[7] *P. Margaretha & K. Schaffner*, Helv. *56*, 2884 (1973).
[8] *D. Bellus, D. R. Kearns & K. Schaffner*, Helv. *52*, 971 (1969).
[9] *E. M. Kosower & T. S. Sorensen*, J. org. Chemistry *28*, 687 (1963).
[10] *S. Gelin & R. Gelin*, Bull. Soc. chim. Fr. *1968*, 288.
[11] *C. S. Rouvier*, Thesis, Univ. d'Aix-Marseille, p. 40 (1968).
[12] *R. Gelin, S. Gelin & R. Dolmazon*, Tetrahedron Letters *1970*, 3657.

246. Reaction of Singlet Oxygen with 2-Methylnorborn-2-ene, 2-Methylidenenorbornane, and their 7,7-Dimethyl Derivatives. The Transition State Geometry for Hydroperoxidation.

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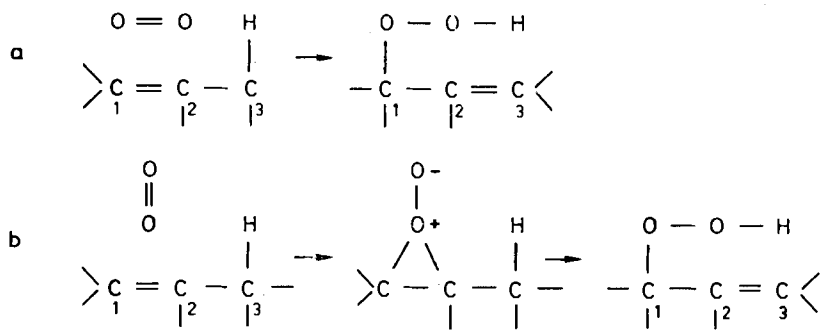
Summary. The dye-sensitized photo-oxygenation of 2-methylnorborn-2-ene (**3**), 2-methylidenenorbornane (**4**) and their 7,7-dimethyl derivatives (**5** and **6**) has been studied. In all cases allylically rearranged hydroperoxides were formed, except that **4** also gave a little norbornanone (presumably from the dioxetane) and **5** gave some *endo*-3,7,7-trimethylnorbornan-2-one as a secondary photoproduct. It was found that the *exo*/*endo* attack ratios by singlet oxygen on **3** and **5** are 66 and 0.19. By exploiting the C (3) monodeuteriated derivatives, **4** and **6** showed ratios of 28 and 0.67.

Rates of reactivity of the olefins **3** and **4** were compared to methylidenecyclopentane, 1-methylcyclopentene and 1-methylcyclohexene as monocyclic standards. Additionally, comparative rates between the 7,7-dimethyl olefins and their parents were measured. When further comparison was made of the rate ratios partitioned for *exo* and *endo* attack, it was seen that oxygen experienced a 500- to 1000-fold rate retardation on approach to the *endo* side of **3** compared to that for its monocyclic analogue. *Exo* rates between the parent norbornene **3** and its 7,7-dimethyl derivative **5** showed a 250-fold decrease. Although four times smaller than the difference reported for epoxidation, the evidence clearly pointed to a one-step cyclic process as the rate determining step for photo-oxygenation. The steric evidence, taken with the low values found for the intermolecular isotope effects of 1.14 ± 0.01 and 1.02 ± 0.01 observed for *exo* and *endo*-3-deuterio-2-methylidenenorbornanes, permits the deduction that the transition state is largely dipolar. In the early stages of the addition bonding between one end of the oxygen molecule and the terminal vinyl carbon is advanced. At the same time positive charge is dispersed by hyperconjugation between the central carbon atom and the allylic carbon-hydrogen bond. At a later stage the anionic oxygen atom abstracts the loosened allylic hydrogen atom to create the hydroperoxide. No evidence for the formation of a discrete perepoxide intermediate was obtained.

Introduction. – The dye-sensitized photo-oxygenation of mono-olefins can follow two distinct courses [1]. The reagent, singlet oxygen, can either attack the double bond directly to give a dioxetane, or the allylic C–H bond can be involved as well, when an allylically rearranged hydroperoxide is formed. Which of the two courses is actually followed for a particular olefin depends mainly on the nature of the allylic part. Dioxetanes are usually formed from strained or electron-rich double bonds [2]. However, the production of hydroperoxides requires not only the presence of an allylic C–H bond, but that it effectively conjugates with the adjacent double bond [3].

On the basis of the experimental evidence obtained so far, the formation of allylic hydroperoxides appears to fit two mechanistic hypotheses. The first of these is the so-called *cis* mechanism in which singlet oxygen approaches the allylic hydrogen and the terminal vinyl carbon atoms to simultaneously break and form C–H and C–O bonds respectively (*Scheme 1 a*) [3]. The second hypothesis is that singlet oxygen behaves as an electrophile, and that it forms an intermediate and fugitive perepoxide which collapses uniquely by abstraction of a contiguous hydrogen atom to give the allylic hydroperoxide (*Scheme 1 b*) [4]. Unfortunately, no case has been made un-

Scheme 1

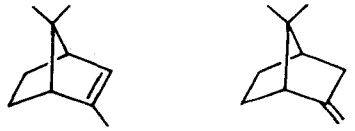


Formation of hydroperoxide by singlet oxygen;
a) one step cyclic process, b) Two step cyclic process

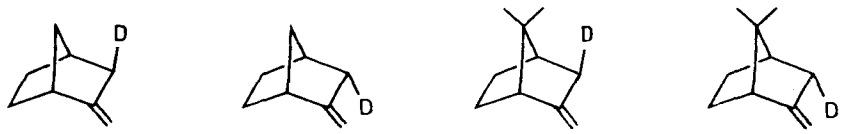
ambiguously as yet for either of these mechanisms. We therefore thought that the distinction between them, they are after all one-step and two-step processes, could be made by designing experiments which exploit the reaction probing properties of norbornene (**1**) and its 7,7-dimethyl derivative (**2**) [5]. It has been reported that those cyclic additions of **1** involving three or four members and which proceed fast on the *exo* face, are not only strongly retarded when olefin **2** is used, but that *endo* products are formed predominantly. Two-step processes show much less differentiation in rate or product composition [6]. In view of this promising possibility of differentiation, we decided to investigate the photo-oxygenation of 2-methylnorborn-2-ene (**3**) and 2-methylidenenorbornane (**4**), together with their 7,7-dimethyl derivatives (**5** and **6**). Additional information, especially that on kinetic isotope effects, was sought by examining the *exo* and *endo* C(3) deuterio derivatives of 2-methylidenenorbornane (**7** and **8**) and its 7,7-dimethyl derivative (**9** and **10**).

