360 MHz produced a positive NOE[23] of the C5 proton. Consequently, the OMe and C5 Me groups have the *trans* configuration. The same experiment with the major epimer (**11**) showed no such effect, confirming that the groups are *cis*. MS (*m/e*): 97 (43), 96 (26), 87 (92), 79 (53), 71 (28), 67 (63). $C_{10}H_{16}O_4$ (220.23). Calc: C, 59.98; H, 8.05. Found: C, 60.00; H, 8.21%.

Photooxygenation of 2-(*methoxymethylidene*)*adamantane* (**12**) *in acetaldehyde at* $-78°$

A soln of **12** (150 mg, 0.84 mmol) in acetaldehyde (10 ml) containing RB (15 mg) was photooxygenated until complete disappearance of **12** (~ 2 hr). Excess acetaldehyde was evaporated and passed through a short florisil column (CH_2Cl_2) to remove RB. Evaporation of solvent and chromatography on a preparative silica gel plate (CH_2Cl_2: hexane = 3:2) gave three products.

Adamantanone (**14**) (39 mg, 31%). Identified by comparison with an authentic sample.

cis-1,2,4-*Trioxane* (**15**) (64 mg, 30%). M.p. 56.5–58°. R_f = 0.52 (CH_2Cl_2, silica gel). IR (NaCl, neat): 1095 (s, —O—). ^{1}H-NMR (360 MHz, $CDCl_3$): 1.3–2.6 (complex m, 14H), 1.36 (d, J = 6, 3H), 3.50 (s, 3H), 4.53 (s, 1H), 5.42 (q, J = 6, 1H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): 17.8 (q), 27.2, 27.8, 29.4, 32.6, 33.1, 33.2, 33.7, 34.4, 38.4, 56.6 (q), 83.8 (s), 99.9 (d), 106.8 (d). The *cis* configuration of **15** was assigned by NOE–FID difference experiments. Irradiation of the OMe group at C5 had no effect on the substituents at C3. Saturation of the C5 proton caused a positive NOE of the C3 proton; thus these protons are diaxial, consequently the Me and OMe groups are diequatorial (**15** and not **15'**). MS (*m/e*): no molecular peak, 194 (2), 178 (9), 166 (3), 165 (22), 164 (8), 162 (4), 152 (3), 151 (30), 150 (100). $C_{14}H_{22}O_4$ (254.33). Calc: C, 66.12; H, 8.72. Found: C, 65.84; H, 8.75%.

trans-1,2,4-*Trioxane* (**16'**) (50 mg, 23%). M.p. 45–50°. R_f = 0.45 (CH_2Cl_2, silica gel). IR (NaCl, neat): 1095 (s, —O—). ^{1}H-NMR (360 MHz, $CDCl_3$): 1.4–2.7 (complex m, 14H), 1.26 (d, J = 6, 3H), 3.47 (s, 3H), 4.90 (s, 1H), 5.68 (q, J = 6, 1H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): 17.4 (q), 27.0, 27.2, 30.0, 31.2, 31.8, 31.9, 33.1, 34.5, 37.8, 55.7 (q), 82.5 (s), 93.5 (d), 95.7 (d). The *trans* configuration of **16'** follows from the saturation of the OMe group which caused a positive NOE on the C3 proton, showing the nuclei to be contiguous. Irradiation of the C3 Me group did not affect the intensity of the C5 protons. Consequently, the preferred conformation places the OMe substituent in the axial position (**16'** and not **16**).[24] MS (*m/e*): no molecular peak, 194 (5), 178 (25), 165 (39), 151 (75), 150 (100), 134 (64). $C_{14}H_{22}O_4$ (254.33). Calc: C, 66.12; H, 8.72. Found: C, 66.36; H, 8.66%.

Photooxygenation of **12** *in THF with propionaldehyde at* $-78°$.

