Reaction of Singlet Oxygen with Norbornenyl Ethers. Characterization of Dioxetanes and Evidence for Zwitterionic Peroxide Precursors[1]

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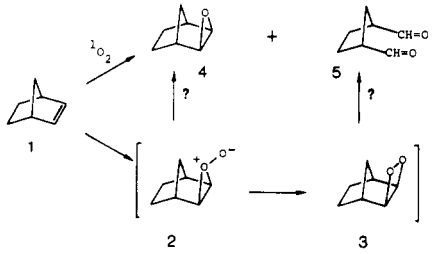
Abstract: Singlet oxygen reacts quickly with 2-trimethylsiloxynorborn-2-ene (**6**) in aprotic solvents at −20 °C to give exclusively the *exo*-3-trimethylsilylperoxynorbornan-2-one (**11**). In methanol the same result is obtained, except that 15% of *exo*-3-hydroperoxynorbornan-2-one (**12**) is also formed. **11** does not give **12** under the experimental conditions. 2-Methoxynorborn-2-ene (**7**) reacts with singlet oxygen similarly in aprotic solvents to give the corresponding exo dioxetane (**19**) (63%) and its cleavage product methyl *cis*-3-formylcyclopentyl ester (**20**) (37%). When deuterated methanol is used as solvent, **19** (58%) and **20** (4%) are still formed, but the *exo*-2-deuteriomethoxy-*endo*-2-methoxy-3-hydroperoxynorbornane (**25**) (38% yield) is produced as well. Photooxygenation in methanol gives no **19**, some **20** (12%), and a new compound, *exo*-(2,2-dimethoxy-3-norbornyl) *exo*-(*exo*-2-hydroxy-*endo*-2-methoxy-3-norbornyl) ether (**28**), which can also be obtained by mixing equimolar parts of **19** and **7** in methanol. The photooxygenation of 1,7,7-trimethyl-2-trimethylsiloxynorborn-2-ene (**9**) and its 7,7-dimethyl derivative (**8**) in carbon tetrachloride give the corresponding *exo*- and *endo*-3-trimethylsilylperoxy-2-norbornanones (**34**/**35** and **36**/**37**) in a ratio of 0.064. The 2-methoxy analogue of **8** (**10**) gives exo (12%) and endo (72%) dioxetanes (**42** and **43**) together with the common cleavage product (**44**) (16%). In summary, the 2-oxy substituents on norbornene stabilize the intermediate ionic peroxides derived from electrophilic attack by singlet oxygen on the double bond so that they are trappable by methanol. However, in the absence of external nucleophile, rearrangement occurs, namely, silatropic shift leading to **11** or **34**–**37**, or closure to dioxetanes (**19**, **42**, and **43**).

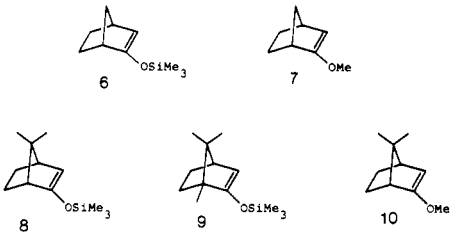
Introduction

Although *N*-oxides are a well-known class of compounds, *O*-oxides or perepoxides appear either not to exist or else they have simply eluded characterization. Nevertheless, they have been invoked as intermediates in the reaction of singlet oxygen with monoolefins.[2] It has been suggested that the latter react with singlet oxygen to give transient perepoxides which subsequently rearrange. When the olefin possesses an allylic carbon–hydrogen bond which is correctly disposed for maximum overlap with the double bond, then the oxide atom of the perepoxide grouping could abstract a hydrogen atom to give the allylically rearranged hydroperoxide (Figure 1a). However, when allylic hydrogen atoms are unavailable then dioxetanes may be formed. These could arise by simple ring expansion; however, they could also be produced directly by [2 + 2] cycloaddition (Figure 1b).

In the case of the photooxygenation of hindered olefins, typified by biadamantylidene, the production of epoxide is now known not to constitute evidence for the intermediacy of a perepoxide.[3] Nonetheless, the latter still remains as a realistic alternative to the concerted process. The crux of the matter is to devise suitable experiments to characterize the putative perepoxides, assuming that they exist. We have recently discovered[4] that norbornene (**1**), originally thought to be inert,[5] reacts slowly with singlet oxygen to give norbornene oxide (**4**) and *cis*-cyclopentane-1,3-dicarboxaldehyde (**5**). In fact, it

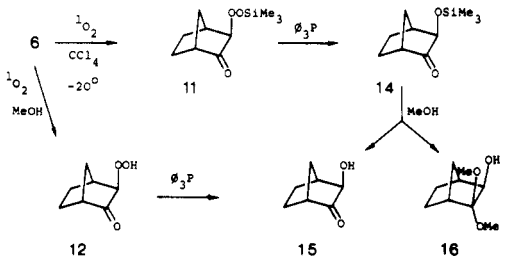


behaves very similarly to the hindered olefins, biadamantylidene[6] and binorbornylidene.[7] Unfortunately, it was not possible to characterize either the norbornane dioxetane **3** or its putative perepoxide precursor **2**. We now report that the 2-trimethylsiloxy (**6**) and 2-methoxy (**7**) derivatives of norbornene react much more rapidly with singlet oxygen. Moreover, clear evidence is obtained for the intermediacy of zwitterionic peroxides. Furthermore, the 2-methoxy group in **7** permits the corresponding dioxetane to be isolated and characterized, both chemically and spectroscopically. In order to obtain information on the nature of the transition states leading to perepoxide or dioxetane, we have synthesized the corresponding 7,7-dimethyl derivatives of the two foregoing norbornene substrates (**8** and **10**) together with the 1,7,7-trimethyl compound **9** and studied their photooxygenation.



Results

Norbornenol Ethers. The siloxy ether **6** in aprotic solvents (e.g., carbon tetrachloride) at −20 °C reacts rapidly and quantitatively with singlet oxygen giving the silylperoxy ketone **11** in 95% yield. Photooxygenation of **6** is equally rapid in protic solvents (e.g., methanol) at −20 °C. Aside from **11** formed in 85% yield, the unstable hydroperoxide **12** is also observed. The



origin of **12** is not **11**, since the latter is recovered unchanged when exposed to the conditions of photooxygenation for a

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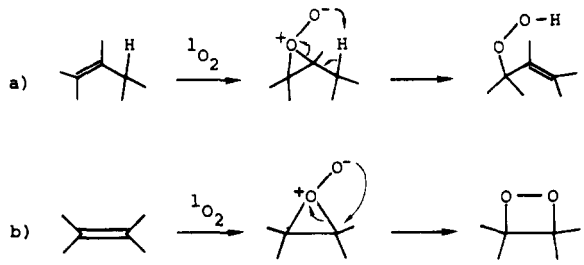
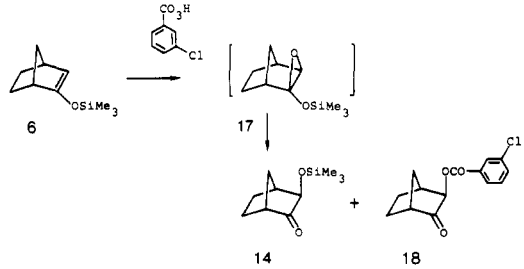


Figure 1. Reaction of singlet oxygen with an olefin to give an allylically rearranged hydroperoxide (a) and a dioxetane (b) via a perepoxide.

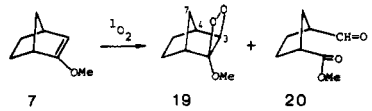
longer period, namely, 30 min of irradiation in perdeuteriomethanol at −20 °C. However, at higher temperatures **11** undergoes slow methanolysis to give **12,** exhibiting a half-life of 32 min at 36 °C.

Several tests demonstrate the involvement of singlet oxygen in these two reactions. Omission of any one of the components, light, oxygen, or sensitizer, stops the reaction. Addition of a radical inhibitor such as di-*tert*-butyl-*p*-cresol[8] has no effect on the rates or product composition regardless of which solvent is used. Dosage with diazobicyclo[2.2.2]octane (Dabco) (5×10^{-3} M) strongly retards the photooxygenation (eightfold) in aprotic solvents.[9] Nevertheless, the silylperoxy ketone **11** is still the only product formed. In protic solvents (CH_3OH, CD_3OD) the same concentration of Dabco slows the oxidation (fivefold), but this time the hydroperoxide **12** also shows up. On raising the concentration of Dabco (5×10^{-2} M), the absorption of oxygen is reduced to 20% of what it was and norbornanone **13** now becomes the main product (Figure 2). In this instance, Dabco is acting as a base, thereby creating methoxide anion (Figure 2a) which, in turn, displaces the trimethylsilyl group in the ether **6** and the ketone **11** to form norbornanone (**13**) and the hydroperoxide **12,** respectively (Figures 2b and 2c). In separate experiments, **6** and **11** in methanol containing Dabco do in fact give **13** and **12.**

The structures of the peroxy compounds **11** and **12** are nicely confirmed by their reduction with triphenylphosphine to the corresponding trimethylsiloxy and hydroxy ketones **14** and **15.** Furthermore, hydrolysis of **14** gives **15.** The treatment of the siloxy ketone **14** with anhydrous methanol for 60 h yields mostly (90%) the ketal **16** together with the keto alcohol **15.** By way of comparison, the siloxy ketone **14** is also obtained in 25% yield by epoxidizing **6** with *m*-chloroperbenzoic acid in methylene chloride. The major product is *exo*-3-*m*-chlorobenzoyloxynorbornan-2-one (**18**), which can be considered as arising from the intermediate epoxide **17,** which also is the origin of **14.**[10]



