273. The Reaction of Singlet and Triplet Oxygen with 2-Phenylnorbornene

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Summary. The reaction of singlet oxygen with 2-phenylnorbornene (**1**) in aprotic solvents gives 3-formylcyclopentyl phenyl ketone (**2**) (10%) and uncharacterized polymer (90%). When methanol is used as solvent, *endo*-2-phenyl-*exo*-2-methoxy-*exo*-3-hydroperoxynorbornane (**4**) and *endo*-2-(*anti*-1′,4′-epidioxy-5′,6′-epoxycyclohex-2′-enyl)-*exo*-2,3-epoxynorbornane (**6** and **7**) are obtained in addition to **2**. Triplet oxygen with **1** gave **2**, *endo*-2-phenyl-*exo*-2,3-epoxynorbornane (**8**), and the trimer **9** or **10** of *exo*-2,3-epidioxy-*endo*-2-phenylnorbornane. With protic solvents the amount of epoxide increased at the expense of trimer. The singlet and triplet oxygen reactions are discussed in the light of possible intermediates.

Introduction. – We have recently demonstrated that, contrary to an earlier report [1], norbornene reacts with singlet oxygen to give norbornene epoxide and *cis*-cyclopentane-1,3-dicarboxaldehyde [2]. We suggested that a transient dioxetane is formed which promptly undergoes cleavage. However, attempts to capture the perepoxide, which is though to be a likely precursor to the dioxetane, proved unavailing. When pinacolone was used as solvent and potential trapping agent, no *t*-butyl acetate could be detected[1]). Either the perepoxide is not formed or if it is, then pinacolone is not sufficiently electrophilic to produce a *Bayer-Villiger*-type intermediate.

In this paper we describe the behaviour of 2-phenylnorbornene towards singlet oxygen in a variety of solvents. Here the phenyl group should offer alternative reaction pathways, not only to the incoming oxygen molecule, but also alternative rearrangement routes to hypothetical intermediates, such as perepoxides.

The presence of the styrene moiety naturally provides the opportunity for *Diels-Alder* reaction with singlet oxygen [4], but also affords a substrate capable of reacting with triplet oxygen [5]. In a second set of experiments, a comparative study of the auto-oxidation of 2-phenylnorbornene in different solvents is made.

Results. – A. *Reaction with Singlet Oxygen.* Photo-oxygenation of 2-phenylnorbornene (**1**) in chloroform, carbon tetrachloride, methylene chloride and acetonitrile using methylene blue or mesotetraphenylporphin as sensitizer gives essentially the same result [6] (*Scheme 1*). The *cis*-ketoaldehyde **2** is the main product, the material balance consisting of polymer (**3**). The ketoaldehyde was easily identified by com-

[1]) The interesting claim has been made that pinacolone is oxidized by the transient perepoxide of adamantylidene adamantane [3].

paring its spectroscopic properties with those of an authentic sample prepared by ozonolysis of 2-phenylnorbornene. As oxygen uptake amounted to some two equivalents of that needed for one equivalent of olefin, it can be deduced that the polymer derives from diperoxides.

Scheme 1

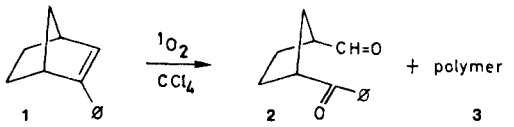
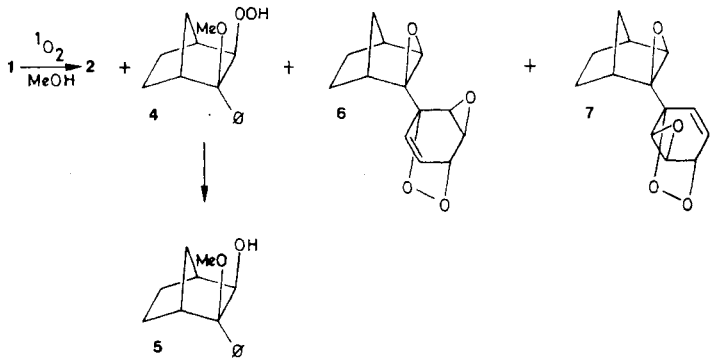