A soln of **12** (297 mg, 1.67 mmol) in dry THF (10 ml) and propionaldehyde (1 ml) containing RB (15 mg) was photooxygenated for 2 hr. Work-up according to the above procedure gave three products.

Adamantanone **14** (104 mg, 42%).

cis-3-*Ethyl*-1,2,4-*trioxane* **17**. Colorless oil (140 mg, 31%). R_f = 0.42 (CH_2Cl_2: hexane = 3:2, silica gel). ^{1}H-NMR (360 MHz, $CDCl_3$): 0.97 (t, J = 7.5, 3H), 1.35–2.55 (complex m, 14H), 2.33 (br.d, J = 12, 1H), 2.56 (br. s, 1H), 3.49 (s, 3H), 4.52 (s, 1H), 5.19 (t, J = 5.5, 1H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): 8.2 (q), 25.1 (t), 27.2 (d), 27.7 (d), 29.3 (d), 32.5 (t), 33.0 (t), 33.2 (t), 33.7 (d), 34.4 (t), 38.4 (t), 56.8 (q), 84.0 (s), 104.0 (d), 106.8 (d). MS (*m/e*): no molecular peak, 178 (28), 151 (35), 150 (100). $C_{15}H_{23}O_4$ (268.35). Calc: C, 67.14; H, 9.01. Found: C, 67.28; H, 9.16%.

trans-3-*Ethyl*-1,2,4-*trioxane* **18'**. M.p. 56–57° (63 mg, 14%). R_f = 0.31 (CH_2Cl_2: hexane = 3:2, silica gel). ^{1}H-NMR (360 MHz, $CDCl_3$): 0.97 (t, J = 7.5, 3H), 1.4–2.1 (complex m, 14H), 2.23 (br. d, J = 12, 1H), 2.66 (br. s, 1H), 3.47 (s, 3H), 4.92 (s, 1H), 5.49 (t, J = 5.5, 1H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): 8.0 (q), 24.9 (t), 27.0 (d), 27.2 (d), 30.0 (d), 31.3 (d), 31.8 (t), 3.20 (t), 33.1 (t), 34.5 (t), 37.8 (t), 55.5 (q), 82.7 (s), 95.7 (d), 97.4 (d). MS (*m/e*): no molecular peak, 178 (48), 151 (32), 150 (100). $C_{15}H_{24}O_4$ (268.35). Calc: C, 67.14; H, 9.01. Found: C, 67.08; H, 9.08%.

Photooxygenation of **12** *in THF with pivalaldehyde at* $-78°$

A soln of **12** (302 mg, 1.70 mmol) in dry THF (10 ml), pivalaldehyde (1 ml) and RB (15 mg) was photooxygenated for 2 hr. Work-up and chromatography gave four products.

Adamantanone **14** (91 mg, 36%).

Epoxide **21** (41 mg, 12%). M.p. 202°. R_f = 0.55 (CH_2Cl_2: hexane = 3:2, silica gel). ^{1}H-NMR (360 MHz, $CDCl_3$): 2.3–1.4 (complex m, 14H), 3.56 (s, 3H), 4.86 (s, 1H). MS (*m/e*): 194 (M^+, 2), 179 (16), 178 (100), 151 (12), 150 (76). $C_{13}H_{18}O_2$ (194.27). Calc: C, 74.19; H, 9.34. Found: C, 74.30; H, 9.47%.

cis-t-*Butyl*-1,2,4-*trioxane* **19**. Colorless oil (50 mg, 10%). R_f = 0.62 (CH_2Cl_2: hexane = 3:2, silica gel). ^{1}H-NMR (360

MHz, $CDCl_3$): 0.99 (s, 9H), 2.3–1.35 (complex, m, 12H), 2.43 (br. d, J = 12, 1H), 2.60 (br. s, 1H), 3.51 (s, 3H), 4.49 (s, 1H), 4.93 (s, 1H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): 24.7 (q), 27.3 (d), 27.9 (d), 29.2 (d), 32.7, 33.1, 33.4, 34.1, 34.4, 34.8, 38.6 (t), 56.5 (q), 84.1 (s), 108.2 (d), 108.5 (d). MS (*m/e*): no molecular peak, 264 (1), 179 (7), 178 (45), 151 (22), 150 (100). $C_{17}H_{28}O_4$ (296.41). Calc: C, 68.89; H, 9.52. Found: C, 68.79; H, 9.61%.