Owing to the strength of the carbon-oxygen bond, the 2-methoxy derivative **7,** unlike **6,** exhibits a significant change in chemical behavior. Photooxygenation in aprotic solvents occurs readily. Oxygen is absorbed quantitatively and just two products are formed, the dioxetane **19** and its cleavage product



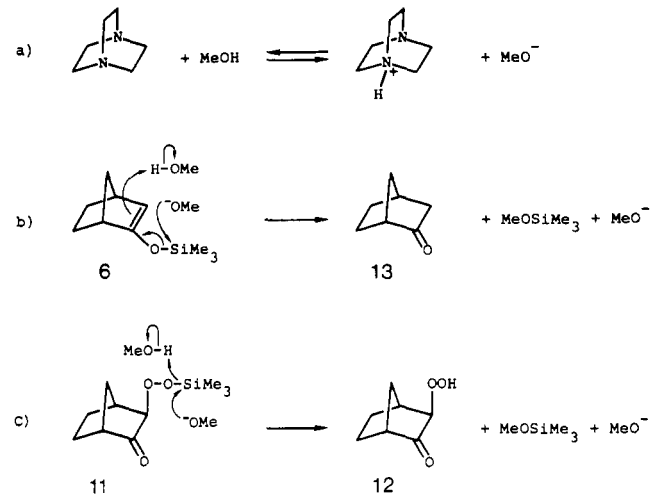
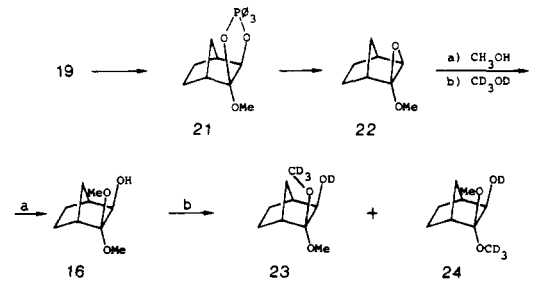


Figure 2. Dabco alters the product composition in methanol in forming methoxide (a), which desilates the ether **6** (b) and its photoproduct **11** (c).

20, in relative yields of 63 and 37%, respectively. Although separation is easy by column chromatography, experiments with **19** are best conducted in solution owing to its explosive nature.

The structure of **19** follows from its NMR spectrum. The C3 proton is strongly deshielded (δ 5.8 ppm), which is typical of trisubstituted dioxetanes.[11] Its endo disposition is amply proved by its long-range coupling with the anti C7 proton which requires a W arrangement of σ bonds.[12] Nonetheless, the vicinal coupling between the endo C3 proton and the bridgehead proton at C4 is not zero (^3J = 1.6 Hz), which can be ascribed to the strain of the dioxygen bridge which reduces the dihedral angle of the C3-H and C4-H bonds from 90 to about 65°.

The structure of **19** is also corroborated by its chemistry. It decomposes in carbon tetrachloride solution to the aldehydic ester **20,** displaying a half-life of 105 min at 36 °C. Reduction of **19** with triphenylphosphine in carbon tetrachloride undoubtedly produces initially the phosphorane **21** and perhaps later the epoxide **22,** although they could not be isolated.[13] Nevertheless, addition of methanol to the solution gives the exo ketal alcohol **16** in quantitative yield. Similar addition of perdeuteriomethanol affords the exo and endo deuteriomethoxy ketals **23** and **24** in a ratio of 66:34.[14]



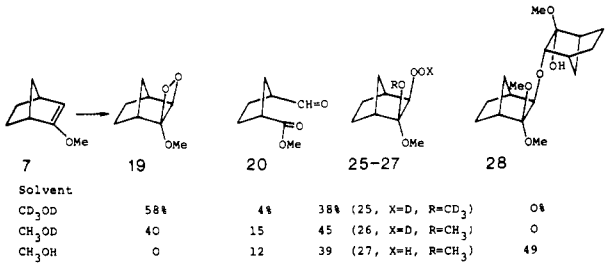
Photooxygenation of **7** in protic solvents, such as CD_3OD and CH_3OD, still gives the dioxetane **19** and the ester **20,** but products incorporating solvent are also formed. The significant products are the hydroperoxy ketals **25, 26,** and **27.** These structures were identified in straightforward fashion by NMR spectroscopy and by their reduction with triphenylphosphine, **26** and **27** both giving the same ketal alcohol **16** and **25** affording **23.**

A dramatic solvent effect is seen with plain methanol. The rate of photooxygenation is slower, with only some 66–70% of the equimolar quantity of oxygen being absorbed (vide infra).

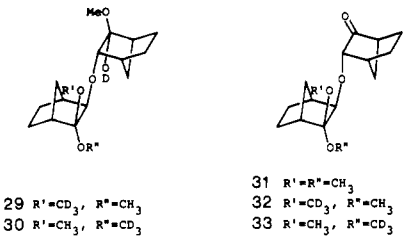
Table I. Rates of Photooxygenation of 2-Methoxynorborn-2-ene (**7**)[a] in Different Solvents

sensitizer[b]	solvent[c]	half-life of **7**, s	lifetime[d] of $^1\Delta_g$ state, μs	solubility[e] of $^1O_2$	rel rate	absorption of oxygen, %
mTPP	CCl_4	192	700	4.892	5.4	100
mTPP	$CHCl_3$	147	60		7.0	100
mTPP	$CDCl_3$	117			8.8	100
MB	CH_3OH	1035	7	16.469	1	70
MB	CH_3OD	450			2.3	100
MB	CD_3OD	220			4.7	100
MB	CH_3CN	240	30		4.3	100

[a] Concentration 0.5 M. [b] Concentration 8.75×10^{-4} M. MB = methylene blue. mTPP = *meso*-tetraphenylporphine. [c] Temperature −20 °C, volume of solution 1 mL. [d] B. Merkel and D. R. Kearns (ref 15). [e] Mol $L^{-1} \times 10^3$, at 298.15 K and 1 atm partial gas pressure (E. Wilhelm and R. Battino, *Chem. Rev.*, **73**, 1 (1973)).



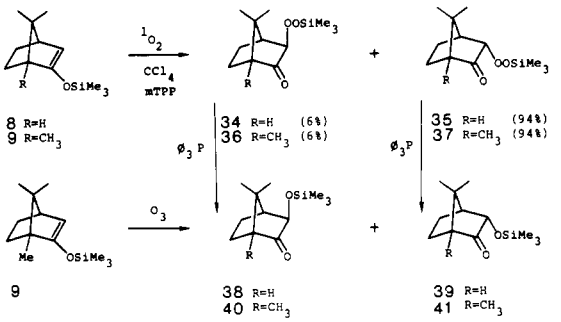
The dioxetane **20** is totally absent, but is replaced by the ether **28** comprising two norbornane residues. The latter arises from the condensation of the dioxetane **19** with the olefin **7** as an independent experiment confirms. The addition of a slight excess of the olefin **7** at 0 °C to a solution of dioxetane **19** in neutral methanol produces the ether **28** as the sole new product. When perdeuteriomethanol is used, the exo and endo deuteriomethoxy derivatives **29** and **30** are obtained in a 66:34 ratio. Traces of *p*-toluenesulfonic acid instantaneously convert the hemiketals **28, 29,** and **30** into their ketones **31, 32,** and **33.**



Supplementary tests characterize the photooxygenation. The dioxetane **19** does not react with methanol, deuterated or not, even under the conditions of photooxygenation. If the irradiation is prolonged, cleavage gives the ester **20.** Furthermore, the ester **20** and the hydroperoxides **25** and **27** are recovered unchanged after irradiation for 1 h in methanol in the presence of oxygen and sensitizer. The olefin **7** is inert to oxygen on irradiation or in the dark. Lastly, 2,6-di-*tert*-butyl-*p*-cresol, a radical inhibitor, has no effect on the photooxygenation.

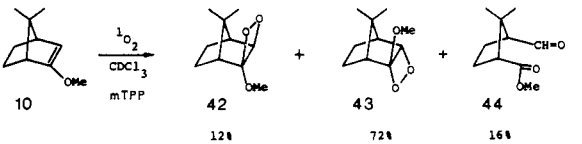
Kinetics. We assume that **28** forms in methanol and not in deuterated solvent, simply because photooxygenation is retarded, thereby permitting the olefin to undergo the secondary reaction with dioxetane. This assumption is borne out by comparing the rates in different solvents. It is seen (Table I) that the rates of photooxygenation of **7** vary little with solvent polarity. The rates of oxygen absorption in acetonitrile and methanol are linear. This means that reaction is zeroth order and that rate is a function of the concentration of sensitizer and of singlet oxygen, viz., its lifetime and its solubility, which depend on the solvent used.[15] In the present case, rates roughly match lifetimes. Moreover, as the rates of photooxygenation attest, singlet oxygen lives longer in a deuterated than in a nondeuterated solvent. Indeed this property is an index for the involvement of singlet oxygen.[16]

7,7-Dimethylnorbornenol Ethers. The photooxygenation of the silyl enol ethers of 7,7-dimethylnorbornanone and camphor (**8** and **9**) in carbon tetrachloride leads in both instances to an exo/endo mixture of silylperoxy ketones (**34/35** and **36/37**).



