Mechanism of the Direct Reaction of Phosphite Ozonides with Olefins

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The direct reaction of triphenyl phosphite ozonide (TPPO) with olefins, occurring at low temperatures where no thermal generation of singlet oxygen occurs, is observed in identical fashion with a caged-ring and two *o*-phenylene phosphite ozonides whose thermal generation of singlet oxygen is very slow compared to TPPO. Biadamantylidene, which is quite reactive toward singlet oxygen, appears totally hindered against the direct reaction with TPPO. In the case of Δ^2-dihydropyran the direct reaction contrasts strongly with the behavior toward singlet oxygen in that (1) ene reaction is only one-tenth as great as dioxetane formation, (2) the importance of ene reaction is not a function of solvent polarity, and (3) ene reaction is inhibited by free-radical scavengers. In the case of tricyclopropylethylene, the formation of allylic hydroperoxides in the case of singlet oxygen is replaced in the direct TPPO reaction by cleavage to ketone and aldehyde under conditions where the hydroperoxides are stable and hence cannot be intermediates. The direct reaction of TPPO with 1,2-dimethylcyclohexene and 2-methyl-2-butene gave mixtures of ene products similar to those from singlet oxygen and, in the case of the former hydrocarbon, quite different from the product of chain oxidation. Dabco, tetramethyl-*p*-phenylenediamine, and other tertiary amines rapidly decompose phosphite ozonides to phosphate and ground-state oxygen, with evidence of electron transfer from the amines. In this and in the direct oxygenation of dihydropyran, the ^{31}P NMR signal goes directly from 63 to 17 ppm, showing that there is no detectable intermediate state of phosphorus between TPPO and phosphate. The facts are accommodated by a mechanism involving initial bond formation between the olefin and the center oxygen atom of the ozonide, with chemical and sterochemical sequels which are discussed. The freezing point of chloroform is depressed to the same extent by TPPO as by triphenyl phosphate, showing that TPPO is monomeric.

Triphenyl phosphite ozonide (TPPO) occupies an important place among agents for thermal generation of singlet oxygen.[1] Its use, however, presents an interesting complication: at low temperatures, e.g., −70 °C, where TPPO is thermally stable, it is capable of reacting directly with certain olefins to donate O_2 and give products often identical with those of singlet oxygen itself. Although such results can be confusing, the criterion for the "direct reaction" is clear-cut: if, under the conditions of the experiment (temperature and time) TPPO is thermally stable, then any reaction that it gives with an olefin is initiated by an encounter between that olefin and TPPO and not by the prior formation of singlet oxygen.[2]

In addition to the mechanistic feature of direct attack, the reaction shows a selectivity between substrates quite different from that of singlet oxygen,[2] often shows different relative rates of dioxetane and hydroperoxide formation, and shows clear evidence of step-wise character as opposed to the concerted nature of singlet oxygen attack: *cis*- and *trans*-diethoxyethylene react stereospecifically with singlet oxygen,[3] but at low temperature each isomer gives with TPPO a mixture of *cis*- and *trans*-dioxetanes.[4]

These observations have suggested a number of experiments bearing on the mechanism. We here report a series of new observations as follows. (1) Triphenyl phosphite ozonide is monomeric. (2) There is no intermediate in the direct reaction that can be detected by ^{31}P NMR on the way from TPPO to the product, triphenyl phosphate. (3) *o*-Phenylene and cage-ring phosphite ozonides are as reactive in the direct reaction as TPPO (no Stephenson effect).[7] (4) Biadamantylidene is inert to the direct reaction, although it is a reactive substrate for free singlet oxygen. (5) The direct ene reaction of TPPO leading to allylic hydroperoxides is easily inhibited by free-radical scavengers. (6) Tricyclopropylethylene in direct reaction with TPPO undergoes oxidative cleavage at the double bond. This is not a Hock cleavage of an allylic hydroperoxide.