Results. – *Syntheses of substrates and reference compounds.* – 2-Methylnorborn-2-ene (**3**) was obtained in abundance by the *Diels-Alder* reaction of ethylene with methylcyclopentadiene dimer [7]. 2-Methylidenenorbornane (**4**) was prepared by standard procedures [8]. The syntheses of the 3-deuterio-2-methylidenenorbornanes (**7** and **8**) required a mild method for the introduction of the methylidene grouping. Controlled deuteriation of norbornanone (**11**) furnished the *exo*-3-deuterio and 3-dideuterionorbornan-2-ones (**12** and **13**) [9]. Careful alkaline hydrolysis of the 3,3-

1 2 3 4



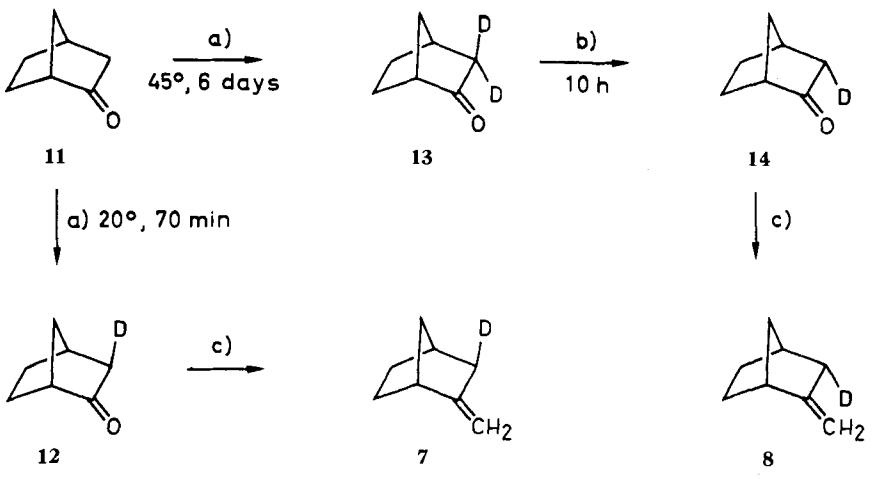
5 6



7 8 9 10

dideuterio derivative (**13**) selectively leached out the *exo*-deuterium substituent to give the *endo*-3-deuterionorbornan-2-one (**14**). Conversion of the ketones (**12** and **14**) to their methylidene derivatives **7** and **8** was achieved by the procedure of *Coates* (*Scheme 2*) [10]. Under these conditions no deuterium exchange was observed.

Scheme 2

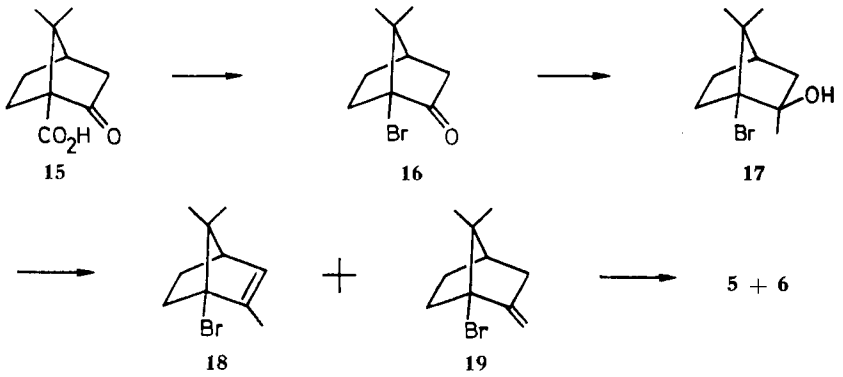


Preparation of 3-Deuterio-2-Methylidenenorbornanes
a) NaOD–D_2O, b) NaOH–H_2O, c) ϕSCH_2Li, Ac_2O, Li–NH_3

The syntheses of the 7,7-dimethyl olefins **5** and **6** in a pure state presented difficulties. Conventional methods always yielded mixtures of at least four to six isomers [11]. Finally a mixture of **5** and **6** (with minor amounts of other isomers)

was obtained by modifying an existing method [12] and by recourse to a new procedure (*Scheme 3*). *Hunsdiecker* reaction of the readily available ketopinic acid **15** [13] afforded the bromoketone **16** [14]. Methylation with *Grignard* reagent gave the tertiary alcohol **17** which on dehydration gave the bridgehead bromo-derivatives **18** and **19** [15]. Reductive dehalogenation with lithium in liquid ammonia furnished the desired olefins **5** and **6**. Separation was achieved by chromatography over a silvernitrate-on-silicagelcolumn (*Scheme 3*).

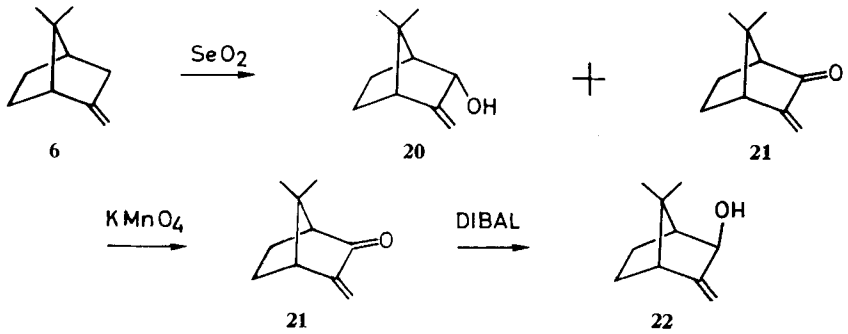
Scheme 3



15 **16** **17** **18** **19**

The *endo* and *exo* C(3) alcohols of 7,7-dimethyl-2-methylidenenorbornane (**20** and **22**) were needed as reference compounds. Their preparation was readily accomplished by allylic oxidation of **6** with selenium dioxide. The desired *endo* alcohol **22** was obtained together with some of the unsaturated ketone **21**. Oxidation was completed with potassium permanganate. Reduction of **21** with di-*t*-butoxyaluminium hydride gave the *exo* alcohol **22** (*Scheme 4*).

Scheme 4

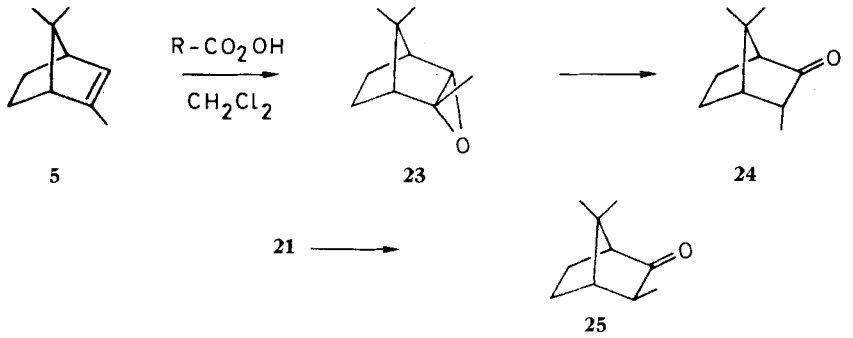


6 **20** **21** **21** **22**

The preparation of *endo*-3-methyl-7,7-dimethylnorbornan-2-one (**24**) (also needed as a reference) was obtained directly by epoxidation of **5** with *m*-chloroperbenzoic acid. Presumably, the intermediate *endo* epoxide **23** underwent an acid induced stereospecific *exo* hydride shift from C(3) to C(2) [16]. In any event the structure of

24 was corroborated by comparison with its *exo* isomer **25** which was obtained from the enone **21** by catalytic hydrogenation (*Scheme 5*).