The exo/endo ratio is the same for both ethers, namely, 0.064. The nonseparable mixture on reduction with triphenylphosphine gives the same ratio of exo and endo silyloxy ketones (**38/39** and **40/41**). By way of contrast, the ozonation[17,18] of **9** in methylene chloride gave the exo and endo ketones (**40** and **41**) in a different ratio, viz., 1.3.

The photooxygenation of the methyl ether **10** in deuteriochloroform gives the exo and endo dioxetanes (**42** and **43**) together with their common cleavage product, the ester **44.** The



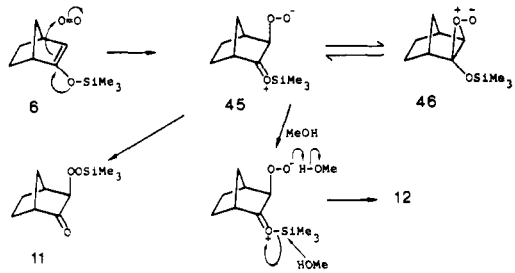
percentage ratios were determined by NMR spectroscopy in view of the thermal instability of the dioxetanes. The stereochemical assignments are based on the magnitude of the vicinal couplings between the protons attached to the C3 and C4 atoms (^3J = 1.5 Hz for **42** and 5.5 Hz for **43**). The half-lives of **42** and **43** are 240 and 300 s at 27 °C.

Discussion

The photooxygenation of the norbornenol ethers, **6** and **7,** in aprotic solvents is similar to that reported for enamines,[19] thioenol ethers,[20] and enol ethers generally.[21] Although 1,2-dioxetanes can form easily and stereospecifically, often they are not isolable and their existence has been assumed from the products of their expected cleavage.[22] In fact, norbornene offers just such an example.[4] Nevertheless, owing to a fortunate choice of substituent, the methoxy group in **7,** we are able to report the first case of the isolation of norbornane dioxetanes, which, in spite of their presumed ring strain, are relatively stable in solution.

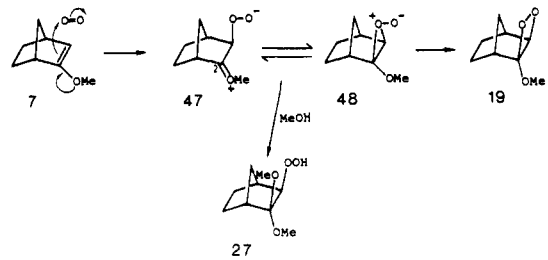
The siloxy substituent in **6** also confers another type of reactivity on the norbornene moiety. The reaction of singlet oxygen with silyl enol ethers is expected to follow an ene-type

mechanism in which the silicon atom mimics the behavior of an allylic hydrogen atom.[23] Allylic rearrangement should occur giving α-ketosilyl peroxide. Indeed, this is precisely what happens, at least formally, with **6** in aprotic solvents. However, the result in methanol indicates that the reaction actually proceeds stepwise. The first event is the formation of the polar peroxide, either in its open (**45**) or cyclic form (**46**). In the



absence of external nucleophile, the dioxetane does not form and instead the charges cancel by transfer of the silyl grouping to the terminal peroxide atom (**45** → **11**). When methanol is present, however, it competes with the rearrangement by attacking and removing the trimethylsilyl group to give the α-hydroperoxy ketone (**12**).

The methoxy group also stabilizes the polar perepoxide, and once again it forms in either its open (**47**) or closed (**48**) form by the attachment of singlet oxygen to the exo face of **7.** Closure of **47** or rearrangement of **48** gives the dioxetane **19.** When

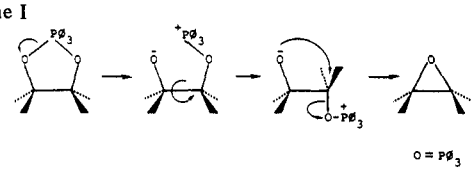


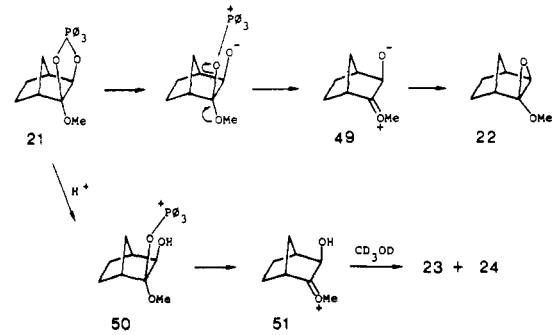
methanol has the chance to intervene, it attacks the C2 atom in **47** or **48,** it is difficult to say which, to give hydroperoxy ketal **27.**

There is some slight indication that the perepoxide **48** may be the favored form, simply because deuteriomethanol, when used as solvent, gives only the exo-deuterated hydroperoxy ketal **25,** no trace of the endo-deuterated hydroxy ketal **24** being found on reduction with triphenylphosphine. This deduction is based on the exo regioselectivity of opening of the exo epoxide of 2-phenylnorbornene and the assumption that perepoxide and epoxide behave the same.[24]

There is doubt about the intermediacy of the epoxide **22** which formally derives from the phosphorane **21.** Normally, epoxides are produced from phosphoranes by rupture of the phosphorus–oxygen bond followed by rotation of the resulting polar fragments about the carbon–carbon bond so that the required trans antiparallel conformation is attained[25] (Scheme I). Of course, this maneuver is impossible in the norbornane skeleton. Consequently, another mechanism must operate. A most likely one is the loss of phosphine oxide to give the zwitterion **49** which could still close to epoxide **22.** However, the results in deuteriomethanol indicate that an open species, such as **49** or its protonated analogue **51** deriving from the protonated phosphorane **50,** is being captured rather than **22,** as both exo and endo deuterioperoxy ketals (**23** and **24**) are formed in a ratio of 66/34.

Scheme I





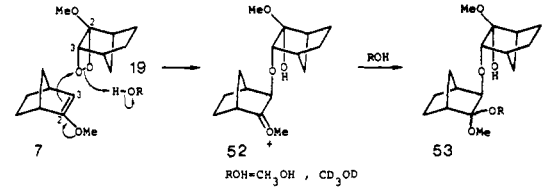
Further corroborative information on the 2-norbornylmethoxonium cation is forthcoming from the reaction of the norbornane dioxetane **19** with 2-methoxynorbornene **7** in methanol. The ether product (**53**) is best explained by an ionic mechanism as added radical inhibitor has no effect. The coupling is undoubtedly initiated by nucleophilic attack of the olefin **7** at its C3 atom on the C3 oxygen atom of the dioxetane **19** breaking the oxygen–oxygen bond to acquire a proton from solvent. The resulting methoxonium cation **52** then further undergoes attack by solvent on its exo and endo sides in an 66:34 ratio as revealed by the product composition when deuteriomethanol is used (Scheme II).

The remarkably high regioselectivity of the process must be due to the almost exclusive exo selectivity of addition of electrophiles to norbornenes in general,[26] combined with the greater electrophilic character of the oxygen substituent on C3 over that on C2 of the dioxetane **19.** The reason why the condensation occurs at all during photooxygenation is purely a question of relative rates. In deuterated solvents, the longer lifetime of singlet oxygen which speeds the oxidation means that the norbornene **7** disappears too fast for any parasitic reaction to occur. Although nucleophilic displacements on dioxetane oxygen atoms are already known,[11] in any event the present unusual result is yet another in the growing list of new reactions of dioxetanes.[27]

It is worth remarking that as the two partners, the norbornene **7** and the dioxetane **19** are chiral and are both present as racemates, namely, A, $\overline{A}$ and B, $\overline{B}$, respectively, the regioselective condensation would lead in principle to two diastereoisomeric pairs of products, A$\overline{B}$ and $\overline{A}$B, together with their corresponding enantiomers, $\overline{A\overline{B}}$ and AB. However, a careful scrutiny of the NMR spectra, in particular the ^{13}C spectrum, of the ketone **31** reveals just a single set of 16 resonances, all of which have been attributed with fair certainty to both portions of the molecule (see Experimental Section). This means that either only one of the two possible diastereomers is formed, it is impossible to say which, or that both are there and that the insulating effect of the ether linkage is such that the chirality of one fragment negligibly influences the other.