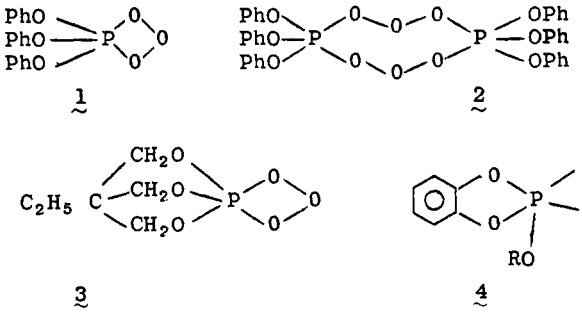
Table I. Freezing Point Depression by TPPO in Chloroform

solute	no. of points	av fp, °C	md[c]	fpd,[a] °C
none	5	−60.98	0.10	0
TPPO[b]	5	−63.52	0.22	2.54 ± 0.32
TPPO[b]	4	−63.65	0.10	2.67 ± 0.20
$(PhO)_3PO$[b] (product)	3	−63.67	0.11	2.69 ± 0.21
$(PhO)_3PO$[b] (control)	5	−63.98	0.14	3.00 ± 0.24

[a] Freezing point depression; uncertainty taken as the sum of the mean deviations for solution and for pure chloroform. [b] There was 4.00 mmol of solute/10 g of solvent. [c] Mean deviation.

Results

Structure of TPPO. Thermochemical considerations and analogy with known ozonides suggest the four-membered ring 1 as the most probable monomeric structure for



a. R=C_2H_5 b. R=Ph

triphenyl phosphite ozonide, a structure consistent with the ^{31}P chemical shift of +63 ppm, normal for a phosphorane.[5] This shift, however, would be equally appro-

(1) For a review of the thermal generation on singlet oxygen see: Murray, R. W. "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; Chapter 3.
(2) (a) Bartlett, P. D.; Mendenhall, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 210. (b) Bartlett, P. D.; Mendenhall, G. D.; Schaap, A. P. *Ann. N.Y. Acad. Sci.* **1970**, *171*, 79.
(3) Bartlett, P. D.; Schaap, A. P. *J. Am. Chem. Soc.* **1970**, *92*, 3223.
(4) Schaap, A. P.; Bartlett, P. D. *J. Am. Chem. Soc.* **1970**, *92*, 6055.
(5) Thompson, Q. E. *J. Am. Chem. Soc.* **1961**, *83*, 845.

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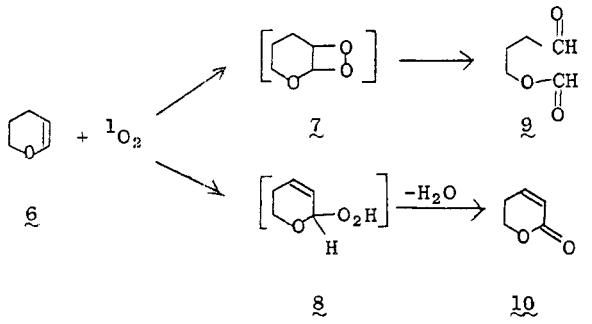
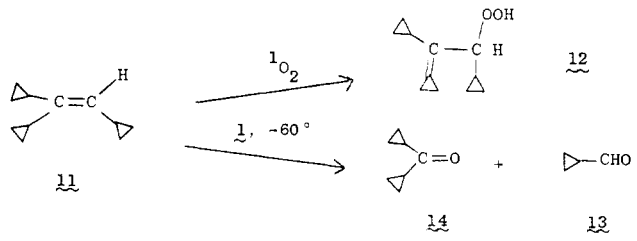
Scheme I

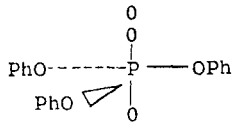


Scheme II



priate for a cyclic dimer **2**, which might be favored by lower ring strain.[6] To settle this point, we ran a series of cooling curves of a solution of TPPO in chloroform before and after complete thermal decomposition to oxygen and triphenyl phosphate, leading to the freezing point depressions shown in Table I. The conclusion is that TPPO is monomeric, with little if any dimer present in a 0.6 M solution in chloroform at −63.5 °C.