Scheme 5



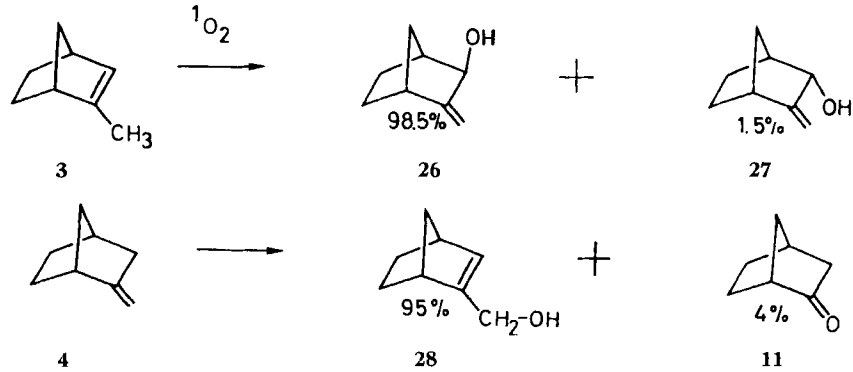
5 23 24 25

The *exo* C(3) deuterio derivatives of the 7,7-dimethyl structure **9** was prepared by the procedure used for the parent structure. Attempts to prepare the *endo* epimer **10** gave mixtures of both.

Photo-oxygenations. – Olefins were photo-oxygenated in acetonitrile at 5–10° for 5–20 min., using two 500 W tungsten filament slide-projector lamps as light source in the presence of methylene blue. The primary photo-products were immediately reduced with sodium borohydride [17] or triphenylphosphine [18] and analysed by GLC. The amount of conversion was similar for all olefins (80–85%).

C_8-olefins. – 2-Methylnorborn-2-ene (**3**) gave only two products *exo*-2-methylidene-norbornan-3-ol (**26**) and its *endo* isomer (**27**), in proportions of 98.5% and 1.5%. This result was reproducible and corresponds to an *exo*/*endo* ratio of 66 for attack by singlet oxygen. Similar reaction of 2-methylidenenorbornane (**4**) for a time sufficiently short so that only about half of the reactant was consumed (~5 min.), gave as products 2-hydroxymethylnorborn-2-ene (**28**) and norbornan-2-one (**11**) in proportions of 95% and 4% respectively (*Scheme 6*). With longer reaction times the first formed hydroperoxide underwent further photo-oxygenation, but at a rate some five times slower than the initial oxygenation.

Scheme 6

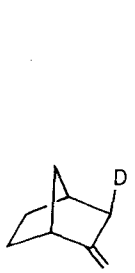


3 26 27

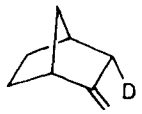
4 28 11

Obviously, oxygen attacks both faces of the double bond of 2-methylidene-norbornane (**4**); in order to ascertain the *exo/endo* ratio, the deuterium content of the photo-products obtained from the *exo* and *endo* 3-deuteriated analogues **7** and **8** was measured by mass spectrometry. The isotope distribution in the resulting pair of 2-hydroxymethylnorborn-2-enes (**29** and **30**) indicates an *exo/endo* attack of ~28 (*Scheme 7*).

Scheme 7



7



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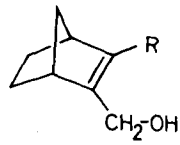


	29 R = H	**30** R = D	Exo/endo Attack ratio by $^1O_2$
7	96.6 %	3.4 %	28.4
8	3.5 %	96.5 %	27.6

Rates I. – In a second series of photo-oxygenations, the intermolecular kinetic isotope effects were measured for 2-methylidenenorbornane (**4**). Internal competition experiments were carried out with 50:50 mixtures of **4** and the *exo* and *endo* 3-deuterio analogues (**7** and **8**) respectively. Four measurements were made for each deuteriated olefin. For the *exo*-3-deuterio-2-methylidenenorbornane (**7**) k_H/k_D was found to be 1.14 ± 0.01; a much smaller value was found for the *endo*-3-deuterio derivative (**8**), viz. 1.02 ± 0.01.

To get a measure of the reactivity of the bridged bicyclic olefins competition experiments were carried out with their monocyclic analogues in order to determine relative rates. The encyclic and ectocyclic[1]) olefins **3** and **4** were compared with methylcyclopentene and cyclohexene (**31** and **32**) and methylidenecyclopentane (**33**) as standards (Table 1). Apart from the relative total rates, a further analysis into partial rates was made; these reflect attack simply from the *exo* and *endo* sides or additionally take into account attack in the ectoclinal mode[2]).

C_{10}-olefins. – Photo-oxygenation of 2,7,7-trimethylnorborn-2-ene (**5**) gave a mixture of three products, the composition of which varied with time. The major products (~95%) were identified as *exo* and *endo* 7,7-dimethyl-2-methylidene-norbornan-3-ols (**22** and **20**). The ratio of the *exo* and *endo* alcohols was estimated by

[1]) Encyclic and ectocyclic olefins possess unsaturated linkages inside and outside the rings respectively. This terminology is chosen to avoid possible confusion between the old terms endocyclic and exocyclic and the prefixes *endo* and *exo*.

[2]) For an explanation of the terms, ectoclinal, etc., see [30].

Table 1. *Relative reactivities of C_8 bridged bicyclic and monocyclic olefin acceptors towards singlet oxygen*

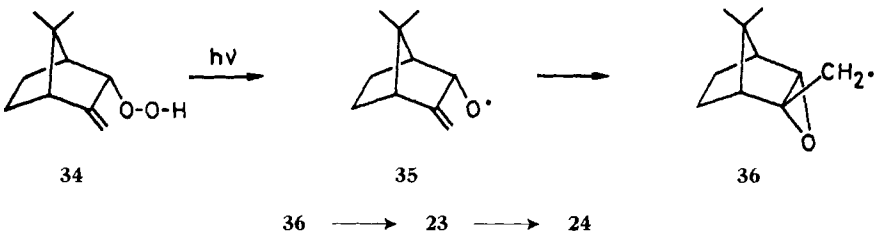
Acceptor		Total Relative Rate[a]	Partial Rates *exo*	*endo*
3		3.2	3.15	0.05
31		115.0[b]	57.7[c] 24.7[d]	57.5[c] 24.7[d]
32		9.5[b]	4.5[c] 2.0[d]	4.5[c] 2.0[d]
4		1.0	0.97	0.03
33		2.3	1.2[c] 0.6[d]	1.2[c] 0.6[d]

[a] Calculated from acceptor disappearance (error ± 20%). [b] From ref. [1]. [c] For attack on the double bond alone. [d] For the ectoclinal mode.

NMR.-spectroscopy, as it proved impossible to separate them by GLC. Mixtures of various compositions of **22** and **20** were prepared independently and their NMR.-spectra were matched with those of the experimental mixtures. The *exo*/*endo* ratio for oxygen attack, as indicated by the primary photo-products, was found to be invariably 0.19.