The placing of the geminal dimethyl grouping at C7 in the enol ethers **8** and **10** affects the chemical outcome in one respect only in that the hitherto energetically unattainable transition state for endo attack now becomes the main reaction course. The exo/endo product ratios for the reaction of singlet oxygen to the silyl (**8**) and methyl ethers (**10**) together with the carbon analogue, 2,7,7-trimethylnorbornene[36] (**54**), are 0.064, 0.25, and 0.19, respectively. The similarity of the last two ratios is significant since **54** affords hydroperoxides, whereas the methyl ether gives dioxetanes. In the case of dioxetane for-

Scheme II



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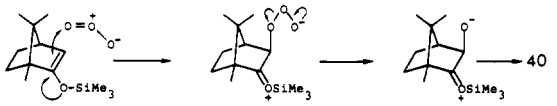
mation, little steric distinction can be made between transition states for perepoxidation or the suprafacial antarafacial arrangement of reactants in the [2 + 2] cycloaddition. Whatever the nature of the rate-determining steps, they appear to be subject to the same steric strictures. These ratios are nevertheless indicative that a tight cyclic transition state is operating.[28] In view of the evidence of the solvent trapping experiments, which points to the prior creation of polar peroxides from **8** and **10,** it is reasonable to assume that the same mechanism holds for the hydroperoxidation of **54.**

An interesting exo/endo ratio is the value of 1.3 found for the ozonation of the silyl ethers derived from camphor (**9**). It has already been suggested that a molecule of ozone approaches **9** in much the same way as it would to a hindered olefin such as biadamantylidene.[18] Thus, the first step is the formation of the zwitterion **55,** which loses a molecule of oxygen to give the new zwitterion **56** which promptly undergoes



9 55 56

silatropic shift to yield product **40.** At first sight, the steric exigencies of ozone and singlet oxygen ought to be of the same order, yet the exo/endo ratio is essentially different. It is also noteworthy that singlet oxygen is at its sterically most discriminating toward the silyl ethers **8** and **9.** Ozone, on the other hand, acts as if it were smaller than singlet oxygen. The logical conclusion is that ozone adds essentially to one end of the double bond where congestion is smaller, while singlet oxygen aims for the sterically more crowded midpoint of the double bond to form perepoxide.

Conclusion

The chief findings can be enumerated as follows. Firstly, the products incorporating solvent can only be adequately explained in terms of a primary zwitterionic intermediate which can be depicted as an open peroxide or preferably as a perepoxide. In the absence of interception by solvent, closure subsequently occurs to dioxetane.

Our results lend experimental support to the theoretical predictions of Dewar,[29] Fueno, and Fukui.[30] For the related example of dihydropyran, calculations[29] show that a zwitterionic peroxide can form which evolves either to give dioxetane, perepoxide, or hydroperoxide. We have demonstrated that such norbornane-type zwitterionic species are in fact chemically discrete and have long enough lifetimes to be captured by solvent before they collapse to dioxetanes which once formed are sufficiently stable to be physically and chemically characterized.[31,33]

Experimental Section

All melting points and boiling points are uncorrected. IR spectra were taken on a Perkin-Elmer Model 257 spectrophotometer. ^{1}H NMR spectra were obtained in the solvent specified on Varian Model T60-A and XL-100 instruments equipped with a variable temperature probe. Temperatures were calibrated with methanol. ^{1}H chemical shifts are reported in parts per million downfield from tetramethylsilane. Coupling constants (J) are expressed in hertz. Signal multiplicity is indicated as follows: s = singlet, d = doublet, t = triplet, m = multiplet higher than first order. Numbering of hydrogen atoms is according to the carbon skeleton; abbreviations, s (syn), a (anti), x (exo), n (endo). Mass spectra were obtained on a Varian SM 1 spectrometer; the most abundant fragments are reported with relative intensities as percent of base peak intensity. Analyses were performed by Dr. K. Eder (Geneva). Precoated silica gel 60 F-254 (Merck) plates were employed for TLC analysis with appropriate hexane-ether mixtures as eluents. Silica gel 70-230 mesh (Merck) and Florisil 100-200 mesh (Fluka AG) were used for column chromatography. Deuterated solvents ($CDCl_3$, CH_3OD, CD_3CN, CD_3OD, Ciba-Geigy) were used as received.

We thank J. P. Saulnier and U. Burger of our department for determining the NMR spectra and A. Buchs and F. Kloeti (Department of Physical Chemistry) for measuring the mass spectra.

2-Methoxynorborn-2-ene (7). A mixture of 2,2′-dimethylnorbornane[35] (37.2 g, 0.238 mol) and *p*-toluenesulfonic acid (2 g) was placed in a 100-mL flask equipped with a 50-cm heating jacket fractionating column and distillation head. The flask was gradually heated to 230 °C. The distillate was collected in a cooled 100-mL flask containing 0.5 g of potassium carbonate. The fraction (35 g) contained methanol and a 3/1 mixture of olefin and ketal, as shown by NMR analysis.

Careful vacuum refractionation using the same apparatus yielded 2-methoxynorborn-2-ene (**7**) as a colorless liquid (15.7 g, 53.2%), bp 73 °C (60 Torr) (lit. 77-79 °C) (75 Torr). The second fraction consisted of pure starting ketal (14.6 g, 39.3%), bp 100°C (60 Torr).

NMR (CCl_4, 60 MHz): 0.9-1.8 (6 H, complex m, H-C(5_{xn}, 6_{xn}, 7_{sa})), 2.63 and 2.80 (2 H, 2 m, bridgehead H), 3.43 (3 H, s, OCH_3), 4.43 ppm (1 H, d, $J_{3,4}$ = 3 Hz, H-C(3)). IR (CCl_4): 2880 m, 2840 m, 1615 s, 1240 s, 1020 s cm^{-1}. MS: *m/e* 124 (M^+) (32), 96 (100), 81 (14), 63 (13).

Photooxygenation of 2-Methoxynorborn-2-ene (7) in Aprotic Solvents. A solution of **7** (363 mg, 2.93 mmol) in dry acetonitrile (5 mL) containing methylene blue (8.75×10^{-4} M) was irradiated under oxygen at −20 °C in the standard manner.[36] The half reaction time was 10 min, and after 30 min oxygen absorption ceased (63 mL at 730 Torr); no sensitizer bleaching occurred. NMR analysis of the crude mixture indicated total consumption of the starting material and formation of just two new compounds: dioxetane **19** (63%) and aldehyde **20** (37%). The blue solution was concentrated under vacuum at 0 °C (not to dryness, otherwise dioxetane explodes) and then chromatographed on Florisil (20 g) at −20 °C using a double jacket column. Elution with pentane gave yellow fractions which were collected at −78 °C; iodometric titration of the combined dioxetane-containing fractions indicated that the actual yield of **19** was 56%. Further elution with 20% ether in pentane gave ester **20** as a colorless liquid (154 mg, 33.7%).

***endo*-2-Methoxy-*exo*-3,4-dioxatricyclo[4.2.1.0^{2,5}]nonane (19).** NMR ($CDCl_3$, 100 MHz): 1.01 (1 H, dm, $J_{7a,7s}$ = 10 Hz, H-C(7s)), 1.35-1.75 (5 H, complex m, H-C(5xn, 6xn, 7a)), 2.22 (1 H, m, H-C(1)), 2.56 (1 H, m, H-C(4)), 3.8 (3 H, s, OCH_3), 5.08 ppm (1 H, t, $J_{3n,4} = J_{3n,7a}$ = 1.6 Hz).

***cis*-1-Carboxaldehyde-3-carbomethoxycyclopentane (20).** NMR ($CDCl_3$, 100 MHz): 1.95 (4 H, large complex m, H-C(4,5)), 2.16 (2 H, t, $J_{2,1} = J_{2,3}$ = 8 Hz, H-C(2)), 2.85 (2 H, wide m, H-C(1,3)), 3.7 (3 H, s, OCH_3), 9.66 ppm (1 H, d, $J_{1,7}$ = 2 Hz, HC=O). IR (CCl_4): 2960 s, 2890 m, 2820 m, 2730 m, 1740 vs, 1450 m, 1380 m, 1225 s, 1185 s cm^{-1}. MS: *m/e* no peak at 156 ($C_8H_{12}O_3$), 128 (27), 125 (22), 96 (16), 87 (100), 79 (15), 67 (41), 59 (11), 55 (29), 41 (26), 39 (12).

Photooxygenation, when carried out at 0 °C, did not alter the quantity of **20.** The molecular weight of **19** was not determined, but its spectral and chemical properties (see below) are consistent with its formulation as a 1,2-dioxetane. The dioxetane was normally obtained in pentane by chromatography. Solution of **19** in other solvents can be effected easily by adding higher boiling solvents (chloroform, carbon tetrachloride, methanol, benzene, etc.) to the pentane solution and then evaporating the pentane under reduced pressure at 0 °C. More higher boiling solvent is added to ensure that the solution is free of pentane. For safety reasons it is advisable to use solutions less than 0.5 M. Iodometric analyses were carried out using the method of Knight and Swern.[37]

Thermal Decomposition of 19. A 0.2 M solution of **19** in nondegassed carbon tetrachloride containing some benzene as internal standards was transferred to an NMR tube which was sealed and placed in the probe of a 60-MHz spectrometer where the temperature was constant at 36 °C. The relative percentages of **19** and **20** were monitored by comparing the area of the signal due to the methoxy hydrogens of **19** (δ 3.8 and 3.7) with that of the benzene signal. The half-life of **19** was found to be 105 min. Conversion to the ester **20** was complete after 3 h, as judged by the NMR signals.

Stability of 19 in the Presence of Methanol. A. A solution of a known

concentration of dioxetane **19** in methanol was prepared. At 0 °C, no decomposition occurred after several hours.

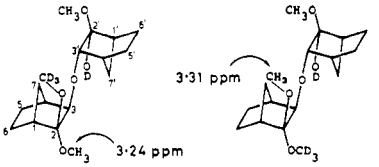
B. The same solution was photooxidized (in the presence of methylene blue) at −20 °C. After 2 h, TLC analysis indicated only the presence of the ester **20** and dioxetane **19.** No trace of hydroperoxide **39** could be detected.

