

SENSITIZED PHOTOOXIDATION OF cis-, AND trans-2-BORNYLIDENE-2-BORNANES:  
A FORMATION OF AN EPOXYCYCLOPROPANE DERIVATIVE  
DURING THE OXYGENATION<sup>1)</sup>

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Singlet oxygen oxidation of the title olefins produced camphor, derived from dioxetanes, and epoxides, reduction products of the intermediary peroxiranes, together with the same keto-aldehyde formed by a rearrangement of isomeric allylhydroperoxides. As a new type of product, an epoxycyclopropane derivative was produced in a stereospecific fashion from the trans-olefin.

Recently, the reaction of singlet oxygen with certain types of unconjugated olefins has become of interests. Thus, the dioxetanes and related epoxides were obtained from bisadamantylidene<sup>2)</sup> and bis-7,7'-norbornylidene,<sup>3)</sup> cage compounds. The formation of dioxetanes in this particular type of simple olefins could be interpreted in terms of a strained nature of the C=C bonds in geometrically rigid molecules. In fact, norbornene, a bridged olefin with a considerable strain, is also shown to give the dioxetane by the oxygenation.<sup>4)</sup> However, the previously studied olefins are structurally forbidden for the other typical mode of the reaction, the ene-process. Indeed, it should be noted that 2-methylnorbornene gave only allylhydroperoxides.<sup>5)</sup> Therefore, it will be worthwhile to examine the reaction with the cage-olefins having allylic hydrogens eligible to cause the ene-reaction. In this paper, we would like to describe the findings obtained from the reaction with such olefins, cis-, and trans-2-bornylidene-2-bornanes (2c and 2t) which could be prepared easily from d-camphor (1).<sup>6,7)</sup>

When a chloroform solution of 2c (1.7 g) and methylene blue was irradiated under oxygen atmosphere at room temperature by means of a 500 W tungsten lamp, a facile reaction has occurred to complete within 1 hr. The major product isolated by silica-gel column chromatography was 1 (63 % yield); the C=C cleavage was thus predominant in this case too.<sup>8)</sup> Second product (3, 0.4 %), colorless needles, mp 82-83°C, was identified to be the cis-anti-epoxide from the PMR [ $\delta_{\text{CDCl}_3}$ : 0.85(3H, s), 0.88(12H, s), and 0.97(3H, s).  $\delta_{\text{C}_6\text{D}_6}$ : 0.78(3H, s), 0.86(3H, s), 0.96(3H, s), and 1.11(3H, s)] evidences. 3 was prepared independently from 2c and m-chloroperbenzoic acid. Another product isolated was a keto-aldehyde, 4, a colorless oil in 10 % yield, which was auto-oxidized into the corresponding keto-carboxylic acid (5), colorless needles, mp 134-135.5°C [ $\delta_{\text{CDCl}_3}$ : 0.80(3H, s), 0.87(6H, s), 0.89(3H, s), 0.93(3H, s), and 1.09(3H, s).  $\nu$ : 3300-2300, 1685  $\text{cm}^{-1}$ .  $m/e$ : 320.2347 ( $\text{M}^+$ ). Calcd for  $\text{C}_{20}\text{H}_{32}\text{O}_3$ : 320.2352]. The analysis of its mass spectral fragmentations deduced the structure as depicted: Thus, occurrences of  $m/e$ : 165 ( $\text{C}_{11}\text{H}_{17}\text{O}$ , base peak), 155 ( $\text{C}_9\text{H}_{15}\text{O}_2$ ), 211 ( $\text{C}_{12}\text{H}_{19}\text{O}_3$ ), and 109 ( $\text{C}_8\text{H}_{13}$ ) ions, determined their compositions by high-resolution measurements, revealed two ways of fragmentations from the molecular ions as illustrated in Chart 2. Other features on the fragmentations observed are also consistent with the formulation.