The third product was recognized as *endo*-3,7,7-trimethylnorbornan-2-one (**24**). However, it turned out to be a secondary photo-product as its concentration increased with irradiation time. The possible origin of **24** was thought to be the primary hydroperoxide (**34**) which on photolysis gives the oxy radical (**35**). Cyclization and capture of a hydrogen atom (**35** → **36** → **23**) leads to the *endo* epoxide and the usual rearrangement (**23** → **24**) (*Scheme 8*)[3]. The fact that methylene blue was completely

Scheme 8



34 **35** **36**

36 → **23** → **24**

[3] Related radical reactions have already been observed [19] [20].

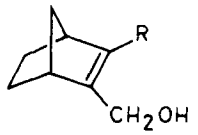
bleached after 20% conversion of **5** is evidence enough for the production of stray UV. light from the projector bulb. Moreover, continued irradiation gave increasing amounts of **24** (Table 2). Significantly the hydroperoxides gave no ketone in the absence of light when kept at 25°; but on heating in benzene the ketone **24** was formed.

Table 2. *Continued irradiation of reaction mixture obtained from* **2** *after complete bleaching of Methylene Blue*

Irradiation Time	% **20** + **22**	% **24**
0 h.	98.7%	1.3%
9	89.5	10.5
24	78.5	21.5
48	66.0	34.0

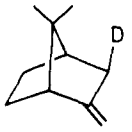
Photo-oxygenation of 7,7-dimethyl-2-methylidenenorbornane (**6**) (followed by reduction) gave solely 7,7-dimethyl-2-hydroxymethylnorborn-2-ene (**37**). The *exo*/*endo* attack ratio was determined by assaying the deuterium content of the pair of alcohols (**38** and **39**) obtained from the *exo* deuteriated analogue **9** (*Scheme 9*).

Scheme 9



Exo/endo Attack ratio by $^1O_2$

38 R = H **39** R = D



9

40% 60% 0.67

Rates II. Owing to the large differences in reactivity between the C_8- and C_{10}-olefins, relative rates could only be properly estimated by comparing half-lives (τ) of the reactants under identical conditions of photo-oxygenation (Table 3). The relative rates were partitioned into *exo* and *endo* partial rates by assuming the product composition to be kinetic in origin.

Discussion. – In order to make an effective evaluation of the present results, it is imperative to present a brief review of the main features of the hydroperoxidation reaction which are unambiguously established [1].

From product composition studies made with simple cyclohexene derivatives and steroidal olefins, two factors emerge as being determinative [21]. The first is an apparent stereoelectronic factor, namely the degree of lateral overlap which exists between the allylic C–H bond and the *p*-orbitals on the double bond. This means for

Table 3. *Relative rates of oxidation of C_8- and C_{10}-olefins*

Acceptors		τ in min.	k_{rel} total	k_{rel} *exo*	k_{rel} *endo*
5		240	1	0.16	0.84
3		6	40	39.4	0.6
6		71	3.4	1.4	2.0
4		18.5	13.0	12.5	0.5

cyclohexenes in the half-chair conformation that the quasi-axial hydrogen atom is abstracted some three times more easily than the quasi-equatorial hydrogen atom.

The second factor is a steric one. The creation of the C–O bond is sensitive to steric congestion around the terminal vinyl carbon, especially when a *syn*-diaxial interaction is in danger of being set up. Faced with such a choice, the least encumbered side or even another vinyl carbon will be attacked by singlet oxygen.

From studies with variously substituted acyclic olefins a third factor or rather property of singlet oxygen emerges; it behaves as a mild electrophile. Rates of peroxidation, bromination and dye-sensitized photo-oxydation of a miscellany of olefins all run parallel [22]. As the rate determining steps of the first two processes, which are considered as exemplars of electrophilic reactivity, involve the formation of a three-membered cyclic intermediate, it has been inferred that singlet molecular oxygen interacts similarly with the double bond to produce an analogous, although electrically neutral, intermediate.

Before starting our discussion it should be said at once that at the moment these three facets of singlet oxygen behaviour appear to be compatible with both processes, the one-step and the two-step mechanism. Nevertheless, there ought to be significant discrepancies. Perepoxidation would entail a three-membered transition state, which should be more sterically demanding than the presumably looser ene-mechanism. Moreover, the stereoelectronic requirement for the allylic carbon-hydrogen bond breakage would now be transformed into one of contiguity with respect to the anionic oxygen atom; however, it is not clear what the geometry of such a perepoxide would be.

The fully concerted singlet oxygen-ene reaction, on the other hand, necessitates a six-membered cyclic transition state in which the steric factor operating at the

vinyl carbon would have to simultaneously operate with the correct stereoelectronic positioning of the allylic carbon-hydrogen bond.

Bearing in mind these factors and the possible discrepancies, it will now be seen if the present results confirm past findings and to what extent a distinction between the two mechanisms can be made.

Comparison of the rates of photo-oxygenation between the C_8-olefins and the monocyclic standards reveals the effect of the bridging element (Table 1). At first glance the total rates of bicyclic and monocyclic olefins are not startlingly different; although methylcyclopentene **31** does stand out as being the most reactive (Table 1). However, to make a meaningful comparison, the rates need to be corrected. This has been done by following two premises, which are based necessarily on the adoption of one of the two mechanisms. Assuming direct attack or fixation of oxygen on the double bond, rates are simply partitioned into *exo* and *endo* modes. For a concerted ene-mechanism, the ectoclinal mode contribution is additionally estimated from the product composition.

Inspection of the *exo* partial rates shows little variation. The only difference worth commenting on is that found between 1-methylcyclopentene **31** and its bicyclic relative **3**. Here the *exo* face of the methyl norbornene (**3**) does present some steric impediment to approaching oxygen, regardless of how the latter is supposed to be oriented with respect to the double bond itself or to the entire allylic moiety (3.15 *vs.* 57.5 or 24.7). Nevertheless, the *exo* partial rates demonstrate and confirm that the steric landscapes of the concave surface of the cyclopentene envelope in **3** and **31** are not dramatically different. Significantly this difference in rate is not observed for the corresponding pair of methylidene isomers **4** and **33**. They have essentially the same reactivity. Clearly attack by oxygen on both ends of the double bond or the creation of a carbon-oxygen bond with the terminal vinyl carbon atom is scarcely affected by the steric environment at the middle carbon atom of the allylic part.

When the minor *endo* partial rates are compared, then striking differences are seen. The placing of an ethane bridge across the 1-methylcyclopentene entity to create the norbornene skeleton brings about a 500- to 1000-fold increase in steric hindrance to incoming oxygen (*cf.* **3** to **31**). Similarly, the formal attachment of the ethane bridge to methylidenecyclopentane causes a corresponding, but smaller retardation of some 20–40 times. The simplest rationalization of these differences in *endo* rates is that no matter how the incoming oxygen molecule approaches the double bond environment, the *endo* C(5) and C(6) hydrogen atoms constitute a steric barrier. As expected the barrier is worse for eventual C–O bond formation on the norbornene skeleton itself. Nonetheless, it is worth noting that the partial rates do not uncover any difference of accessibility to the *endo* sides of 2-methylnorborn-2-ene (**3**) and 2-methylidenenorbornane (**4**).