trans-t-*Butyl*-1,2,4-*trioxane* **20′** (58 mg, 12%). M.p. 91–92°. R_f = 0.42 (CH_2Cl_2 : hexane = 3 : 2, silica gel). ^{1}H-NMR (360 MHz, $CDCl_3$): 0.96 (s, 9H), 2.1–1.4 (complex m, 12H), 2.24 (br. d, J = 12, 1H), 2.62 (br. s, 1H), 3.45 (s, 3H), 4.93 (s, 1H), 5.19 (s, 1H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): 24.5 (q), 27.0 (t), 27.2 (t), 30.0 (d), 31.3 (d), 31.8 (d), 32.0 (d), 33.1 (t), 34.4 (s), 34.6 (t), 37.9 (t), 55.3 (q), 82.6 (s), 95.7 (d), 101.1 (d). MS (*m/e*): no molecular peak, 264 (1), 179 (12), 178 (100), 151 (14), 150 (71). $C_{17}H_{28}O_4$ (296.41). Calc: C, 68.89; H, 9.52. Found: C, 68.76; H, 9.68%.

X-ray crystallographic data[25] *of compound* **20′**

A suitable crystal of **20′** was obtained by recrystallization from hexane. Orthorhombic, **a** = 22.033 (5), **b** = 6.3679 (7), **c** = 11.502 (2) Å, space group $Pna2_1$, Z = 4, d_c = 1.220 g cm^{-3}. The lattice parameters and intensities were measured at room temp on an automatic four-circle Philips PW 1100 diffractometer equipment with a graphite monochromator and using MoK_α radiation. 1182 independent reflections were recorded ($\omega - 2\theta$ scan) of which 605 had $|F_0| > 3\sigma(F_0)$ and $|F_0| > 8.0$. Three standard reflections were measured at intervals of 90 min. Substantial crystal degradation was observed causing loss of about 20% of the diffracted intensities. However, all intensities were corrected for this drift.[26]

The structure was solved by direct methods using the Multan-80 program[27] and refined by full-matrix least-square analysis using the X-ray system;[26] anisotropic temperature factors were employed for the non-H atoms. The positions of the H atoms were calculated. The final *R* factor, based on the 605 reflections observed, was 0.038. The positional and vibrational parameters (Table 3) together with the bond lengths and principal torsional angles were determined (Table 4).

Control experiments

(A) *Irradiation of* **12** *in acetaldehyde without RB at* −78°. A soln of **12** (50 mg, 0.28 mmol) in acetaldehyde was irradiated with continuous passage of O_2 for 2 hr. On evaporation of solvent, chromatography over a short florisil column (hexane) gave **12** (45 mg, 90%).

(B) *Photooxygenation of* 1,2-*dioxetane* **13** *in acetaldehyde at* −78°. A soln of **12** (42 mg, 0.24 mmol) in acetone (5 ml) was photooxygenated with RB (6 mg) for 1 hr at −15°. TLC (CH_2Cl_2, silica gel) showed the quantitative formation of **13** (R_f = 0.57, CH_2Cl_2). In another experiment, **13** was isolated in 63% yield by column chromatography over florisil at −10°. Acetone was evaporated and replaced by acetaldehyde (5 ml) (no decomposition of **13** was observed during this operation, as checked by TLC). Photooxygenation was resumed at −78° for 2 hr. Work-up gave **13** (7 mg, 14%) and **14** (30 mg, 83%). No trioxane was formed.