Photo-oxygenation of **1** in methanol at $-10°$ with one equivalent of oxygen using rose bengal as sensitizer gave four products, but significantly very little polymer (*Scheme 2*). Apart from the ketoaldehyde **2** (7%), the chief product was the methoxy-

Scheme 2



hydroperoxide **4** (63%). The configuration of **4** was established by its reduction to the known *endo*-2-phenyl-*exo*-2-methoxy-*exo*-3-hydroxynorbornane **5** [7]. The other two products, **6** and **7**, isolated in feeble quantities (3%), are the result of a double addition of oxygen. Their structures were deduced from their NMR. spectra. It was not possible to separate the mixture of diastereoisomers, however from the NMR. data the isomer ratio was established as 1:4.

From these results it follows that photo-oxygenation of 2-phenylnorbornene is essentially the same in inert solvents and methanol, the difference being that polymer has the chance to form in the absence of the nucleophilic solvent. A clue to the origin of the polymer was forthcoming by repeating the photo-oxygenation at $-78°$ in methylene chloride until just half an equivalent of oxygen was absorbed. After addition of methanol, analysis revealed the presence of the ketoaldehyde **2** and the methoxyhydroperoxide **4**. This provides a good indication that the dioxy precursor to the ether **4**, whatever it may be (*v. infra*), leads on further oxidation to the polymer **3**.

B. *Auto-oxidation.* In carrying out the tests for singlet oxygen as the authentic oxidation species, it was discovered that 2-phenylnorbornene undergoes auto-oxidation although at a much slower rate than the photo-oxygenation. Under irradiation conditions, two sets of oxidations are competing with a ten-fold or so difference of rate (Table 1). In fact, care had to be exercised by using short reaction times and

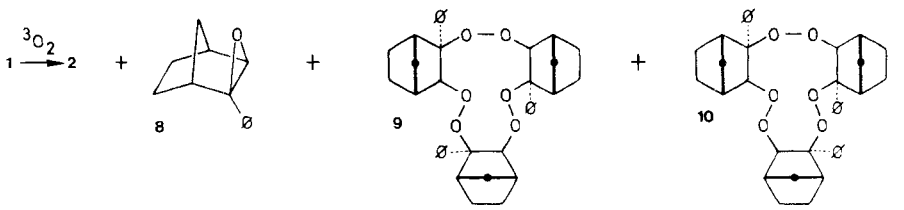
Table 1. *Relative rates of auto-oxidation*[a]) *and photo-oxygenation of* **1**

Conditions	$^3O_2$, dark	$^3O_2$ irradiation	$^3O_2$, dark, radical inhibitor	$^1O_2$
Rel. rate	1	3.6	0	47

[a]) In CH_3OH, concentration of substrate 0.5M.

weak concentrations of substrate to ensure that the products were derived from the singlet state. However, when ground state oxygen was the reagent, just three products were formed, the ketoaldehyde **2**, the epoxide **8** and a product which was thought to be the elusive dioxetane **11** (*Scheme 3*). The suspected dioxetane was a

Scheme 3



white solid and exploded on warming to give a quantitative yield of ketoaldehyde **2**. In other words, it appeared to be a *bona fide* dioxetane as characterized by its decomposition mode; however from its molecular weight determined by osmometry, the product was a dioxetane trimer. Although its structure has not been unequivocally determined, it is probably of the all *exo* configuration with either the three-fold head-to-tail arrangement **9** or the less symmetric alternative **10**.

The product composition varied with solvent. The amount of ketoaldehyde **2** remained more or less constant, with the trimer-epoxide ratio decreasing with increasing polarity of solvent (Table 2).

Table 2. *Auto-oxidation of 2-phenylnorbornene in various solvents*

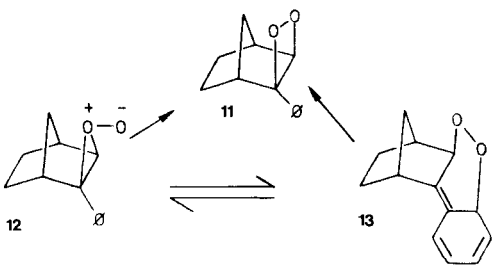
Solvent	Trimer **9** or **10**	Ketoaldehyde **2**	Epoxide **8**
	%	%	%
C_6H_6	75	20	5
$CHCl_3$	72	20	8
CH_3CN	62	13	25
CH_3OH	47	22	31[a])

[a]) **5** is formed.