For 2-methylnorborn-2-ene (**3**) the optimal stereoelectronic disposition of the allylic C–H bond is presumably always attainable by virtue of the free rotation of the methyl group. In the methylidenenorbornanes (**4**, **7** and **8**), the C(3) hydrogen atoms are denied such mobility, nevertheless models indicate that overlap is equally satisfactory for the *exo* and *endo* hydrogen atoms. Consequently, information on allylic C–H bond breaking should be forthcoming from the intermolecular isotope

effects shown by **7** and **8**[4]). Essentially no effect is observed for the *endo* C(3) deuterio isomer **8**, ($k_H/k_D = 1.02$) which is not surprising as only 3.5% of the oxygen molecules manage to attack the deuterium substituent. Attacks are more frequent on the *exo* C(3) deuterium in **7**, but even here the isotope effect is feeble ($k_H/k_D = 1.14$). Two interpretations may be advanced to account for this. If it is to be considered as a secondary isotope effect, then an initial rate determining perepoxidation is indicated[5]). If on the other hand the effect is primary, then the tiny value suggests that the allylic C–H bond in the transition state is either almost completely ruptured or hardly broken at all [25]. Clearly, as the transition state is reactant-like, as evidenced by the importance of ground state steric factors, only the second possibility is feasible[6]).

These findings receive further support and amplification when comparisons are made between the norbornene and the 7,7-dimethyl substituted substrates (Table 3). Here it is seen that the partial *endo* rates are roughly the same for the C_8- and C_{10}-olefins reaffirming that oxygen experiences the same degree of steric impediment on getting to the *endo* side of the ectocyclic or the encyclic allylic parts. In striking contrast, the *exo* rates display important differences. The most significant of these is the 250-fold decrease observed on passing from the norbornene **3** to its *gem*-dimethyl relative **5**. Although sizeable, this difference is several times smaller than those observed for the *exo*-face reactions of phenylsulfenyl chloride, peracid and diimide with the norbornene/7,7-dimethylnorbornene pair, viz. 1820, 1000 and 950 [6]. Since these last reactions are classed as *bona fide* one-step cyclic processes, accordingly all that can be said about the singlet oxygen mechanism is that it too is a cyclic one-step process, but one which occurs through a loose arrangement, certainly looser than epoxidation. Naturally, caution has to be exercised in suggesting a close geometric parallel between the reaction of a peracid with an olefin and the hypothetical perepoxidation, but it does appear that singlet oxygen is not forming two C–O bonds simultaneously with the ends of the double bond. If this were so, then both events would be subject either separately or jointly to steric retardation in the structures under study, especially when the newly forming bond is located at the corner of the norbornane skeleton; on C(2) and C(3) in the norbornenes and on C(2) in the methylidenenorbornanes. Further inspection of Table 3 shows that *exo* rate differences between the *gem*-dimethyl compound **6** and its parent **4** are negligible.

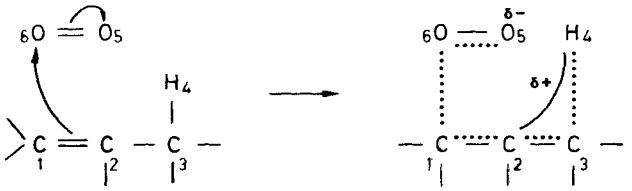
In summary, the steric evidence is entirely compatible with the establishment of a one-point attachment by oxygen to the terminal vinyl carbon of the allylic fragment. Moreover, the formation of the C–O bond is very sensitive to interference by 1,3 type non-bonded interactions, whereas 1,2 interactions have little effect. Therefore the transition state is best described by a one-step process which in its early stages has much dipole character. As bonding advances between the oxygen molecule and the vinyl end of the allylic portion, positive charge is set up on the central carbon atom, but which in turn is delocalized by hyperconjugation with the allylic C–H bond (*Scheme 10*). Naturally such delocalization will be facilitated when the local molecular geometry favours σ–π overlap. This transition state possesses many

[4]) Intramolecular isotope effects have been reported [23].

[5]) Similar small effects are seen in the solvolysis of 3-deuterionorborn-2-yl brosylates [24].

[6]) Isotope effects in ene-type reactions have been little investigated [26].

Scheme 10



Creation of Dipolar Transition State Leading to Allylic Hydroperoxide

of the features of the perepoxide mechanism, but with the capital difference that a discrete perepoxide is not formed. In the later stages of the transition state the anionic oxygen abstracts preferentially whichever of the allylic hydrogens available is best hyperconjugated. This is the main requirement. The subsidiary requirement is one of contiguity. However the abstraction itself should not require a precise orientation of the two atoms as the 1s orbital on hydrogen has good all-round overlap properties and the positioning of the oxygen with respect to it should not be crucial.

This dipolar transition state accounts, at least qualitatively, for the previously observed dependence of rates and product composition on solvent [27]. The interesting finding that a nucleophilic solvent can compete with oxygen for allylic hydrogen is inconsistent with the conventional fully concerted ene mechanism, but fits the mechanism proposed here [28].

By way of epilogue it is worth mentioning that in these photo-oxidations no rearranged products were observed. Norbornene epoxides and *exo* onium type intermediates of norbornene are notorious for the facility of their skeletal rearrangement, consequently the consistent observation of hydroperoxides of unrearranged structure renders the intermediacy of a perepoxide unlikely [29].

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Experimental Part

General. Gas liquid chromatography (GLC.) was carried out on models F11 (analytical) and 990 (semi-preparative)*Perkin-Elmer* instruments. IR.-spectra were recorded on a model 402 *Perkin-Elmer* spectrophotometer. NMR.-spectra were determined at 60 MHz on a model R-12 *Perkin-Elmer* instrument and at 100 MHz on a model XL-100 *Varian* spectrometer using CCl_4 as solvent. Chemical shifts are expressed as ppm with reference to tetramethylsilane taken as zero. Signal intensities are reported in proton units (1H, 2H, etc.), multiplicities are expressed as singlet (*s*), doublet (*d*), triplet (*t*) and multiplet (*m*).

Mass-spectra, recorded on an *Atlas* model CH-4, operating at 12 eV, were performed by Mrs. *F. Kloeti*.

All boiling and melting points are uncorrected.

Preparation of olefins. 2-Methylnorborn-2-ene [7], 2-methylidenenorbornane [8], 2,7,7-trimethylnorborn-2-ene (ξ-fenchene) and 7,7-dimethyl-2-methylidenenorbornane (α-fenchene) [4] [12] were prepared by the best methods available.

exo-*3-Deuterionorbornan-2-one* (**12**). To 80 mg (2 mmol) of NaOH in 60 g dioxane and 30 g D_2O, 20 g (0.19 mol) of norbornanone were added. After stirring for 70 min. at room temperature, the mixture was extracted three times with 100 ml of pentane. The organic phase was dried over

$MgSO_4$ and the pentane removed. Dioxane (20 g), D_2O (30 g) and NaOH (70 mg) were added to the residue and the mixture kept at room temperature for 70 min. Extraction with pentane followed by distillation through a *Vigreux* column gave 15 g (75%) of *exo*-deuteriated norbornanone (**12**).