Photooxygenation of 1,1-*di*-t-*butyl*-2-*methoxyethene* (**22**) *in acetaldehyde at* −78°. A soln of **22** (153 mg, 0.90 mmol) was treated according to the above procedure.

1,2,4-*Trioxanes* **23** and **24** colorless oil (64 mg, 31%). R_f = 0.59 (CH_2Cl_2, silica gel). ^{1}H-NMR (360 MHz, $CDCl_3$): pairs of characteristic peaks, 1.15 (s, t-Bu, major), 1.22 (s, t-Bu, minor), 1.25 (s, t-Bu, minor), 1.35 (s, t-Bu, major), 1.32 (d, J = 5.5, Me, minor), 1.34 (d, J = 5.5, Me, major), 3.46 (s, OMe, minor), 3.50 (s, OMe, major), 4.86 (s, MeO—C—H, minor), 4.99 (s, MeO—C—H, major), 5.43 (q, J = 5.5, Me—C—H, major), 5.67 (q, J = 5.5, Me—C—H, minor). ^{13}C-NMR (90.6 MHz, $CDCl_3$): pairs of characteristic peaks, 18.0 (q) and 18.1 (q), two pairs; 29.4 (q), 29.7 (q), 29.8 (q), and 31.4 (q), two pairs; 40.6 (s), 40.8 (s), 40.9 (s), and 41.2 (s), 55.6 (q) and 55.7 (q), 87.2 (s) and 91.1 (s), two pairs; 96.9 (d), 98.1 (d), 98.9 (d), and 102.1 (d). MS (*m/e*): no molecular peak, 213 (1), 196 (1), 142 (3), 131 (4), 129 (6), 103 (5), 101 (6), 85 (14), 61 (39), 57 (100). $C_{13}H_{26}O_4$ (246.35). Calc: C, 63.38; H, 10.64. Found: C, 63.44; H, 10.71%.

Condensation of 1,2-*dioxetanes* **13** *and* **25** *with acetaldehyde catalyzed by trimethylsilyl trifluoromethanesulfonate (TMSOTf)*

(A) Dioxetane **13** (23.7 mg, 0.113 mmol) was dissolved in dry CH_2Cl_2 (2 ml) with acetaldehyde (200 µl). Next, TMSOTf (15 µl, 0.7 eq.) was added and the soln stirred for 1 hr at −78°. After addition of Et_3N (10 µl), the mixture was diluted with CH_2Cl_2 (20 ml), washed with H_2O (3 × 20 ml) and dried (Mg SO_4). After evaporation of solvent, chromatography on a

Table 3. Crystallographic coordinates and equivalent isotropic temperature factors, U_{eq} ($\times 10^3$ Å^2) with experimental standard deviations in parentheses for trioxane **20′** ($C_{17}H_{28}O_4$)

Atom*	X	Y	Z	U_{eq}
O(1)	0.4518(3)	0.2096(10)	0.7580	36(3)
O(2)	0.4214(3)	0.5465(10)	0.8118(8)	36.3(24)
O(3)	0.3584(3)	0.4930(10)	0.7770(9)	37.8(24)
O(4)	0.3759(3)	0.1521(11)	0.6210(9)	43(3)
C(1)	0.3468(4)	0.2756(17)	0.8081(10)	32(4)
C(2)	0.3910(5)	0.1398(16)	0.7395(11)	40(4)
C(3)	0.4596(5)	0.4296(18)	0.7373(12)	46(4)
C(4)	0.5256(4)	0.4879(17)	0.7648(11)	45(4)
C(5)	0.5380(5)	0.4603(24)	0.8949(12)	68(5)
C(6)	0.5355(5)	0.7173(18)	0.7323(12)	60(5)
C(7)	0.5669(4)	0.3472(19)	0.6887(13)	64(5)
C(8)	0.4090(5)	0.0088(21)	0.5515(11)	63(5)
C(9)	0.2799(5)	0.2421(17)	0.7750(10)	38(3)
C(10)	0.2387(4)	0.3991(17)	0.8396(11)	39(4)
C(11)	0.2469(5)	0.3680(18)	0.9725(10)	39(4)
C(12)	0.3139(5)	0.4011(16)	1.0059(11)	40(4)
C(13)	0.3544(5)	0.2472(16)	0.9416(10)	34(4)
C(14)	0.2616(4)	0.0135(17)	0.8091(11)	39(4)
C(15)	0.2682(5)	−0.0156(17)	0.9402(11)	45(4)
C(16)	0.3347(4)	0.0163(18)	0.9752(10)	42(4)
C(17)	0.2280(5)	0.1421(18)	1.0066(12)	48(4)