C. To a solution of dioxetane **19** in methanol (0.64 mmol) was added under stirring an excess of 2-methoxynorborn-2-ene (**7,** 99 mg, 0.8 mmol). After a few minutes at 0 °C, the yellow color of the solution faded. TLC analysis indicated the presence of a new major compound (**28**) which was isolated pure by column chromatography (Florisil/ether–pentane). Fractions containing **28** were mixed and concentrated and the resulting paste was recrystallized from hexane at −30 °C to give white crystals of **28** (143 mg, 72%), mp 72–78 °C. The ketal **28** was easily converted to the corresponding ketone **31** in CCl_4 solution by adding a trace of *p*-toluenesulfonic acid, and stirring at room temperature for a few minutes.

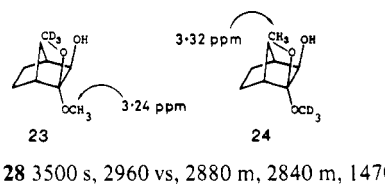
D. The above experiment was also carried out in CD_3OD. The corresponding exo and endo deuteriomethoxy compounds **29** and **30** were obtained (hemiketals) which could be converted to the ketones **32** and **33.** The identity of compounds **28–33** was established from their spectral properties.

1. Hemiketal Form (28, 29, 30). NMR ($CDCl_3$, 100 MHz): **28** 1.1–2.1 (12 H, complex m, CH_2(5,5′, 6,6′, 7,7′)), 2.2–2.5 (4 H, m, H-C(1,1′, 4,4′)), 3.15 (1 H, d, J = 2.4 Hz, H-C(3′n)), 3.31 (masked) (1 H, d, H-C(3n)), 3.24 (3 H, s, OCH_3), 3.31 (3 H, s, OCH_3), 3.4 (3 H, s, OCH_3), 4.56 ppm (1 H, exchanges with D_2O, OH).

The spectrum of the nonresolved mixture (**29 + 30**) was superimposable on the spectrum of **28,** but the singlet at 3.4 ppm was absent. Total integration of the signals at 3.24 and 3.31 ppm was only 3 H. These two peaks were respectively in a ratio 66/34 and assignments of structures **29** (66%) and **30** (34%) were made by comparison with the alcohols **23** and **24** (see below).



29 30



23 24

IR (CCl_4): **28** 3500 s, 2960 vs, 2880 m, 2840 m, 1470 m, 1450 m, 1370 m, 1340 m, 1320 m, 1190 s, 1130 vs, 1060 vs, 980 s, 920 m, 890 m cm^{-1}. No carbonyl band.

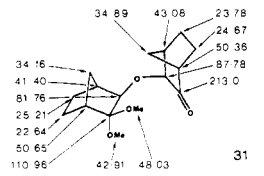
29 + 30 superimposable on above spectrum. Additional bands at 2250 m, 2225 m, 2130 w, 2080 m cm^{-1}.

MS: *m/e* **28** no peak at 312 ($C_{17}H_{28}O_5$), 281 (4), 280 (5), 249 (6), 171 (100), 156 (5), 141 (6), 139 (9), 124 (33), 111 (8), 101 (9), 96 (55), 81 (20), 79 (19).

29 + 30 no peak at 316 ($C_{17}H_{24}O_5D_4$), 283 (0.8), 280 (0.9), 251 (1), 249 (2), 174 (100), 159 (3), 139 (3), 127 (14), 124 (22), 104 (9), 99 (20), 96 (31), 81 (16), 79 (16).

Anal. Calcd for $C_{17}H_{28}O_5$: C, 65.36; H, 9.03. Found: C, 65.43; H, 9.14.

2. Ketonic Forms (31, 32, 33). The ^{13}C NMR spectrum of **31** was determined in C_6D_6 solution with respect to tetramethylsilane as internal reference at 25.2 MHz (see below). The attribution of the resonances, which is tentative, was made by exploiting the ^{13}C–H off-resonance multiplicities and by comparison with the shifts of norbornane, norbornanone, and their derivatives.



31

NMR ($CDCl_3$, 100 MHz): **31** 0.9–2.1 (11 H, complex m, CH(5,5′, 6,6′, 7a, 7s, 7′a)), 2.2 and 2.3 (3 H, 2 m, H-C(1,4,7′s)), 2.58 (2 H, m, H-C(1′,4′)), 3.24 (3 H, s, OCH_3 endo), 3.34 (s, 3 H, OCH_3 exo), 3.30 (1 H, d, J = 2.4 Hz, H-C(3′n)), 3.46 ppm (1 H, d, J = 2.4 Hz, H-C(3n)).

32 + 33 same as **31,** but integration sum for singlets at 3.24 and 3.34 was only 3 H. Area for 3.24/area for 3.34: 66/34.

IR (CCl_4): **31** 2970 vs, 2890 m, 2850 m, 1750 vs, 1460 m, 1340 m, 1330 m, 1190 m, 1145 s, 1130 vs, 1090 vs, 1060 vs, 980 m, 950 m cm^{-1}, no alcohol band.

32 + 33 superimposable on above spectrum; additional bands at 2250 m, 2225 m, 2130 w, 2080 m cm^{-1}.

MS: *m/e* **31** no peak at 280 ($C_{16}H_{24}O_4$), 249 (1.5), 234 (1.5), 171 (100), 165 (8), 101 (8), 81 (20), 79 (23).

32 + 33 no peak at 283 ($C_{16}H_{21}O_4D_3$), 177 (36), 174 (100), 171 (54), 165 (24), 81 (50), 79 (50).

3-Hydroxy-2,2-dimethoxynorbornane (16). To a solution of dioxetane **19** in CCl_4 (2 mL, 0.968 mmol) was added dry methanol (2 mL). Triphenylphosphine (253 mg, 0.968 mmol) was added in small portions to the cooled solution (0 °C). After 10 min of stirring, the solution was concentrated and the residue triturated with cold pentane from which triphenylphosphine oxide precipitated. After filtration, the residue was chromatographed on a small column (Florisil). Elution with pentane/ether (10%) gave pure alcohol **16** (151 mg, 91%) as a colorless liquid.

NMR ($CDCl_3$, 100 MHz): 1.04–1.90 (6 H, complex m, H_{5xn}, H_{6xn}, H_{7a} (1.15, dm) (+0.2), H_{7s} (1.79, dt) (+0.4)), 2.1 (1 H, m, H-C(4) (+0.38)), 2.4 (1 H, m, H-C(1) (+0.34)), 3.24 (3 H, s, OCH_3 endo (+0.24)), 3.32 (3 H, s, OCH_3 exo (+0.38)), 3.24 (1 H, 2 s, exchanged with D_2O, OH), and 3.48 ppm (1 H, 2 d, $J_{3n,7a}$ = 2.5 Hz (+0.63), characterized as an AB system, $J_{3n,OH}$ = 6 Hz).

IR (CCl_4): 3540 vs, 2950 vs, 2870 m, 2830 m, 1455 s, 1385 s, 1238 s, 1180 s, 1150 vs, 1090 vs, 1050 vs, 1040 s, 1000 s, 920 m, 890 w cm^{-1}.

MS: *m/e* 172 (M^+, $C_9H_{16}O_3$) (79), 144 (22), 141 (34), 115 (66), 101 (53), 88 (100), 81 (39), 79 (29), 75 (31).

When CD_3OD was used instead of methanol, a mixture of the exo and endo deuteriomethoxy compounds **23** and **24** was obtained in a 66/34 ratio. The correct attribution of structures and percentages was achieved by NMR analysis using shift reagent. Positive figures in brackets are the observed deshieldings when shift reagent was added ($Eu(fod)_3$, 2 mg) (vide supra).

IR (CCl_4): as for **16** except extra bands at 2245 m, 2220 m, 2130 w, 2080 m cm^{-1}.

MS: *m/e* 175 (M^+, $C_9D_3H_{13}O_3$) (62), 147 (15), 144 (16), 118 (63), 104 (48), 91 (100), 81 (30), 79 (26), 78 (30).

Photooxygenation of 7 in Methanol. Freshly distilled **7** (1 g, 8.06 mmol) in 10 mL of dry methanol (containing methylene blue, 8.75 × 10^{-4} M) was irradiated at −20 °C under oxygen. After 140 min, the absorption ceased and only 115 mL of oxygen was consumed (66%). The dye remained unbleached. The blue solution was concentrated in vacuo (0 °C, 0.5 Torr) to 2 mL and stored at −30 °C. After 2 days, colorless crystals deposited and were quickly filtered at subambient temperatures. Pure crystalline **28** was obtained by recrystallization from hexane (0.345 g, 13.7%). The mother liquors were mixed and chromatographed at −20 °C in a jacketed chromatography column containing 50 g of Florisil. Elution with pentane (containing increasing concentrations of diethyl ether from 1 to 10%) gave more **28** but as its ketone **31** (0.358 g, 15.8%), the hydroperoxide **20** (23%, in solution, titrated by iodometry), and the ester **20** (0.088 g, 7%).

2,2-Dimethoxy-3-*exo*-hydroperoxynorbornane (27). NMR ($CDCl_3$, 100 MHz): 1.16 (1 H, dm, $J_{7a,7s}$ = 10 Hz, H-C(7a)), 1.2–1.75 (4 H, complex m, H-C(5_{xn}, 6_{xn})), 1.9 (1 H, dm, $J_{7a,7s}$ = 10 Hz, H-C(7s)), 2.2 (1 H, m, H-C(1)), 2.52 (1 H, m, H-C(4)), 3.34 (3 H, s, OCH_3 endo), 3.36 (3 H, s, OCH_3 exo), 3.94 (1 H, d, $J_{3n,7a}$ = 2 Hz, H-C(3n)), 9.65 ppm (1 H, wide peak, OOH).