Deuterium assay by MS.: 0% d_0, 97% d_1, 3% d_2.

endo-*3-Deuterionorbornan-2-one* (**14**). A solution of 20 g (0.19 mol) of norbornanone and 240 mg (6 mmol) of NaOH in 80 ml dioxane and 40 g D_2O was heated to 45° for 6 days. The solution was diluted with 500 ml of water and extracted several times with pentane. The organic phase was washed and dried over $MgSO_4$. Distillation through a *Vigreux* column gave 19 g (95%) of dideuteriated norbornanone. A solution of the latter and 250 mg NaOH in 40 ml H_2O and 80 ml dioxane was stirred for 10 h at room temperature. Work-up as described above gave 13.0 g (65%) of *endo*-3-deuterionorbornan-2-one (**14**).

Deuterium assay by MS.: 14.0% d_0, 83,5% d_1, 2.5% d_2.

2-Methylidene-exo-*3-deuterionorbornane* (**7**). A mixture of 4.4 g (0.04 mol) **12** in 20 ml THF was added to a solution of phenylthiomethyllithium (0.05 mol) in THF at 0°. The solution was stirred for 3 h at 25° and recooled to 0° when 8.2 g (0.08 mol) of acetic anhydride in 5 ml THF were added. After further stirring for 1.5 h at room temperature, water was added and the solution extracted with ether. The organic layer was washed with 10% HCl solution and water and dried over $MgSO_4$. Evaporation of solvent gave 12.0 g (100%) of crude product. Direct treatment with 5 drops of BF_3-etherate and 5 ml of acetic anhydride, followed by stirring at room temperature for 1 h and extraction with ether, washing with 10% $NaHCO_3$ and water, gave on evaporation of the solvent 10.5 g (88%) of *exo*-3-deuterio-*endo*-2-phenylthiomethyl-2-norbornyl acetate. – NMR.: 1.7 (*s*, 3H); 3.22 and 3.77 *ABq* (J_{AB} = 5.0 Hz).

To a stirred refluxing solution of 3.7 g (0.55 mol) Li in 250 ml of liquid ammonia a solution of 10.5 g (0.035 mol) of *exo*-3-deuterio-*endo*-2-phenylthiomethyl-2-norbornyl acetate in 15 ml ether was added during 20 min. 30 Min. later, pentane and ammonium chloride were added until the blue colour disappeared. The ammonia was allowed to evaporate and the pentane layer was washed with 10% aqueous NaOH and water, dried over $MgSO_4$ and distilled through a *Vigreux* column. Final distillation gave 2.1 g (50% yield) 2-methylidene-*exo*-3-deuterionorbornane (**7**). B.p. 120–122°.

Deuterium assay by MS.: 2.7% d_0, 96.0% d_1, 1.3% d_2.

2-Methylidene-endo-*3-deuterionorbornane* (**8**). From 5.0 g (0.05 mol) of *endo*-3-deuterionorbornane-2-one and using the previous procedure, 2.2 g (53% yield) of 2-methylidene-*endo*-3-deuterionorbornane (**8**) was obtained.

Deuterium assay by MS.: 14.6% d_0, 82.1% d_1, 3.3% d_2.

exo-*1-Bromo-2,7,7-trimethylnorbornan-2-ol* (**17**). To a stirred suspension of 4.8 g (0.2 mol) magnesium turnings in 200 ml ether was added a solution of 30 g (0.21 mol) methyl iodide in 20 ml ether. The resulting *Grignard* solution was treated dropwise with 14.2 g (0.066 mol) 1-bromo-7,7-dimethylnorbornanone (**16**) [14] in 200 ml of ether. The mixture was stirred at room temperature for 5 h and then hydrolysed with a saturated aqueous ammonium chloride solution. Extraction with ether, followed by evaporation of the solvent, yielded 14.5 g (95%) of unreacted ketone (**16**) and addition product (**17**); repeating the addition of *Grignard* reagent three times furnished *exo*-1-bromo-2,7,7-trimethylnorbornan-2-ol in about 90% purity (m.p. 172–174°). – NMR. (CCl_4): δ 1.00 (*s*, 3H); 1.20 (*s*, 3H); 1.27 (*s*, 3H). – IR. (CCl_4): 3560 cm^{-1}.

1-Bromo-2,7,7-trimethylnorborn-2-ene (**18**) *and 1-Bromo-7,7-dimethyl-2-methylenenorbornane* (**19**). 8.9 g (38.2 mmol) of the addition product (**17**) in 12 ml acetonitrile was added dropwise to a stirred solution of 10.8 g (45.5 mmol) carboxysulfamoyltriethylammonium hydroxide inner salt methyl ester ($MeO_2CNSO_2NEt_3$) in 25 ml acetonitrile [15]. The resulting mixture was heated for 1.5 h at 60°, after cooling it was treated with 20 ml water, extracted with ether and the organic layer was washed, dried with $MgSO_4$ and evaporated. The residue (8.1 g) was directly treated with lithium without further purification.

7,7-Dimethyl-2-methylidenenorbornane (**6**) *and 2,7,7-trimethylnorborn-2-ene* (**5**). To a stirred solution of 2.6 g (0.37 mol) Li in 150 ml of liquid ammonia was added 7.0 g (0.033 mol) of the mixture **18** and **19** in 10 ml dry ether. Stirring was continued for 30 min more and ammonium chloride added while the ammonia was allowed to evaporate slowly. The residue was extracted

with ether, the organic phase washed with water, dried over $MgSO_4$ and the solvent distilled to give 3.5 g (79%) of a mixture of **5** and **6** in a ratio of 9:91. Separation was achieved on a 10% $AgNO_3$ silica gel column using pentane as eluant.

2,7,7-Trimethylnorborn-2-ene (**5**). NMR. (CCl_4): δ 0.9 (*s*, C (7)—CH_3); 1.0 (*s*, 3H, C (7)—CH_3); 1.75 (*d*, 3H, C (2)—CH_3; J = 2 Hz); 5.50 (br. *s*, 1H, C (3)—H).

7,7-Dimethyl-2-methylidenenorbornane (**6**). NMR. (CCl_4): δ 1.0 (*s*, 6H, C (7)—CH_3); 4.63 and 4.84 (br. *s*, 2H, C (2)=CH_2).