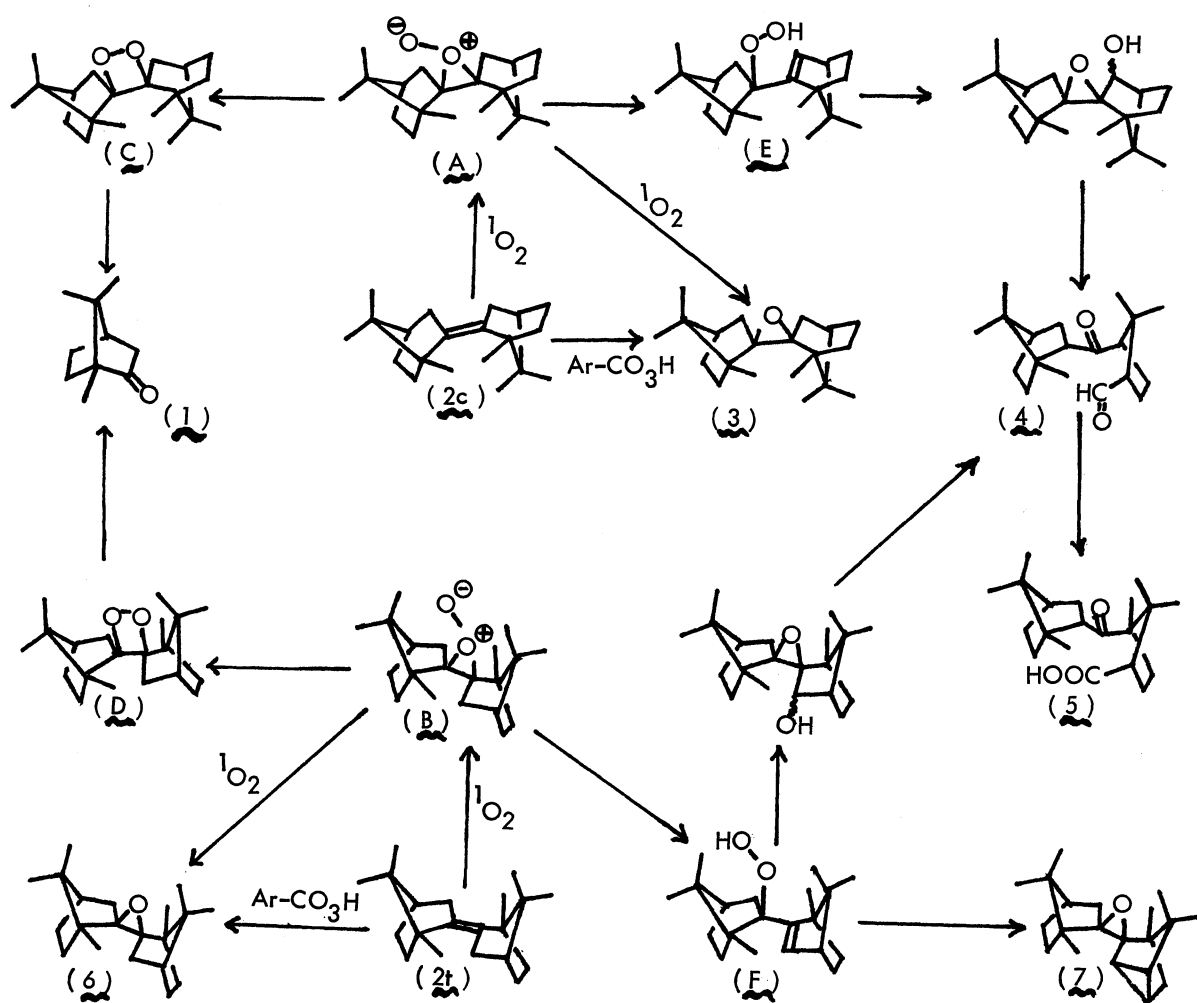


Fig. 1

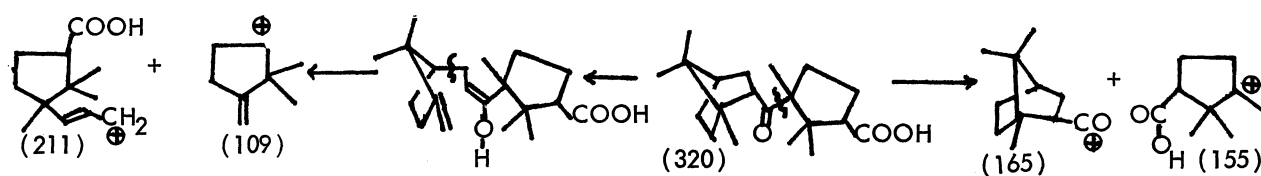


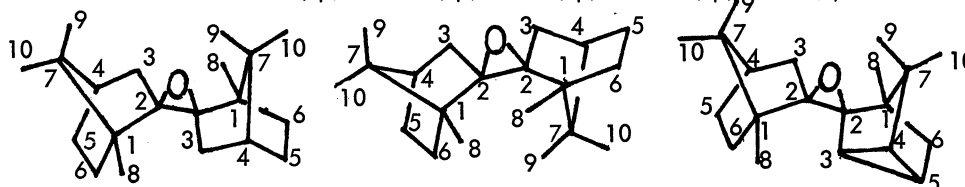
Fig. 2

On the other hand, when **2t** was irradiated under comparable conditions with **2c**, it has required 51 hr to complete the reaction. Four products detectable on a thin layer chromatogram were isolated and characterized. The major product was again **1**, formed in 57 %. Second product was another epoxide (**6**, 4 %), colorless needles, mp 132–134°C, which was identical with the sample prepared from **2t** and *m*-chloroperoxybenzoic acid. The PMR [ $\delta^{CDCl_3}$ : 0.72(6H, s), 0.84(6H, s), and 0.97(6H, s).  $\delta^{C_6D_6}$ : 0.78(6H, s), 0.79(6H, s), and 1.24(6H, s)] spectral findings revealed the retention of trans-syn-stereochemistry. Third product (**7**, 6 %), colorless needles, mp 129–131°C, was shown to be  $C_{20}H_{30}O$  by high-resolution mass spectral determination [ $m/e$ : 286.2256 ( $M^+$ ). Calcd: 286.2296]. The PMR [ $\delta^{CDCl_3}$ : 0.66(3H, s), 0.81(3H, s), 0.86(3H, s), 0.96(3H, s), 0.98(3H, s), and 0.99(3H, s)] evidences disclosed a loss of the molecular symmetry. The IR spectrum revealed no  $\nu_{OH}$  but  $\delta_{C-O-C}$  at 915  $cm^{-1}$ .

Hence, 7 must be a dehydro-epoxide. The intactness of one of the bornane-parts was confirmed by occurrences of same  $C_{11}H_{16}O$  (a ketene)- and  $C_{10}H_{16}O$  (camphor)-ions as well as  $C_{10}H_{16}$  (bornylidene)- and  $C_{10}H_{17}$  (bornyl)-ions similarly to that of 6. Further evidences on the structure were obtained by the CMR spectral comparisons with those of 3 and 6. The assignments by an aid of off-resonance experiments were deduced as listed in Table 1.<sup>9)</sup>

Table 1. The CMR Figures of Epoxides 3, 6, and 7

Compounds :	<u>6</u>	<u>3</u>	<u>7</u>			
Chemical Shifts for :	A	A	B	A	C	
No. of Carbon	1	48.6 ( s )	49.3 ( s )	52.0 ( s )	48.0 ( s )	43.2 ( s )
	2	71.2 ( s )	74.6 ( s )	79.3 ( s )	76.9 ( s )	82.6 ( s )
	3	38.7 ( t )	41.3 ( t )	43.0 ( t )	39.7 ( t )	28.8 ( d )
	4	44.9 ( d )	44.5 ( d )	41.7 ( d )	44.6 ( d )	15.4 ( d )