In methanol, the epoxide **8** is immediately captured to yield the methoxy-alcohol **5**, but a search revealed no trace of the corresponding methoxyhydroperoxide **4**. Moreover, the rates of oxidation in methanol were indifferent to light or dark when sensitizer was absent, but were some 47 times slower than that observed under singlet oxygen conditions. Auto-oxidation was stopped completely when small quantities of radical inhibitor (3-*t*-butyl-4-methoxyphenol) were added (Table 1).

Discussion. – As a working hypothesis, the results from the singlet oxygen experiments can be conveniently interpreted in terms of three primary intermediate 1:1 adducts, the dioxetane **11**, the perepoxide **12** and the *Diels-Alder* adduct or *endo* peroxide **13** (*Scheme 4*). It is difficult to say whether these adducts are formed

Scheme 4

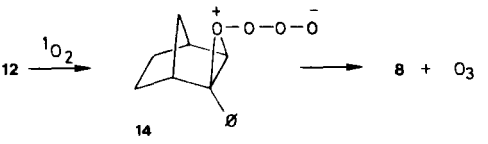


simultaneously or consecutively. Formally they are all connected, although complete reversibility between them is doubtful. Their different chemical properties will make them differently interceptible by solvent and singlet oxygen. In the absence of nucleophiles, **12** could expand to **11** or **13**. The *endo* peroxide **13** in its turn could either revert to perepoxide or rearrange to dioxetane. In any event, as soon as the dioxetane **11** is attained, it will undergo irreversible cleavage.

In inert solvents the only reagent available is singlet oxygen itself. The *endo* peroxide **13**, having a *cis*-diene function at the ready, is expected to react further to give a double peroxide, which will eventually give polymer (*v. infra*).

Another possible outcome, as singlet oxygen is known to react with nucleophiles, such as anions [8], is its adjunction to perepoxide **12** to create the tetra-oxy zwitterion **14** which could fall apart to epoxide **8** and ozone[2][3] (*Scheme 5*). However, in methanol none of the methoxy-alcohol **5** was isolated, which argues against this possibility.

Scheme 5

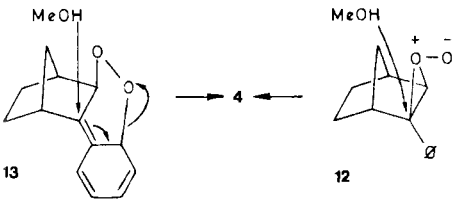


[2] On the basis of kinetic evidence *P. D. Bartlett* has proposed such a mechanism (private communication, May 1975).

[3] In our experiment the ozone is lost. In any event we were unable to detect it, probably owing to its ready reaction with olefin.

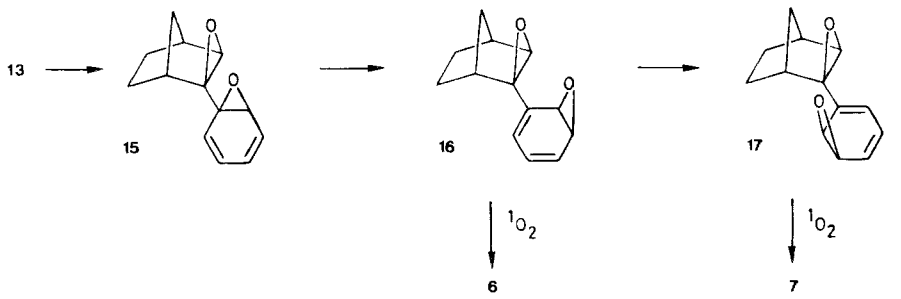
On the other hand, evidence for the intermediacy of **13** finds solid support from the products obtained in methanol. The *endo* peroxide **13** and the perepoxide **12** should both be susceptible to nucleophilic attack by methanol. *Exo* attack on C(2) of **13** finds sound mechanistic precedent in that an S_N2' process is expected [9]. Here nucleophile and nucleofuge, the peroxy anion, respectively enter and leave on the same face of the molecule. The result is the hydroperoxide **4**. Equally plausible is *exo* attack by methanol on the perepoxide **12** to give the same result (*Scheme 6*).