Reduction of Hydroperoxide 27. A solution of **27** in carbon tetrachloride (0.26 mmol) was reduced by triphenylphosphine in ether (68 mg, 0.26 mmol) at 0 °C with stirring. TLC analysis indicated alcohol **16** as the only detectable product. Filtration on a short column and elution with 20% ether–pentane gave pure **16** (43 mg, 95%), whose NMR spectrum in $CDCl_3$ is identical with that of an authentic sample.

Photooxygenation of 7 in Deuteriomethanol (CD_3OD). Photooxygenation of **7** (300 mg, 2.42 mmol) in 99.5% CD_3OD (5 mL)/methylene blue (8.75 × 10^{-4} M) was performed at −20 °C. The reaction was completed in 10 min, 51.5 mL (724 Torr) of oxygen being absorbed (97.7%). The crude mixture consisted of three compounds as revealed by TLC and low-temperature NMR analysis (−20 °C): the

dioxetane **19** (58%), the ester **20** (4%), and the hydroperoxide **25** (38%). No trace of its isomeric endo hydroperoxide could be detected. The relative percentages were derived from NMR signal integrations of the singlets at 3.80 (3 H, OCH_3, **19**), 3.65 (3 H, OCH_3, **20**), and 3.26 ppm (3 H, OCH_3, **25**). The crude mixture was diluted with 20 mL of carbon tetrachloride and concentrated at low temperature (0 °C, 0.1 Torr). At least 2 mL of solution was maintained as both **19** and **25** decomposed easily when dry. The solution was transferred to a jacketed chromatography column containing 20 g of Florisil at −20 °C. The dioxetane **19** was eluted with pentane and the hydroperoxide **25** with 1% ether in pentane. The fractions containing **19** (yellow) and **25** (colorless) were concentrated to 50 mL, then diluted with the same volume of CCl_4 and concentrated (0 °C, 0.1 Torr) to remove pentane. The carbon tetrachloride solutions were found to contain pure **19** and **25** as revealed by TLC and NMR. Iodometric titration indicated that the actual yields of **19** and **25** were respectively 52 and 31%. Further elution of the column with 5% ether–pentane removed the ester **20** (4%).

***exo*-2-Trideuteroxy-*endo*-2-methoxy-*exo*-3-hydroperoxynorbornane (25).** NMR ($CDCl_3$, 100 MHz): spectrum superimposable on that of pure hydroperoxide **27**, with the exception of the singlet at 3.36 ppm (OCH_3 exo) which is absent.

Reduction of Hydroperoxide 25. Using the same procedure as for hydroperoxide **27**, alcohol **23** was obtained (93%), whose NMR spectrum in $CDCl_3$ was identical with that of alcohol **16** with the exception of the singlet at 3.32 ppm (3 H, exo methoxy).

2-Trimethylsilyloxynorborn-2-ene (6) was prepared according to the general method of House.[38] To a solution of diisopropylamine (12.4 g, 0.12 mol) in dry THF (100 mL) at −70 °C was slowly added by syringe a solution of *n*-butyllithium (0.115 mol) in hexane. 2-Norbornanone (11 g, 0.1 mol) in dry THF (135 mL) was then added dropwise. After stirring for 45 min at −70 °C, the solution was treated with freshly distilled HMPT (15 mL) and trimethylsilyl chloride (11.93 g, 0.11 mol) in pentane (20 mL). On warming to room temperature, the mixture was diluted with pentane (250 mL) and washed rapidly in succession with portions of cold aqueous 2% HCl and aqueous $NaHCO_3$. The resulting solution was dried and evaporated. Vacuum distillation of the residual oil gave **6** (12.15 g, 66.7%) as a colorless liquid which was judged to be pure by NMR spectroscopy and GLC (Apiezon 20%/Chromosorb W, 200 °C) analysis (bp 77 °C (20 Torr)).

NMR ($CDCl_3$, 100 MHz): 0.18 (9 H, s, $OSi(CH_3)_3$), 0.95–1.8 (6 H, complex multiplet, H-C(5x, n, 6x, n, 7a, s)), 2.56 (1 H, broad s, H-C(1)), 2.76 (1 H, H-C(4)), 4.7 ppm (1 H, d, $J_{3n,4}$ = 3.2 Hz, H-C(3)).

IR (CCl_4): 1612 vs, 1455 m, 1340 s, 1260 s, 1235 s, 935 s, 910 s, 850 vs cm^{-1}.

MS: *m/e* 182 (M^+) (21), 167 (15), 154 (100), 73 (85).

***exo*-3-Trimethylsilylperoxy-2-norbornanone (11).** The irradiation in the presence of oxygen of 2.69 g (14.7 mmol) of **6** in 25 mL of CCl_4 containing 20 mg of mTPP as sensitizer was complete in less than 30 min. The volume of oxygen consumed was 321 mL (100%) at −20 °C (725 Torr). The rate appears to be zeroth order indicating that **6** is a very reactive acceptor as the rate-determining step is not the reaction of singlet oxygen with **6**, but the rate of formation of singlet oxygen which is dependent on the sensitizer concentration, light intensity, and oxygen concentration. The photooxygenated mixture was concentrated under vacuum and then distillated to give **11**, bp 51 °C (0.025 Torr) (2.99 g, 94.5%).

NMR (CCl_4, 100 MHz): 0.16 (9 H, s, O-Si$(CH_3)_3$), 1.3–2.0 (5 H, complex m, H-C(5x, n, 6x, n, 7a)), 2.1 (1 H, 2 t, $J_{7a,7s}$ = 10, $J_{7a,1}$ = $J_{7a,4}$ = 1.25 Hz, H-C(7s)), 2.46 (1 H, m, H-C(4)), 2.83 (1 H, m, H-C(1)), 3.72 ppm (1 H, d, $J_{2,7a}$ = 3.2, $J_{2n,1}$ = 0 Hz, H-C(2n)).

IR (CCl_4): 1775 vs, 1460 w, 1255 s, 1220 m, 1113 m, 1080 m, 880 vs, 850 vs cm^{-1}.

MS: *m/e* 199 (M − 15) (10), 186 (3), 171 (5), 169 (3), 149 (6), 75 (100).

***exo*-3-Hydroperoxy-2-norbornanone (12).** The reaction of deuteriomethanol (CD_3OD, 0.5 mL) with pure **11** (50 mg) was followed by NMR at 36 °C, monitoring the singlets (9 H) at δ 0.18* (**11**) and 0.09* ppm ($CD_3OSi(CH_3)_3$). The half reaction time was 32 min and the solvolysis was complete in 1 h. In fact, the hydroperoxide **12** slowly decomposed at this temperature. Attempts to isolate pure **12** failed. (*δ are referred to the typical quintet for CD_3OD at 3.30 ppm.)

Photooxygenation of 6 in Methanol. A solution of **6** (39 mg, 0.21 mmol) in 99.5% CD_3OD containing either methylene blue or rose bengal as sensitizer (8.75×10^{-4} M) was photooxygenated at temperatures ranging from −5 to −78 °C. In all cases, 1 equiv of oxygen was taken up (4.6 mL at −20 °C, 730 Torr). Low-temperature NMR analysis (−20 °C) of the crude mixture revealed *exo*-3-trimethylsilylperoxy-2-norbornanone (**11**, 85%) and *exo*-3-hydroperoxy-2-norbornanone (**12**, 15%). These compounds were identified by their endo C(3) hydrogen signal: **11**, doublet at δ 3.89 (J = 3 Hz) and **12**, doublet at δ 3.83 (J = 3 Hz). Further irradiation of the crude photooxygenated solution at −20 °C for 2 h gave an identical NMR spectrum. Furthermore, a pure sample of **11** (55 mg, 0.3 mmol) in 0.5 mL of CD_3OD containing methylene blue did not absorb oxygen on irradiation at −20 °C. NMR analysis after 30 min irradiation indicated no change.

***exo*-3-Trimethylsilyloxy-2-norbornanone (14).** Triphenylphosphine (2.88 g, 10.98 mmol) was added in small portions to a stirred, cooled (0 °C) solution of **11** (2.35 g, 10.98 mmol) in carbon tetrachloride. The temperature was allowed to warm to room temperature. After 20 min, the solvent was evaporated and the residue triturated with cold pentane. Triphenylphosphine oxide was filtered off and washed carefully with cold pentane. All the pentane fractions were concentrated under vacuum and the residue distilled to give pure 3-trimethylsilyloxy-2-norbornanone (**14**) as a colorless liquid (2.04 g, 94%), bp 57 °C (0.6 Torr).

NMR ($CDCl_3$, 60 MHz): 0.18 (9 H, s, $OSi(CH_3)_3$), 1.1–2.2 (6 H, complex m, H-C(5_{xn}, 6_{xn}, 7_{sa})), 2.5 (2 H, m, H-C(1.4)), 3.43 (1 H, d, $J_{3n,7a}$ = 3 Hz, H-C(3n)).

IR (CCl_4): 2960 vs, 2880 m, 1760 vs, 1255 s, 1125 vs, 1100 s, 1085 m, 1035 m, 895 s, 875 s, 850 s cm^{-1}.

MS: *m/e* 198 (M^+) (10), 183 (19), 170 (14), 129 (100), 73 (51).