	5	28.1 ( t )	28.6 ( t )	27.6 ( t )	26.9 ( t )	13.6 ( d )
	6	30.4 ( t )	30.8 ( t )	31.8 ( t )	31.7 ( t )	37.9 ( t )
	7	48.6 ( s )	49.0 ( s )	48.0 ( s )	47.3 ( s )	52.0 ( s )
	8	11.1 ( q )	12.8 ( q )	16.0 ( q )	13.3 ( q )	8.9 ( q )
	9	19.7 ( q )	20.0 ( q )	20.7 ( q )	20.7 ( q )	22.0 ( q )
	10	19.4 ( q )	19.7 ( q )	20.2 ( q )	20.5 ( q )	21.0 ( q )



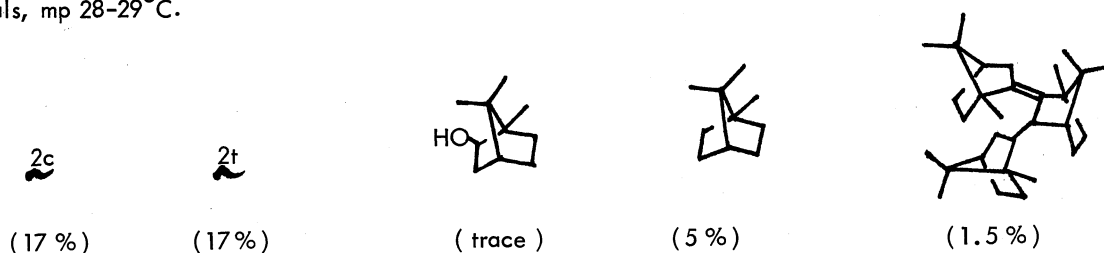
Dividing into two  $C_{10}$ -moieties respectively, these epoxides should be expressed as A-A(6), A-B(3), and A-C(7) according to relative geometries of the oxygen function. As could be seen in the table, the signals ascribable to carbons of the A-moiety exhibited a close resemblance in each other, it was then possible to assign the other carbon signals of the molecules, B-part of 3, and C-part of 7. Clearly, the signals shifted to up-field ( $C_{3C}$ ,  $C_{4C}$  and  $C_{5C}$ ) are attributable to the formation of a cyclopropane ring.<sup>10)</sup> Observed signals for other carbons also agree with expectations. Independently, an evidence for the formula was provided also by the mass spectral analysis of 7 which yielded  $C_{17}H_{25}O$  (M-acetylene-Me)-,  $C_{11}H_{14}O$  (dehydroketene)-, and  $C_{10}H_{14}O$  (dehydrocamphor)-ions. The remaining product (10%) was identified to be 4 by direct comparisons with authentic sample prepared from 2c. The stereochemistry of 6 and 7 was deduced from the mechanism of stereospecific formation of 7 from 2t. As depicted, the cyclopropane ring closure must be occurred by the anti-parallel, probably in concerted, dehydration of the intermediate allyhydroperoxide(F). This requires the  $\beta$ -oxygenation unless C-C bond rotation has occurred to cause a conversion of F into E which should be formed from 2c. This is obviously inconsistent with the fact that 2c does not afford 7. The stereochemistry deduced is thus reverse to the original assignment reported by Wynberg *et al.*<sup>6, 11)</sup> On the other hand, 4, whose formation can be visualized as shown, has been obtained *via* an epimerization step to result in the same compound from the different allyhydroperoxides.