Scheme 6



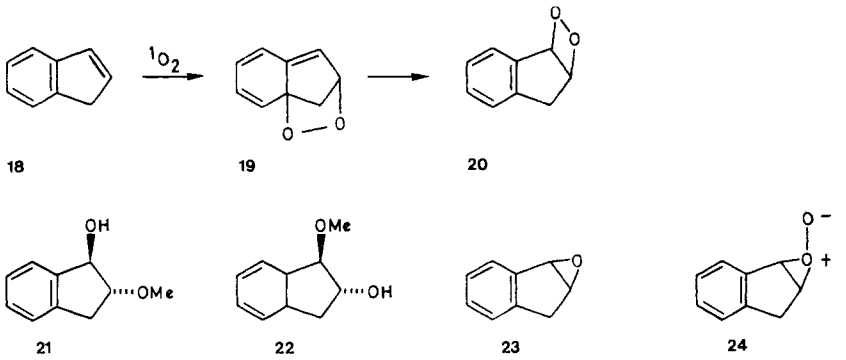
The *endo* peroxide **13** is not completely trapped by methanol, as it is clearly the source of the epoxy epimers **6** and **7**. How these arise from **13** may be rationalized as follows. Firstly, homolytic rupture of the oxygen-oxygen bond gives the diepoxide **15**; precedent for this reaction is provided by the decomposition of ascaridole [10] [11]. Next, an oxygen migration [12] can give rise to an enantiomeric pair of the more reactive dienes **16** and **17** which are trapped by another molecule of singlet oxygen [13]. For reasons of steric hindrance, this attack will occur to give the *trans* isomers [14] (*Scheme 7*).

Scheme 7



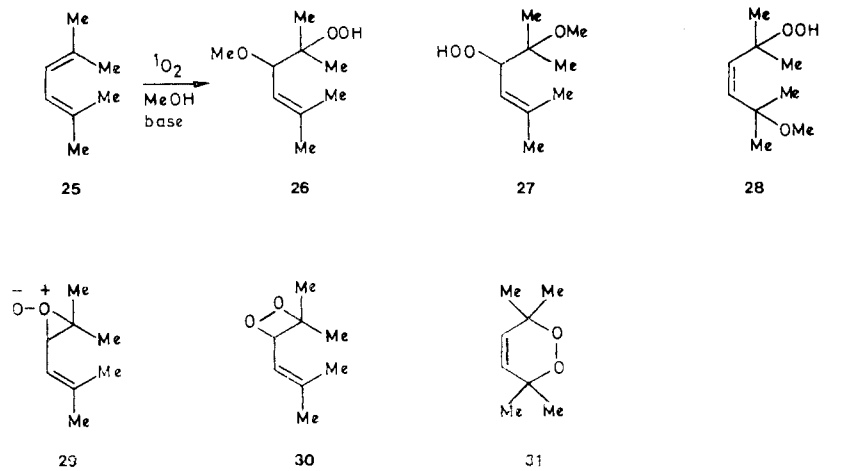
These findings are pertinent to others obtained with diene systems of the styrene type. The photo-oxygenation of indene (**18**) in methanol is now thought to involve the primary formation of an *endo* peroxide **19** and the secondary formation of the dioxetane **20** [15]. It has been suggested that the origin of the epimeric *trans*-methoxy-alcohols **21** and **22** could be the consequence of attack by methanol on **19** or **20**. We believe that the latter course is unlikely for a dioxetane and that the former would lead to a methoxyhydroperoxide of *cis* configuration. Moreover, the intermediacy of the corresponding epoxide **23** or perepoxide **24** would better account for the presence of **21** and **22** (*Scheme 8*).

Scheme 8



Another related experiment where comment is warranted is that performed with 2,5-dimethyl-2,4-hexadiene (**25**) [16]. Photo-oxygenation in methanol containing base gave the isomeric methoxyhydroperoxides **26**–**28**. These results were interpreted in terms of a primary perepoxide **29** which is intercepted by methanol attacking the three-membered ring or the terminal unsaturated carbon atom. In plain methanol the dioxetane **30** was also isolated and was thought to arise from the perepoxide **29**. This interpretation parallels our own, but neglects to mention the possibility of solvent incorporation with the hypothetical intermediate peroxide **31**, for which there is good precedent [17] (*Scheme 9*).