***exo*-3-Hydroxy-2-norbornanone (15).** Silyl ether **14** (1 g, 5.05 mmol) was refluxed overnight in a 10% water–methanol solution. As much solvent was distilled as possible and the residue was dissolved in ether, dried over $MgSO_4$, and filtered on a short Florisil column.

NMR ($CDCl_3$, 100 MHz): 1.10–1.95 (5 H, complex m, H-C(5_{xn}, 6_{xn}, 7_a)), 2.20 (1 H, 2 m (first part of an AB system), $J_{7a,7s}$ = 10 Hz, H-C(7s)), 2.56 (2 H, m, H-C(1.4)), 3.50 (1 H, d, $J_{3n,7a}$ = 3 Hz, H-C(3n)).

IR (CCl_4): 3580 m, 3430 vs, 1760 vs, 1130 s, 1090 s, 950 m, 920 m cm^{-1}.

MS: *m/e* 126 (M^+) (17), 98 (11), 57 (100).

When silyl ether **14** (0.2 g, 1.01 mmol) was refluxed during 60 h in dry methanol (5 mL), and methanol distilled at atmospheric pressure, the major product was 2,2-dimethoxy-*exo*-3-hydroxynorbornane (**16**, 90%) with only a small amount of the expected alcohol **15** (10%). (Relative percentages were derived from GLC analysis/FFAP 5% Chromosorb W realized on the crude mixture.) Both compounds can be isolated by preparative chromatography (Florisil); elution with a pentane–ether mixture (10/1) gave pure **16** (0.137 g, 79%) and **15** (7.6 mg, 6%), whose spectral data were identified with those of authentic samples. The ketal **16** (0.1 g, 0.58 mmol) can be converted to the corresponding ketone **15** by reflux in water for 5 min followed by distillation at atmospheric pressure until the solution becomes limpid. Extraction with ether, drying, and evaporation of solvent gave pure **15** (0.066 g, 91%).

Epoxidation of 2-Trimethylsilyloxy-2-norbornene (6). Solid *m*-chloroperbenzoic acid (436 mg, 2.19 mmol) was added portionwise to a stirred mixture of **6** (400 mg, 2.19 mmol) in methylene chloride (25 mL) and 0.5 M aqueous sodium bicarbonate (8 mL, pH 8.3). Stirring was continued at 0 °C for 2 h (the consumption of peracid was tested with starch–iodide paper) and the phases were separated. The organic layer was washed successively with 1 N sodium hydroxide and water and dried (Na_2SO_4). Methylene chloride was evaporated. The residue was recrystallized from a pentane–ether mixture. Pure **18** was filtered (317 mg, 55%), mp 75 °C, and the mother liquors were chromatographed on a short column (Florisil, pentane–ether) to yield **14** as a colorless liquid (80 mg, 18.5%).

18: NMR (CCl_4, 60 MHz): 1.0–2.3 (6 H, complex m, H-C(5_{xn}, 6_{xn}, 7_{as})), 2.63 (2 H, m, H-C(1.4)), 4.76 (1 H, d, J = 3 Hz, H-C(3n)), 7.3–7.8 ppm (4 H, complex m, aromatic H).

IR (CCl_4): 1780 vs, 1745 vs, 1320 m, 1310 m, 1270 vs, 1140 s, 1095 m, 1090 m, 745 s, 690 m cm^{-1}.

MS: *m/e* 264 (M^+) (21), 266 (M^+ + 2) (7), 141 (33.8), 139 (100), 125 (67).

7,7-Dimethylnorbornanone. A solution of 1-bromo-7,7-dimethylnorbornanone[39] (10 g, 46 mmol) in dry ether was added dropwise to a solution of lithium (3.8 g) in liquid ammonia (100 mL). After stirring overnight, excess lithium was carefully destroyed with NH_4Cl and finally with an ether–methanol solution. The mixture was dissolved in water and extracted with ether, washed with water, and fi-

nally dried over $MgSO_4$. Solvent evaporation yielded 7 g of a crude, yellow paste. This crude mixture was dissolved in acetone (20 mL) and oxidized by dropwise addition of a 8 N chromic acid solution maintaining the reaction temperature at 20 °C. About 15 mL of oxidant solution was required; oxidation was complete when the orange color persisted. The mixture was stirred overnight at room temperature. Solid sodium bisulfite was added in portions to reduce the excess oxidant. The dark green chromic sulfate sludge was extracted ten times with ether, and the ether extracts were washed with aqueous $NaHCO_3$ solution and water and dried. After evaporation, the white solid residue was sublimed (80 °C, 12 Torr) to give pure ketone (5.1 g, 80%), mp 113-113.5 °C.

NMR (CCl_4): 1.05 (6 H, s, CH_3), 1.3-2.6 ppm (8 H, complex m).

IR (CCl_4): 1765 vs cm^{-1}.

7,7-Dimethylnorbornanonetrimethylsilyl enol ether (8) was prepared from 7,7-dimethylnorbornanone according to the general procedure[38] in 80% yield, bp 91-92 °C (17 Torr).

NMR (CCl_4, 60 MHz): 0.2 (9 H, s, $OSi(CH_3)_3$), 0.95-2.3 (6 H, complex m, C-H), 0.93 and 1.1 (3 H each, 2 s, 2 CH_3), 4.56 ppm (1 H, d, J = 3.5 Hz, H-C(3)).

IR (CCl_4): 3080 w, 1630 s, 1340 s, 1150 s, 1020 m, 930 s, 905 s, 855 vs cm^{-1}.

Camphortrimethylsilyl enol ether (9) was prepared from camphor according to the general procedure[38] in 86% yield, bp 81-82 °C (10 Torr) (lit.[40] 84-88 °C (12 Torr)).

NMR ($CDCl_3$, 100 MHz): 0.2 (9 H, s, $OSi(CH_3)_3$), 0.74 (3 H, s, CH_3), 0.90 (6 H, s, CH_3), 0.8-2.0 (4 H, complex m, CH_2), 2.22 (1 H, t, J = 4 Hz, H-C(4)), 4.66 ppm (1 H, d, J = 3.5 Hz, H-C(3)).

IR (neat): 3090 w, 1630 s, 1340 s, 1265 s, 1150 s, 1015 m, 930 s, 905 s, 855 vs cm^{-1}.

MS: *m/e* 224 M^+ (15), 209 (26), 196 (100), 181 (40), 73 (87).

Photooxygenation of Camphortrimethylsilyl Enol Ether (9). The irradiation in the presence of oxygen of 1.84 g (8.22 mmol) of **9** in 30 mL of carbon tetrachloride containing 22 mg of mTPP as sensitizer was performed at −5 °C under 728 Torr. The reaction was complete in 3 h (half reaction time 47 min) with an oxygen uptake of 188 mL. The mixture was concentrated and distilled under vacuum to give a pale yellow oil (1.81 g, 85%), bp 60-63 °C (0.005 Torr), which consisted of **37** and **36** in a 94/6 ratio.

NMR ($CDCl_3$, 100 MHz): **37** 0.22 (9 H, s, $OSi(CH_3)_3$), 0.88 (3 H, s, CH_3), 0.9 (3 H, s, CH_3), 1.0 (3 H, s, CH_3), 1.0-2.0 (4 H, complex m, H-C(5,6)), 2.48 (1 H, m, H-C(4)), 4.6 ppm (1 H, d, $J_{3x,4}$ = 4.5 Hz, H-C(3x)).

NMR of **36** was the same except 4.17 ppm (1 H, s, H-C(3n)).

IR (neat): 1770 vs, 1260 s, 895 s, 880 s, 855 s cm^{-1}.

***endo*- and *exo*-3-Trimethylsilyloxy-1,7,7-trimethyl-2-norbornanone (41 and 40).** A trimethylsilylperoxy mixture of **36** and **37** (0.5 g, 2.23 mmol) in ether (30 mL) was reduced with excess triphenylphosphine (0.65 g, 2.5 mmol) at 0 °C. The temperature was allowed to warm to 20 °C. The solvent was evaporated and the residue triturated with cold pentane. Triphenylphosphine oxide was filtered off and washed carefully with cold pentane. Pentane fractions were concentrated under vacuum and the residue was distilled to give a pure mixture of **40** and **41** (56-62 °C (0.05 Torr)).

NMR ($CDCl_3$, 100 MHz): of **41:** 0.14 (9 H, s, $OSi(CH_3)_3$), 0.84 (3 H, s, CH_3), 0.88 (3 H, s, CH_3), 0.96 (s, 3 H, CH_3), 1.2-2.2 (5 H, complex m, H-C(4,5,6)), 4.1 ppm (1 H, d, $J_{3x,4}$ = 5 Hz, H-C(3x)).

NMR of **40** was the same except at 3.64 ppm (1 H, s, H-C(3n)).

IR (CCl_4): 1765 vs, 1260 s, 1140 s, 1090 w, 1015 m, 910 s, 850 s cm^{-1}.

MS: *m/e* 240 (M^+) (3), 225 (3), 169 (4), 129 (100), 122 (25), 73 (44).

Photooxygenation of 7,7-Dimethyl-2-norbornanonetrimethylsilyl Enol Ether (8). Compound **8** (0.6 g, 2.85 mmol) was photooxygenated in carbon tetrachloride (9 mL)/mTPP at 10 °C. Quantitative oxygen absorption (69 mL) was complete in 40 min. Evaporation of solvent and distillation of the residue in a bubble tube gave a pure mixture of **35** and **34** in a 94/6 ratio (40-60 °C, 0.0001 Torr) as a yellow liquid (0.606 g, 88%).