Stephenson and McClure[7] observed that phosphite ozonides, such as **3** and **4**, in which the pseudorotations expected about trigonal bipyramidyl phosphorus are hindered, were much slower in evolving singlet oxygen than was TPPO; these authors suggested that the evolution of singlet oxygen occurred by way of the rearranged species **5** in which one O–O bond was already broken and that it



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was the formation of this molecule, with its implied requirement of apical O and O_2 groups and equatorial phenoxy, which was hindered in the caged or *o*-phenylene phosphite ozonides. It may be expected that in the direct reaction too the initiating step will involve the breaking of an O–O bond. We therefore compared the reactions of **3**, **4a**, and **4b** toward tetramethylethylene with that of TPPO, all at −70 °C; as followed by NMR, the rates of the four direct reactions were all very similar. Thus the hindrance imposed by caged or small rings on the evolution of singlet oxygen does not operate in the direct oxygenation reaction of olefins by phosphite ozonides. The implication of this for the mechanism is discussed below.

Δ^2-Dihydropyran. This cyclic enol ether is an interesting substrate for the direct reaction with TPPO because it gives both dioxetane and allylic hydroperoxide in measurable amounts in its reaction with singlet oxygen.[2b] The oxygenation products undergo thermal conversion as shown in Scheme I into aldehydoformate **9** and dihydropyrone **10**, which are stable in VPC analysis. The ratio of **9** to **10** obtained with singlet oxygen varied with the polarity of the solvent over a 59-fold range, polar solvents favoring dioxetane formation.[2b]

Dihydropyran was allowed to react at −60 °C with TPPO in methylene chloride, acetone, and *n*-butyronitrile without any notable difference in rate among the three solvents. In a 5-h reaction time, **9** and **10** were formed in the ratio of 10:1. The ene-derived product **10**, however, was absent in reactions carried out in the presence of the free-radical scavenger di-*tert*-butyl-*p*-cresol. Thus the direct reaction lacks the polar solvent dependence noted for the concerted reaction of singlet oxygen, while it gives evidence of a radical-like intermediate.

Tricyclopropylethylene (11). The interest of this hydrocarbon in the present connection is that in dye-sensitized photooxidation[8] it yields the ene product 1,2-dicyclopropyl-1-cyclopropylidene-2-(hydroperoxy)ethane (**12**) as the only detectable product by NMR (Scheme II). When **11** was treated for 24 h with TPPO at −60 °C, on the other hand, the product observed by VPC consisted of equal amounts of cyclopropylcarboxaldehyde (**13**) and dicyclopropyl ketone (**14**) and no ene product. A control experiment showed that the ene product **12**, under the conditions of the reaction, does not undergo Hock cleavage and hence cannot be involved in the formation of the carbonyl products.

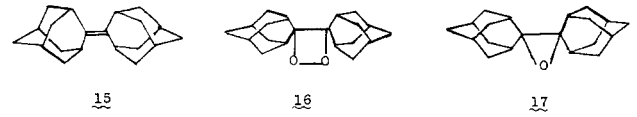
In the cases of both dihydropyran and tricyclopropylethylene, the dioxetane precursor of the carbonyl cleavage products was never isolated. Therefore, the following two experiments were carried out to test for its occurrence.

A solution containing equal amounts of TPPO and dihydropyran in dichloromethane was allowed to stand at −78 °C for 5.5 h. A small amount of 9,10-dibromoanthracene (DBA) was then added, and the mixture was allowed to warm to room temperature in the dark. A strong blue luminescence, characteristic of fluorescing 9,10-dibromoanthracene, was observed. A control experiment showed that TPPO alone with DBA did not give this luminescence.