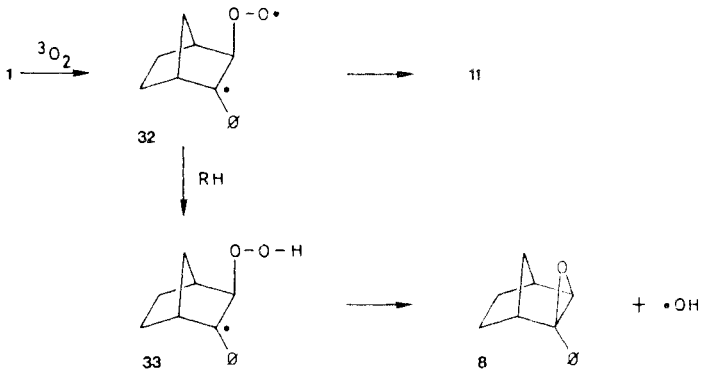
Scheme 9



The essential and significant difference between the singlet and triplet oxygen reactions is that in the latter only the epoxide **8** and the trimer **9** or **10** are formed. This difference can only be explained in terms of a radical mechanism. The first step is the addition of triplet oxygen to the double bond of 2-phenylnorbornene (**1**) to yield the tertiary benzylic radical **32**, which can then close to dioxetane **11** or ab-

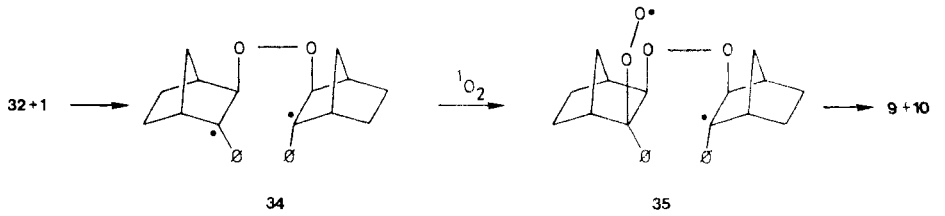
stract a hydrogen atom from the solvent. In more protic solvents this latter course becomes dominant. The resulting hydroperoxide radical **33** can then yield epoxide **8** by homolysis of the oxygen-oxygen bond (*Scheme 10*). It is interesting to note that

Scheme 10



epoxide forms at the expense of trimer (Table 2). Apart from closing to dioxetane **11**, the benzylic radical **32** has the opportunity to react with 2-phenylnorbornene to give the double benzylic radical **34**, which in turn can acquire a molecule of oxygen to form the peroxy radical **35**. Repetition of this process gives **9** and **10** (*Scheme 11*). This behaviour is not unexpected, in view of the propensity to dimerization already noted with the *exo*-2,3-epoxide of 2-phenylnorbornene [7].

Scheme 11



Such examples of auto-oxidation are uncommon. However, two have been recently described in which no radical initiator was present. Aerial oxidation of α,β-unsaturated ketones [18] and 3,4,6-triphenylbicyclo[3.1.0]hex-2-ene furnished the corresponding epoxides [5]. An older example is the auto-oxidation of α-styrene which is reported to give epoxide and some *Diels-Alder* adduct [19] [20].

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Experimental Part. – *General.* Gas liquid chromatography was carried out on a model F11 *Perkin-Elmer* instrument. IR. spectra were recorded on a model 402 *Perkin-Elmer* spectrometer (absorptions in cm^{-1}). Band intensities are characterized as very strong (*vs*), strong (*s*), medium (*m*) and weak (*w*). NMR. spectra were determined at 100 MHz on a model XL-100 *Varian*

instrument using CCl_4 or $CDCl_3$ as solvents. Chemical shifts are expressed as ppm with reference to tetramethylsilane (= 0 ppm). Signal intensities are reported in proton units (1H, 2H, *etc.*), multiplicities are expressed as singlet (*s*), doublet (*d*) and multiplet (*m*), the coupling constant J are given in Hz. Mass spectra were recorded on SM1 or EM600 *Varian* instruments. Mass numbers are given in *m/e*. 2-Phenylnorbornene (**1**) was purchased from *Aldrich Chemical Co.*