NMR (CCl_4, 60 MHz): 0.1 (9 H, s, $Si(CH_3)_3$), 1.00 (6 H, s, 2 CH_3), 1.0-2.5 (6 H, complex m, H-C(1,4,5,6)), 3.86 ppm (1 H, s, H-C(3n)), relative integration 6%, characterized **34;** 4.40 ppm (1 H, d, H-C(3x), $J_{3x,4}$ = 4.5 Hz, relative integration 94%) characterized **35.**

IR (CCl_4): 1765 vs, 1260 s, 1140 s, 1090 w, 1015 m, 910 s, 850 s cm^{-1}.

The mixture of **34** and **35** (0.2 g, 0.83 mmol) reduced in ether by 220 mg of triphenylphosphine gave a 94/6 mixture of **39** and **38** after purification by column chromatography (Florisil/pentane-ether, 1%) (0.17 g, 90%).

NMR (CCl_4, 60 MHz): 0.13 (9 H, s, $OSi(CH_3)_3$), 1.03 (6 H, s, 2 CH_3), 1-2.1 (6 H, unresolved m, H-C(1,4,5,6)), 3.46 ppm (1 H, s, H-C(3n), relative integration 6%) characterized **38;** 4.05 ppm (1 H, d, $J_{3x,4}$ = 4.5 Hz, H-C(3x), relative integration 94%) characterized **39.**

IR (CCl_4): 1765 vs, 1260 s, 1150 s, 1015 m, 910 s, 850 s cm^{-1}.

Ozonation of Camphortrimethylsilyl Enol Ether (9). Ozone from a generator was passed into a −78 °C solution of **9** (2 g, 8.92 mmol) in methylene chloride (50 mL). After the ozone was passed for 1 h, the blue solution was concentrated under vacuum. The yellow residue was distilled to give 1.63 g (76%) of a 56/44 ratio of **40** and **41,** bp 56-62 °C (0.05 Torr). The exo/endo ratio was determined by NMR analysis of the singlet (3.64 ppm) of **40** and of the doublet (4.1 ppm) of **41.**

Photooxygenation of Camphortrimethylsilyl Enol Ether (9) in CD_3OD. A solution of enol ether **9** (120 mg, 0.53 mmol) in CD_3OD (1 mL) containing methylene blue was photooxygenated at −20 °C. After 4 h the reaction was complete (12 mL oxygen uptake). NMR analysis of the crude mixture (recorded at −20 °C) indicated an exo/endo mixture of **36** and **37.** No trace of α-hydroxyperoxy ketone could be detected. Furthermore, the NMR spectrum was unchanged after 2 h warming of the NMR sample at 30 °C.

7,7-Dimethyl-2,2-dimethoxynorbornane. In a 50-mL flask were placed 7,7-dimethylnorbornanone (6 g, 43.5 mmol), dry methanol (20 mL), *p*-toluenesulfonic acid (pTSA, 0.1 g), and trimethyl orthoformate (6.91 g, 65.2 mmol). After 2 h reflux under nitrogen, the dark solution was cooled, a little potassium *tert*-butoxide was added to neutralize the acid, and the solvent was removed. Vacuum distillation gave pure product (6.2 g, 78%), bp 80 °C (12 Torr).

IR (neat): 2840 s, 1340 s, 1330 w, 1125 s, 1080 s, 1060 s, 900 m, 850 m cm^{-1}.

NMR ($CDCl_3$, 60 MHz): 0.95 + 1.15 (3 H each, 2 s, 2 CH_3), 1.0-2.4 (8 H, m, H-C(1,3,4,5,6)), 3.16 ppm (6 H, 2 s, 2 OCH_3).

7,7-Dimethyl-2-methoxynorborn-2-ene (10). A mixture of the above compound (6.2 g, 34 mmol) and pTSA (25 mg) was placed in a 25-mL flask equipped with a 30-cm Vigreux column and distillation head and gradually heated to 230 °C. The distillate was collected in a cooled flask containing 0.2 g of K_2CO_3. Careful vacuum refractionation using the same apparatus yielded **10** as a colorless liquid (2.05 g, 40%), bp 72 °C (22 Torr).

IR (neat): 3100 w, 2860 m, 1630 s, 1030 s, 790 s, 740 s cm^{-1}.

NMR ($CDCl_3$, 60 MHz): 0.83 + 1.05 (3 H each, 2 s, 2 CH_3), 1.6-2.4 (6 H, m, H-C(1,4,5,6)), 3.46 (3 H, s, OCH_3), 4.45 ppm (1 H, d, $J_{3,4}$ = 3 Hz, H-C(3)).

MS: *m/e* 152 (M^+) (42), 137 (96), 124 (73), 109 (100).

Photooxygenation of 7,7-Dimethyl-2-methoxynorborn-2-ene (10). A solution of **10** (170 mg, 1.12 mmol) in $CDCl_3$ (2 mL) containing *meso*-tetraphenylporphine was irradiated under oxygen at −20 °C. The half reaction time was 15 min and after 45 min the oxygen uptake ceased (22 mL under 725 Torr, 90%). NMR analysis of the crude mixture (−14 °C NMR) indicated a little **10** and three new compounds: the exo dioxetane **42** (12%), the endo dioxetane **43** (72%), and the aldehyde **44** (16%). No attempts were made to separate the mixture, but all components were easily identified by NMR spectroscopy.[41]

***endo*-2-Methoxy-*exo*-3,4-dioxa-9,9-dimethyltricyclo[4.2.1.$0^{2,5}$]-nonane (42).** NMR ($CDCl_3$, −14 °C, 100 MHz): 0.83 (3 H, s, CH_3) 1.03 (3 H, s, CH_3), 1.5-2.5 (6 H, m, H-C(1,4,5,6)), 3.82 (3 H, s, OCH_3), 5.2 ppm (1 H, d, $J_{3n,4}$ = 1.5 Hz, H-C(3n)). Half-life time: 240 s/27 °C (followed by NMR).

***exo*-2-Methoxy-*endo*-3,4-dioxa-9,9-dimethyltricyclo[4.2.1.$0^{2,5}$]-nonane (43).** NMR ($CDCl_3$, −14 °C, 100 MHz): 0.88 (3 H, s, CH_3), 1.08 (3 H, s, CH_3), 1.5-2.5 (6 H, m, H-C(1,4,5,6)), 3.78 (3 H, s, OCH_3), 5.68 (1 H, d, $J_{3x,4}$ = 5.5 Hz, H-C(3x)). Half-life time: 300 s/27 °C (followed by NMR).

***cis*-1-Carboxaldehyde-3-carbomethoxy-2,2-dimethylcyclopentane (44).** A solution of **10** (0.317 g, 2 mmol) in $CDCl_3$-mTPP (3 mL) was photooxygenated at −20 °C. Oxygen uptake was 40 mL (88%). The solution was allowed to stand at 30 °C for 0.5 h. Solvent was evaporated and the residue distilled in a bubble-tube apparatus giving a pale yellow oil, **44** (0.272 g, 74%), oven temperature 50 °C, pressure 0.1

Torr.

IR (neat): 2740 w, 1750 vs, 1180 s cm^{-1}.

NMR ($CDCl_3$, 60 MHz): 0.83 (3 H, s, CH_3), 1.33 (3 H, s, CH_3), 1.7–2.9 (6 H, m, H-C(1,2,3,4)), 3.66 (3 H, s, $COOCH_3$), 9.71 (1 H, d, J = 2 Hz, CHO).

MS: *m/e* 184 (M^+) (absent), 169 (6), 153 (19), 152 (16), 138 (29), 124 (32), 115 (13), 114 (26), 95 (70), 87 (100).

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Stereoselective Conversion of Keto Groups into Methyl Vinyl Quaternary Carbon Centers†,[1]

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Abstract: In the presence of bis(triphenylphosphine)nickel dichloride both *trans*- (**1b**) and *cis*-4-*tert*-butyl-1-vinylcyclohexanol (**1c**) reacted with methylmagnesium bromide affording *r*-4-*tert*-butyl-*t*-1-methyl-1-vinylcyclohexane (**4a**), 1-*n*-propylidene-4-*tert*-butylcyclohexane (**3b**), and *r*-4-*tert*-butyl-*c*-1-methyl-1-vinylcyclohexane (**5a**) in a 19:5:1 ratio. This reaction was applied to vinylcarbinols prepared from four manool-derived 13-hydrophenanthrones (**8, 9a, 10a,** and 7-dehydro-**10a**) for diterpene synthesis. In the cases leading to terminal olefins 8,14-dihydropimaradiene (**14b**), 7,8-dihydroisopimaradiene (**15b**), and $\Delta^{7(8)}$-pimaradiene (**17b**) were produced. The first olefin was transformed into the tetracarbocyclic diterpene hibaene (**23**) in five high-yielding steps.

Recent studies of the reaction of Grignard reagents with allyl alcohols have shown that in the presence of bis(triphenylphosphine)nickel dichloride catalyst the hydroxy group of the alcohols is replaced by hydrogen or by alkyl or aryl groups depending on the nature of the organometallic reagents.[4] Grignard reagents containing β hydrogens yield hydrogenolysis

† Dedicated to Professor Edgar Lederer on the occasion of his 70th birthday.

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