Attempted Preparation of endo-*2,7,7-trimethyl-2,3-epoxynorbornane* (**23**). A quantity of 200 mg (1.5 mmol) of 2,7,7-trimethylnorborn-2-ene **5** in 2.5 ml methylene chloride was added to a solution of 325 mg (1.60 mmol) 85% *m*-chloroperbenzoic acid in 3.5 ml methylene chloride at 0°. After stirring for 1 h the excess peracid was decomposed by addition of 10% sodium sulfite solution. Extraction with methylene chloride followed by the usual work-up gave 150 mg (67%) crude material, which was identified as *endo*-2,7,7-trimethylnorbornan-3-one (**24**). – NMR. ($CDCl_3$): δ 1.10 (*s*, 6H, C (7)—CH_3). – IR. (CCl_4): 1745 cm^{-1}.

endo-*7,7-dimethyl-2-methylidenenorbornan-3-ol* (**20**). To a refluxing solution of 3.0 g (22.0 mmol) of olefin **6** in 20 ml dioxane was added a hot solution of 1.24 g (11.2 mmol) SeO_2 in 50 ml dioxane and 3.3 ml water. Refluxing was continued for a further 20 h. Evaporation of the dioxane yielded 2.0 g (60%) of crude mixture of *endo* alcohol **20** and enone **21**. Separation of the two products was achieved by GLC., using a FFAP column. – NMR. ($CDCl_3$): δ 1.00 (*s*, 6H, C (7)—CH_3); 4.62 (br. *s*, 1H, (C (3)—H); 5.00 (br. *s*, 2H, C (2)=CH_2). – IR. (CCl_4): 3615 cm^{-1}.

7,7-Dimethyl-3-methylidenenorbornan-2-one (**21**). A solution of 2.96 g $Na_2Cr_2O_7 \cdot 2H_2O$ (10 mmol), 2.45 ml conc. sulfuric acid and 12.3 ml water was added to 4.0 g (26.4 mmol) of a mixture of alcohol **20** and enone **21** in 16 ml ether over a period of 15 min. Stirring was continued for 4 h. The mixture was then poured onto crushed ice, extracted with ether, washed with $NaHCO_3$ and water and the ether finally dried over $MgSO_4$. Evaporation yielded 2.0 g (51%) of ketone **21**. – NMR. ($CDCl_3$): δ 1.03 (*d*, 3H, C (7)—CH_3, J = 3 Hz); 1.08 (*s*, 3H, C (7)—CH_3); 5.16 and 5.80 (*s*, 2H, C (2)=CH_2). – IR. (CCl_4): 1745 cm^{-1}.

exo-*3,7,7-Trimethylnorbornan-2-one* (**25**). A solution of 200 mg of enone **21** in 5 ml ether was hydrogenated in a *Parr* apparatus with 4 atm. hydrogen over 10% Pd/C. The catalyst and solvent were removed to yield 110 mg (55%) ketone **25** which was purified by GLC. (FFAP column). – NMR. (CCl_4): 1.10 (br. *s*, 6H, C (7)—CH_3). – IR. (CCl_4): 1750 cm^{-1}.

Although the *exo* and *endo* ketones **25** and **24** exhibit almost identical spectra, they were easily distinguished by GLC. (FFAP column).

Preparative photo-oxygenation. About 200–400 mg of olefin and 2 ml of solvent/sensitizer reagent (acetonitrile and methylene blue, 10^{-3} M), were placed in the irradiation cell [32]. Air was replaced by oxygen and the system connected to a gas burette. The solution was saturated with oxygen and allowed to come to thermal equilibrium. After about 10 min the lamps (two 500 W projector bulbs, *Sylvania* FFX) were turned on. The reaction was followed by measuring the amount of oxygen absorbed. Photo-oxygenation was usually stopped after 95% completion. The reaction mixture was treated with 200–400 mg $NaBH_4$ in methanol and kept at room temperature for about 2 h. Water was added and then the aqueous layer extracted twice with ether. After washing with water and drying over $MgSO_4$ the solvent was removed. The residue (usually 180–400 mg) was analysed by GLC. using a FFAP/chromosorb W column. When triphenylphosphine/ether was used to reduce the hydroperoxide, the resulting reaction mixture was directly analysed by GLC.

Determination of the mode of attack on the 2-methylidenenorbornanes (**7**, **8**, and **9**). Photo-oxygenation of the deuteriated olefins was carried out according to the general procedure. The crude reduced products were directly analysed by mass spectroscopy. From the *exo*-deuteriated olefin **7** (2.7% d_0, 96.0% d_1, 1.3% d_2) the isotopic distribution in 2-hydroxymethylnorborn-2-ene was found to be 95.5% d_0, 4.5% d_1 and 0% d_2 indicating *exo* and *endo* attacks of 96.5% and 3.5%. Photo-oxygenation of **8** (14.6% d_0, 82.1% d_1, 3.3% d_2) gave the same alcohol with the isotopic distribution 17.7% d_0, 82.3% d_1, 0% d_2. This indicates *exo* and *endo* attacks of 96.4% and 3.6%.

In the case of the *gem*-dimethylated olefin **9** (92.5% d_0, 7.5% d_1, 0% d_2) the isotopic distribution found in the corresponding 7,7-dimethyl-2-hydroxymethylnorborn-2-ene was found to be

95.5% d_0, 4.5% d_1 and 0% d_2. This distribution reflects *exo* and *endo* attacks of 40%, and 60% respectively.

Determination of the kinetic deuterium isotope effect. An approximately 50:50 mol % mixture (totalling 70–150 mg) of undeuteriated **4** and deuteriated **7** or **8** was prepared. This mixture was poured into the oxidation apparatus and 1.5 ml of solvent/sensitizer reagent added. The solution under an oxygen atmosphere was allowed to stand 15 min. The t = 0 volume was read and the lamps turned on.

Irradiation time: 9–12 min.

Concentration of methylene blue: 10^{-3} mol/l.

Oxidation: 39–53%.

After turning off the light source, the volume of absorbed oxygen was determined and the acetonitrile and unreacted olefin were removed by distillation under reduced pressure (15 mm Hg, trap cooled with acetone/CO_2). The unoxidized starting material was separated from the solvent by GLC. (20% Apiezon L, chromosorb W). The isotope effect was calculated from Equation a.

$$k_H/k_D = \frac{\log (E_{oH}/E_{tH})}{\log (E_{oD}/E_{tD})} \quad (a)$$

E_{oD}, E_{tD}, E_{oH} and E_{tH} designate the concentration of the labelled and unlabelled olefin before and after photo-oxygenation. These concentrations were obtained from a knowledge of the total amount of initial olefin, the conversion factor (amount of oxygen absorbed, corrected to 760 mm Hg and 0°) and the mass spectrometric isotope ratios of deuteriated and undeuteriated olefin mixture before and after photo-oxygenation [31].