1. *Photo-oxygenation of* **1** *in acetonitrile.* 500 mg of **1** were dissolved in 5 ml of CH_3CN/methylene blue reagent. Following our standard photo-oxygenation procedure [6] absorption of 98 ml (150%) of oxygen was observed within 30 min. Filtration of the residue through a silica gel column gave 21 mg (10%) of the ketoaldehyde **2**. – NMR. ($CDCl_3$): 1.9–2.4 (*m*, 6H), 2.85 (*m*, 1H, H–C(3)); 3.85 (*m*, 1H, H–C(1)); 7.5 (*m*, 3H); 7.95 (*m*, 2H); 9.65 (*d*, 1H, J = 2.0, CHO). – IR. (CCl_4): 2880*m*, 2810*m*, 1720*s*, 1690*s*, 1455*s*, 700*s*. – MS.: 202 (M^+, 5.5), 174 (15), 154 (5.1), 133 (11), 123 (8.9), 105 (100), 97 (19), 77 (39).

Identical results were obtained in chloroform, carbon tetrachloride, and methylene chloride.

3-Formylcyclopentyl phenyl ketone (**2**) was also prepared by ozonolysis of **1** in methanol at –78°.

2. *Photo-oxygenation of* **1** *in methanol.* Photo-oxygenation of a solution of 740 mg (4.4 mmol) of **1** and 20 mg of 2,6-di-*t*-butyl-*p*-cresol in 6 ml of methanol/rose bengal at –10° was stopped after 60 min irradiation time, when 73 ml (3.3 mmol) of oxygen were absorbed. Column chromatography (silica gel, pentane/ether 9:1) permitted the isolation of four products, namely unreacted 2-phenylnorbornene (250 mg), the methoxyhydroperoxide **4** (425 mg, 63%), the ketoaldehyde **2** (40 mg, 7%), and a mixture of the two diepoxides **6** and **7** (20 mg, 3%); total yield of oxidized product: 73%.

endo-*2-Phenyl*-exo-*2-methoxy*-exo-*3-hydroperoxynorbornane* (**4**). – NMR. (CCl_4): 1.0–1.8 (*m*, 5H); 2.15 (*m*, 1H); 2.3 (*m*, 1H); 2.9 (*m*, 1H); 2.93 (*s*, 3H, O–CH_3); 4.33 (*d*, 1H, J = 1.6, H–C(3)); 7.1–7.7 (5 *m*, 5H); 9.4 (*s*, 1H, exchangeable with D_2O, O–O–H). – IR. (CCl_4): 3500*m*, 3400*s*, 2840*m*, 1490*m*, 1455*m*, 1080*s*, 705*s*, 665*m*. – MS.: 234 (M^+, 0), 216 (4), 174 (9), 147 (9), 136 (28.5), 105 (100), 91 (16.7), 77 (43).

endo-*2-Phenyl*-exo-*2-methoxy*-exo-*3-hydroxynorbornane* (**5**). Compound **5** was obtained in 85% yield by the $NaBH_4$ reduction of hydroperoxide **4** in methanol, and by the treatment of *endo*-2-phenyl-*exo*-2,3-epoxynorbornane with methanol at room temp. for a few minutes [16]. – NMR. ($CDCl_3$): 0.9–1.6 (*m*, 5H); 2.02 (*d*, 1H, J = 12, *anti* –H–C–(7); 2.08 (*m*, 1H); 2.76 (*m*, 1H); 2.88 (*s*, 3H, O–CH_3); 39 (*d*, 1H, J = 2.0, H–C(3)); 3.9 (*s*, 1H, exchangeable with D_2O, OH), 7.3 (*m*, 5H). – IR. (CCl_4): 3510*m*, 2880*m*, 1400*m*, 1130*m*, 1090*s*, 705*s*, 665*w*. No change in the position of the band at 3510 cm^{-1} (OH, assoc.) is observed on dilution (0.5M to 0.05M). – MS.: 218 (M^+, 10), 203 (52),186 (16), 142 (68), 121 (100), 105 (40), 91 (24), 77 (20).

endo-*2-*(anti-*1'4'-Epidioxy-5',6'-epoxycyclohex-2'-enyl*)-exo-*2,3-epoxynorbornane* (**6** and **7**). White crystals from CCl_4/pentane, m.p. 86–88°.