*The numbering of atoms is that shown in Fig. 1.

Table 4. Bond lengths (Å) with estimated standard deviations in parentheses and principal torsional angles (°) for trioxane **20'** ($C_{17}H_{28}O_4$)[a]

O(1)—C(2)	1.427(12)	C(4)—C(6)	1.524(16)
O(1)—C(3)	1.432(13)	C(4)—C(7)	1.549(17)
O(2)—O(3)	1.484(9)	C(9)—C(10)	1.541(15)
O(2)—C(3)	1.413(14)	C(9)—C(14)	1.560(15)
O(3)—C(1)	1.453(13)	C(10)—C(11)	1.552(17)
O(4)—C(2)	1.406(16)	C(11)—C(12)	1.542(15)
O(4)—C(8)	1.415(15)	C(11)—C(17)	1.548(16)
C(1)—C(2)	1.523(15)	C(12)—C(13)	1.518(15)
C(1)—C(9)	1.538(14)	C(13)—C(16)	1.582(15)
C(1)—C(13)	1.555(16)	C(14)—C(15)	1.526(18)
C(3)—C(4)	1.534(14)	C(15)—C(16)	1.534(15)
C(4)—C(5)	1.531(19)	C(15)—C(17)	1.541(16)

C(3)—O(1)—C(2)—O(4)	68
C(3)—O(1)—C(2)—C(1)	−52
C(2)—O(1)—C(3)—O(2)	59
C(2)—O(1)—C(3)—C(4)	178
C(3)—O(2)—O(3)—C(1)	68
O(3)—O(2)—C(3)—O(1)	−65
O(3)—O(2)—C(3)—C(4)	177
O(2)—O(3)—C(1)—C(2)	−62
O(2)—O(3)—C(1)—C(9)	177
O(2)—O(3)—C(1)—C(13)	60
C(8)—O(4)—C(2)—O(1)	67
C(8)—O(4)—C(2)—C(1)	−172
O(3)—C(1)—C(2)—O(1)	54
O(3)—C(1)—C(2)—O(4)	−67
C(9)—C(1)—C(2)—O(1)	168
C(9)—C(1)—C(2)—O(4)	47
C(13)—C(1)—C(2)—O(1)	−67
C(13)—C(1)—C(2)—O(4)	172
O(3)—C(1)—C(9)—C(10)	−58
O(3)—C(1)—C(9)—C(14)	−178
C(2)—C(1)—C(9)—C(10)	−175
C(2)—C(1)—C(9)—C(14)	65
O(3)—C(1)—C(13)—C(12)	55
O(3)—C(1)—C(13)—C(16)	174
C(2)—C(1)—C(13)—C(16)	−67

[a]The numbering of atoms is that shown in Fig. 1.

preparative silica gel plate (CH_2Cl_2 : hexane = 3 : 2) gave **15** (16.7 mg, 58%) and **16'** (10.9 mg, 38%), identical with those obtained from photooxygenation of **12**.

(B) *Dioxetane* **25** (13.5 mg, 0.067 mmol) and acetaldehyde (200 μl) were treated with TMSOTf (10 μl, 0.8 eq.) as described above. Work-up gave **24** (10.5 mg, 64%) identical with the major isomer obtained by photooxygenation of **22**.