Determination of relative rates of photo-oxygenation (Tables 1 and 3). The determination of the relative reactivities of the bridged bicyclic olefins amongst themselves (Table 3) or with respect to standard monocyclic olefins (Table 1) was accomplished by comparing their half-lives under the conditions of photo-oxygenation or by measuring the rate of acceptor disappearance in appropriate competition experiments. When half-lives were measured, care was taken to ensure that the conditions of photo-oxidations were identical. For the estimation of relative rates of reactivities for a pair of olefins A and B then equation b was used. Here, A_o and A_t are the concentrations of olefin A at time o and t respectively. The quantities B_o and B_t denote the corresponding concentrations of olefin B. The determination of the olefin concentrations was estimated from peak areas obtained from GLC. calibrated with an internal standard. For each oxidation of a particular olefin the experimental k_{rel} was determined at 20%, 50%, and 75% conversions. The results indicated an error of about ± 20%.

$$k_{rel_{A/B}} \frac{\log (A_o/A_t)}{\log (B_o/B_t)} \quad (b)$$

REFERENCES

[1] *C. S. Foote*, Accounts chem. Res., *1*, 104 (1968); Pure Appl. Chem. *27*, 635 (1971); *D. R. Kearns*, Chem. Rev. *71*, 395 (1971); *R. W. Denny & A. Nickon*, Org. Reactions, *20*, 133 (1973).

[2] *P. D. Bartlett & A. P. Schaap*, J. Amer. chem. Soc. *92*, 3223 (1970); *S. Mazur & C. S. Foote, ibid., 92*, 3225 (1970); *A. P. Schaap & G. R. Faler, ibid., 95*, 3381 (1973); *P. D. Bartlett & M. S. Ho, ibid., 96*, 627 (1974).

[3] *A. Nickon, J. B. DiGiorgio & P. J. L. Daniels*, J. org. Chemistry *38*, 533 (1973) and references therein.

[4] *D. B. Sharp*, Abstracts, 139th National Meeting of the American Chemical Society, New York, N.Y., Sept. 1960, p. 79; *K. R. Kopecky & H. J. Reich*, Canad. J. Chemistry *43*, 2265 (1965); *W. Fenical, D. R. Kearns & P. Radlick*, J. Amer. chem. Soc., *91*, 7771 (1969); *N. Hasty, P. B. Merkel, P. Radlick & D. R. Kearns*, Tetrahedron Letters 49 (1972).

[5] *C. W. Jefford, M. H. Laffer & A. F. Boschung*, J. Amer. chem. Soc. *94*, 8904 (1972), preliminary paper.

[6] *H. C. Brown & K. T. Liu*, J. Amer. chem. Soc. *93*, 7335 (1971); *H. C. Brown, J. H. Kawakami & K. T. Liu, ibid., 95*, 2209 (1973).

[7] *C. W. Jefford & W. Wojnarowski*, Helv. *55*, 2244 (1972); *C. W. Jefford, S. Mahajan, J. Waslyn B. Waegell*, J. Amer. chem. Soc. *87*, 2183 (1965).
[8] *S. Bank, C. A. Rowe, Jr., A. Schriesheim & C. A. Naslund*, J. Amer. chem. Soc. *89*, 6897 (1967).
[9] *T. T. Tidwell*, J. Amer. chem. Soc. *92*, 1448 (1970).
[10] *R. L. Sowerby & R. M. Coates*, J. Amer. chem. Soc. *94*, 4758 (1972); *R. M. Coates & R. L. Sowerby*, ibid. *94*, 5386 (1972).
[11] *F. Petit & M. Blanchard*, Bull. Soc. chim. France, 1611 (1972).
[12] *M. Hanack*, Chem. Ber. *94*, 1082 (1961).
[13] *P. D. Bartlett & H. Knox*, Org. Synthesis *45*, 14, 55 (1965).
[14] *W. C. Fong, R. Thomas & K. V. Scherrer, Jr.*, Tetrahedron Letters 3789 (1971).
[15] *E. M. Burgess, H. R. Penton, Jr., & E. A. Taylor*, J. org. Chemistry *38*, 26 (1973).
[16] a) *J. K. Crandall*, J. org. Chemistry *29*, 2830 (1964); b) *R N. McDonald & R. N. Steppol*, J. Amer. chem. Soc. *91*, 782 (1969).
[17] *L. Horner & H. Hoffmann*, Angew. Chem. *68*, 473 (1956).
[18] *J. A. Sousa & A. L. Bluhm*, J. org. Chemistry *25*, 108 (1960).
[19] *A. Suzuki, N. Miyaura, M. Itoh, H. C. Brown, G. W. Holland & E. Negishi*, J. Amer. chem. Soc. *93*, 2792 (1971).
[20] *J. E. Lyons & J. O. Turner*, J. org. Chemistry *37*, 2881 (1972).
[21] *K. Gollnick & G. O. Schenk*, Pure appl. Chemistry *9*, 507 (1964); *A. Nickon, N. Schwartz, J. B. DiGiorgio & D. A. Widdowson*, J. org. Chemistry *30*, 1711 (1965); *E. Klein & W. Rojahn*, Tetrahedron, *21*, 2173 (1965).
[22] *K. R. Kopecky & H. J. Reich*, Canad. J. Chemistry *43*, 2265 (1965); *C. S. Foote & R. W. Denny*, J. Amer. chem. Soc. *93*, 5162, 5168 (1971).
[23] *A. Nickon, V. T. Chuang, P. J. L. Daniels, R. W. Denny, J. B. DiGiorgio, J. Tsunetsugu, H. G. Vilhuber & E. Werstiuk*, J. Amer. chem. Soc. *94*, 5517 (1972).
[24] *B. L. Murr & J. A. Conkling*, J. Amer. chem. Soc. *92*, 3464 (1970).
[25] *F. H. Westheimer*, Chem. Rev. *61*, 265 (1961); *R. A. More O'Ferrall*, J. chem. Soc. *B*, 785 (1970); *C. J. Collins & N. S. Bowman*, Isotope Effects in Chemical Reactions, Van Nostrand Reinhold Company, New York 1970, p. 242.
[26] *S. H. Dai & W. R. Dolbier, Jr.*, J. Amer. chem. Soc. *94*, 3953 (1972); *R. Huisgen & H. Pohl*, Chem. Ber. *93*, 527 (1960).
[27] *N. M. Hasty & D. R. Kearns*, J. Amer. chem. Soc. *95*, 3380 (1973); *P. D. Bartlett & A. F. Boschung*, unpublished work; *E. C. Blossey, D. C. Neckers, A. L. Thayer & A. P. Schaap*, J. Amer. chem. Soc. *95*, 5820 (1973).
[28] *L. M. Stephenson, D. E. McClure & P. K. Sysak*, J. Amer. chem. Soc. *95*, 7888 (1973).
[29] *C. W. Jefford, A. F. Boschung, R. M. Moriarty, C. G. Rimbault & M. H. Laffer*, Helv. *56*, 2649 (1973).
[30] *C. W. Jefford, A. F. Boschung & C. G. Rimbault*, to appear.
[31] *K. Biemann*, 'Mass Spectrometry. Organic Applications', McGraw-Hill, New York 1962, p. 223 ff.
[32] *C. W. Jefford, A. F. Boschung, C. G. Rimbault & M. H. Laffer*, to appear.

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247. The Reaction of Singlet Oxygen with Norbornene

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(9. VIII. 74)

In recent years there has been considerable speculation concerning the existence of perepoxide or peroxirane intermediates [1]. Two particular, but related instances are provided by the dye-sensitized photo-oxygenation of monoolefins to give hydro-

[1]) Preliminary paper. A full account will appear in Helv.