Major isomer. – NMR. ($CDCl_3$): 0.84 (*d*, 1H, J = 9.5, *anti* –H–C(7)); 1.2–1.9 (*m*, 5H); 2.6 (*m*, 1H, H–C(4)); 2.7 (*m*, 1H, H–C(1)); 3.4 (br. *s*, 1H, *endo*–H–C(3)); 3.44 (*d*, 1H, J = 5.0, H–C(6')); 3.66 (*t*, 1H, J = 5.0, H–C(5')); 5.06 (*m*, 1H, H–C(4')); 6.2–6.6 (*m*, 2H, H–C(2') and H–C(3')).

Minor isomer: NMR. ($CDCl_3$): The same chemical shifts and coupling constants are observed with the following exceptions: 2.7 (*m*, 1H, H–C(4)); 2.8 (*m*, 1H, H–C(1)); 3.3 (br. *s*, 1H, *endo* –H–C(3)); 3.7 and 3.8 (*AB*, 2H, H–C(5') and H–C(6')); 6.26 (*m*, 2H, H–C(2') and H–C(3')). – IR. (CCl_4): 2980*s*, 2885*m*, 1480*m*, 1460*m*, 1400*m*, 1379*s*, 1320*m*, 1275*m*, 1240*w*, 1145*w*, 1045*m*, 1010*m*, 1000*m*, 970*m*, 950*s*, 930*s*, 910–860*vs*. – MS.: 234 (M^+, 0), 202 (80), 174 (48), 173 (40), 145 (48), 133 (100), 105 (93), 81 (73), 79 (70).

3. *Photo-oxygenation of* **1** *in methylene chloride at* –78°. 100 mg (0.59 mmol) of 2-phenylnorbornene (**1**) in 3 ml of CH_2Cl_2/methylene blue reagent were photo-oxidized at –78°. After absorption of 6.6 ml (3.0 mmol) of oxygen, the oxidation was stopped and the mixture quenched by the addition of 3 ml of methanol. Thin layer chromatography (silica gel, hexane/ether/ethanol 6:3:1) revealed the presence of a trace of the hydroperoxide **4** besides ketoaldehyde **2** and unreacted olefine **1**.

4. *Auto-oxidation of* **1** *in methanol.* Freshly distilled 2-phenylnorbornene (0.5 g, 2.9 mmol) was dissolved in 5 ml of methanol and the solution stirred at room temp. in the dark under an atmo-

sphere of oxygen for 36 h, after which 66 ml (100%) of oxygen were absorbed. Filtration of the mixture afforded 263 mg (44%) of trimer **9** or **10** as a white precipitate. Column chromatography (silica gel, hexane/ether 95:5) of the residue gave 185 mg (29%) of **5** and 121 mg (20.5%) of **2**. Total yield 93%.

Trimer **9** or **10**: white solid, m.p. 66–67°. – NMR. ($CDCl_3$, poor resolution:) 0.5–4.0 (*m*, 9H); 6.8–8.1 (*m*, 5H). – IR. (KBr): 1720*s*, 1680*s*, 1600*m*, 1580*w*, 1450*s*, 1010*m*, 1000*m*, 965*m*, 762*s*, 700*s*. – MS.: 202 (1.3), 175 (3.1), 174 (23.8), 133 (15.6), 106 (8.1), 105 (100), 97 (2), 77 (28.1), 55 (4), 51 (44). – Molecular weight: 606 (measured on a *Perkin-Elmer* osmometer model 115).

$C_{39}H_{42}O_6$ (606.75) Calc. C 77.20 H 6.98% Found C 77.01 H 7.21%

5. *Auto-oxidation of* **1** *in aprotic medium.* When the auto-oxidation of **1** was carried out in aprotic solvents such as benzene, chloroform or acetonitrile, epoxide **8** was isolated instead of the methoxy-alcohol **5**. For the product distribution consult table 2.

endo-*2-Phenyl*-exo-*2,3-epoxynorbornane* (**8**). – NMR. ($CDCl_3$): 0.83 ($d \times m$, 1H, J = 10, *anti*-H—C(7)); 1.15–1.75 (*m*, 5H); 2.56 (*m*, 1H, H—C(4)); 2.82 (*m*, 1H, H—C(1)); 3.36 (*m*, 1H, H—C(3)); 7.3 (*s*, 5H.) – IR. (CCl_4): 3100*w*, 3080*w*, 2890*m*, 1610*w*, 1508*m*, 1480*w*, 1460*m*, 1270*s*, 970*w*, 950*m*, 870*m*, 700*s*, 675*w*.