Consequently, 2c and 2t are capable to give 1 predominantly through dioxetane intermediates on the reaction with singlet oxygen, and it is interesting to note that the yields of 1 and 4 are similar for both olefins, but the yields of epoxides 3 and 6 are markedly different. This contrast should mean that peroxirane A, derived from 2c, would have shorter mean life than the other peroxirane B derived from 2t, and thus would quickly rearrange

into dioxetane C and allylhydroperoxide E prior to intermolecular reduction with another singlet oxygen<sup>12)</sup> to result in 3.<sup>13)</sup> According to inspections by a molecular model, 2c, having a confronted orientation for two bridge-head methyl groups, is more strained than 2t,<sup>6)</sup> and for both series, the strains increase in order of olefins  $\longrightarrow$  peroxiranes  $\longrightarrow$  dioxetanes. Since 2c is more reactive than 2t towards the oxygenation, observed lower yield of 3 from 2c should not be a result of steric hindrance of A against a further attack of singlet oxygen, as a reducing agent, but should be due to a decrease of life time for more strained peroxirane A. Finally, it seems to be no precedence for a cyclopropane ring formation during the oxygenation. We are currently studying to include this process in a terpenoid synthesis.

#### References and Notes

- 1) A part of this study has been presented at 19th Symposium on Terpenes, Essential Oils, and Aromatic Chemistry (Oct. 1975, Fukuoka). Cf. Abstract Papers, p. 166.
- 2) A. P. Schaap and G. R. Faler, J. Amer. Chem. Soc., 95, 3382 (1973).
- 3) P. D. Bartlett and M. S. Ho, *ibid.*, 96, 628 (1974).
- 4) C. W. Jefford and A. F. Boschung, Helv. Chim. Acta, 57, 2257 (1974).
- 5) C. W. Jefford, M. H. Laffer, and A. F. Boschung, J. Amer. Chem. Soc., 94, 8904 (1972).
- 6) H. Wynberg, K. Lammertsma, and L. A. Hulshof, Tetrahedron Lett., [43], 3749 (1975).
- 7) By an independent preparation of the olefins with the same procedure, we obtained a parallel result with those of Wynberg *et al.*. But there are some minor discrepancies on accompanied by-products; in our hands, following products were isolated and characterized. Originally, 2c was described as an oil, but it was low melting crystals, mp 28-29°C.



- 8) The yields described for 1 were based on the glc analyses, and others are those of actually isolated.
- 9) We thank Mr. K. Fujita, JEOL Co., Akishima, for elaborate measurements of the CMR spectra.
- 10) J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, J. Amer. Chem. Soc., 92, 7107 (1970).
- 11) We have no knowledge on the evidence of Wynberg's assignment. At least on stereo-model considerations, it does not seem to favor the  $\alpha$ -epoxidation. Spectral data alone could not distinguish the stereochemistry.
- 12) M. J. S. Dewar, A. C. Griffin, W. Thiel, and I. J. Turchi, J. Amer. Chem. Soc., 97, 4439 (1975).
- 13) We have observed a remarkable time-lag in the formation of 1 from 2c. In a controlled irradiation in  $\text{CHCl}_3$ , 2c has consumed after 15 min, but the yield of 1 at this time was analyzed to be 23 % and was then gradually increased to show 63 % after 30 min. On the other hand, a peak with a certain integration was detected after 15 min in less volatile regions of chromatograms. Although the transient species responsible for the glc peak were unsuccessful to be isolated or characterized spectroscopically, it is highly probable to be the dioxetane C. If so, this would constitute an experimental proof for incapability of dioxetanes to epoxide formation by singlet oxygen reduction.

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