Photooxygenation of 2-(methylmercaptomethylidene)adamantane (**26**)

(A) *In* CH_2Cl_2 *at* −78°. A soln of **26** (326 mg, 1.68 mmol) in CH_2Cl_2 (5 ml) containing MB (10 mg) was photooxygenated for 135 min. Work-up and chromatography over silica gel gave two products. *Sulfoxide* **28**: (118 mg, 33%), m.p. 97–98° (recrystallized from hexane). IR (CCl_4): 1630 (m, C=C), 1050 (s, S=O). ^{1}H-NMR (100 MHz, $CDCl_3$): 1.6–2.1 (m, 12H), 2.60 (s, 3H), 2.4–265 (m, 1H), 3.35–3.15 (m, 1H), 6.02 (s, 1H). MS (*m/e*): 210 (M^+, 46), 195 (43), 194 (80), 193 (100), 163 (24), 145 (43). *Adamantanone* **14**: (145 mg, 58%).

(B) *In acetaldehyde–*CH_2Cl_2 *at* −78°. A soln of **26** (405 mg, 2.09 mmol) in acetaldehyde (15 ml) and CH_2Cl_2 (5 ml) containing RB (23 mg) was photooxygenated for 1.5 hr. Work-up gave **14** (251 mg, 80%) and a trace of **26**.

(C) *In acetaldehyde–THF at* −78°. A soln of **26** (216 mg, 1.11 mmol) in acetaldehyde (2 ml) and THF (10 ml) containing RB (15 mg) was photooxygenated for 2 hr. Evaporation of solvent and chromatography gave two products. *Adamantanone* **14**: (65 mg, 41%) and *cis and* trans-3-*methylmercapto*-1,2,4-*trioxanes* (**29** *and* **30**): (8 mg, 3%, ratio 3 : 1). R_f = 0.50 (silica gel, CH_2Cl_2). ^{1}H-NMR (360 MHz, $CDCl_3$): 6.01 (q, J = 5.5, HCMe, major), 5.42 (s, HCSMe, major), 5.41 (q, J = 5.5, HCMe, minor), 4.85 (s, HCSME, minor), 2.26 (SMe, minor), 2.16 (s, SMe, major), 1.45 (d, J = 5.5, HCMe, minor), 1.30 (d, J = 5.5, HCMe, major, adamantyl) 1.85–1.25 (complex m). MS (*m/e*): 270 (0.2, M^+), 237 (3), 223 (7), 210 (7), 194 (8), 181 (25), 164 (12), 151 (48), 150 (100), 135 (15), 117 (18), 105 (16), 91 (45). $C_{14}H_{22}O_3S$ (270.39). Calc: C, 62.19; H, 8.20; S, 11.86. Found: C, 62.14; H, 8.35; S, 11.65%.

(D) *TMSOTf-catalyzed condensation with acetaldehyde.* A soln of **26** (210 mg, 1.08 mmol) in CH_2Cl_2 (7 ml) was photooxygenated with tetraphenylporphine (2 mg) for 2 hr at −78°. After irradiation, acetaldehyde (0.5 ml) and TMSOTf (150 μl, 0.83 mmol) were added and stirred 1 hr at −78°. Et_3N (80 μl) was next added, followed by CH_2Cl_2 (~ 30 ml). The soln was washed (H_2O, 3×), and dried ($MgSO_4$). Work-up and TLC afforded **29** and **30** (24 mg, 9%) identical with those obtained in C, except that the isomer ratio = 15 : 1.

Photooxygenation of 2-(phenoxymethylidene)adamantanes (**31**) *in the presence of acetaldehyde at* −78°. A soln of **31** (0.7 mmol) in acetaldehyde (15 ml) and THF (5 ml) containing RB (20 mg) was photooxygenated for 4 hr. Work-up and inspection of the ^{1}H-NMR spectra of the crude mixture

revealed only signals corresponding to the expected **32**. The signals characteristic of authentic samples of **33** and **34** were absent.

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