6. *Thermal decomposition of trimer* **9** *or* **10**. A solution of 39.1 mg (0.065 mmol) of trimer **9** or **10** in 0.5 ml of $CDCl_3$ with 1,1,2,2-tetrachloroethane as internal standard was heated in a NMR. tube for 50 min at 45°. Comparison of the NMR. integration with an independently obtained calibration curve revealed the presence of 36.75 mg (0.18 mmol) of ketoaldehyde **2**. The thermal decomposition of one mol of trimer yields therefore 3 mol of ketoaldehyde **2**.

REFERENCES

[1] *F. A. Litt & A. Nickon*, 'Oxidation of Organic Compounds III', Advances in Chemistry series, No. 77, American Chemical Society, Washington D.C. 1968, p. 118.

[2] *C. W. Jefford & A. F. Boschung*, Helv. *57*, 2257 (1974).

[3] *A. P. Schaap & G. R. Faler*, J. Amer. chem. Soc. *95*, 3381 (1973).

[4] *K. Gollnick & G. O. Schenck* in '1,4-Cycloaddition Reactions', J. Hamer, Ed., Academic Press, New York, N.Y., 1967, p. 235; *M. Matsumoto & K. Kondo*, Tetrahedron Letters *1975*, 3935.

[5] *A. Padwa & L. Brodsky*, Tetrahedron Letters *1973*, 1045.

[6] *C. W. Jefford & A. F. Boschung*, Helv. *57*, 2242 (1974).

[7] *T. J. Gerteisen, D. C. Kleinfelter, G. C. Brophy & S. Sternhell*, Tetrahedron *27*, 3013 (1971).

[8] *D. P. Higley & R. W. Murray*, J. Amer. chem. Soc. *96*, 3330 (1974); *H. H. Wasserman & J. E. Van Verth*, ibid. *96*, 585 (1974); *R. H. Young & H. Hart*, Chem. Commun. *1967*, 827; *R. H. Young*, ibid. *1970*, 704.

[9] *F. G. Bordwell*, Accounts. chem. Res. *3*, 281 (1970); *C. W. Jefford, A. Sweeney & F. Delay*, Helv. *55*, 2214 (1972).

[10] *J. Boche & O. Runquist*, J. org. Chemistry *33*, 4285 (1968).

[11] *D. R. Kearns*, Chem Rev. *71*, 395 (1971).

[12] *P. Y. Bruice, G. J. Kasperek, T. C. Bruice, H. Yagi & D. M. Jerina*, J. Amer. chem. Soc. *95* 1674 (1973); *iidem*, ibid. *95*, 6041 (1973).

[13] *C. H. Foster & G. A. Berchtold*, J. org. Chemistry *40*, 3743 (1975).

[14] *G. Rio, D. Bricourt & L. Lacombe*, Tetrahedron *29*, 3553 (1973).

[15] *W. Fenical, D. R. Kearns & P. Radlick*, J. Amer. chem. Soc. *91*, 3396 (1969); *C. S. Foote, S. Mazur, P. A. Burns & D. Lerdal*, ibid. *95*, 586 (1973); *P. A. Burns, C. S. Foote & S. Mazur*, J. org. Chemistry *41*, 899 (1976).

[16] *N. M. Hasty & D. R. Kearns*, J. Amer. chem. Soc. *95*, 3380 (1973).

[17] *C. S. Foote, M. T. Wuesthoff, S. Wexler, I. G. Burstain, R. W. Denny, G. O. Schenk & K. H. Schulte-Elte*, Tetrahedron *23*, 2853 (1967); *J. Rigaudy, N. K. Cuong & J. F. Rothschild*, Tetrahedron Letters *1973*, 4439. *R. H. Young, N. Chinh & C. Mallon*, Ann. N.Y. Acad. Sci. *171*, 130 (1970).

[18] *H. Hart & P. B. Lavrick*, J. org. Chemistry *39*, 1794 (1974).

[19] *H. Hock & M. Siebert*, Chem. Ber. *87*, 546 (1954).

[20] *F. R. Mayo & A. A. Miller*, J. Amer. chem. Soc. *80*, 2480 (1958).