Similarly, equivalent amounts of TPPO and tricyclopropylethylene were allowed to stand in the presence of an equivalent amount of 2,6-di-*tert*-butyl-*p*-cresol for 24 h. Addition of DBA and warming in the dark again resulted in strong blue luminescence.

These experiments show that the carbonyl products in these direct reactions were formed in an excited state *after* the direct reaction with TPPO. This is characteristic of carbonyl fragments from the cleavage of a dioxetane; the alternative process, cleavage of a linear polyperoxide, has not been observed to produce such excited products.

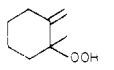
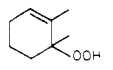
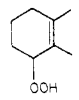
Biadamantylidene. With singlet oxygen, biadamantylidene (**15**) reacts with great efficiency to yield the dioxetane **16**[8] and with certain sensitizers results in the



concomitant formation of epoxide **17**.[9] Direct treatment of **15** with a 25-fold excess of TPPO in acetone at −60 °C for 24 h failed to produce any reaction. However, a solution warmed to room temperature over a period of 30 min

(6) Mendenhall, G. D., private communication
(7) Stephenson, L. M.; McClure, D. E. *J. Am. Chem. Soc.* **1973**, *95*, 3074.
(8) Rousseau, G.; Le Perchec, P.; Conia, J. M.; *Tetrahedron* **1978**, *34*, 3475.
(9) (a) Wieringa, J. H.; Strating, J.; Wynberg, H.; Adam, W. *Tetrahedron Lett.* **1972**, 169. (b) Jefford, C. W.; Boschung, A. F. *Helv. Chim. Acta*, **1977**, *60*, 2673.

Table II. Products of Oxidation of 1,2-Dimethylcyclohexene

method of oxidation	products		
			
radical autoxidation[a]	6	39	54
radical autoxidation[b]	5	34	61
photooxygenation[a]	89	11	0
photooxygenation[c]	85	15	0
TPPO[d,e,i] (1)	95	5	0
3[f,i]	95	5	0
4a[g,i]	95	5	0
4b[h,i]	95	5	0

[a] Reference 10. [b] Free-radical initiator AIBN. [c] Methylene blue sensitization. [d] At −78 °C, total of seven runs, one run with 2,6-di-*tert*-butyl-*p*-cresol added, one run with 2,2-diphenyl-1-picrylhydrazyl added. [e] Similar results have also been reported; see ref 2 and 17. [f] At −60 °C, total of three runs. [g] At −60 °C, total of two runs. [h] At −78 °C, total of two runs, one run with 2,6-di-*tert*-butyl-*p*-cresol added. [i] Direct reaction.

Table III. Direct Reaction with 2-Methyl-2-butene

method of oxidation	products	
		
photooxygenation[a]	48	52
TPPO[b,d]	54	46
TPPO[c,d]	52	48
3[c,d]	36	64

[a] Reference 10. [b] Reference 18. [c] −78 °C, 5 h. [d] Direct reaction.

yielded **16** and **17** in the ratio 79:21.

Direct Reaction of Phosphite Ozonides with 1,2-Dimethylcyclohexene. 1,2-Dimethylcyclohexene has been used to advantage to contrast different mechanisms of olefin oxidation.[10] Table II shows that the products from TPPO and the caged and *o*-phenylene phosphite ozonides with this olefin are all alike and bear much more resemblance to the singlet oxygen products than to the products of radical-initiated autoxidation.

2-Methyl-2-butene. With 2-methyl-2-butene the direct reaction of TPPO leads to products similar to those of singlet oxygen, and the cage-ring ozonide **3** differs from it only a little in the distribution between the isomeric hydroperoxides. As with singlet oxygen, there is no sign of a dioxetane or an oxidative cleavage, unlike the case of tricyclopropylethylene. The results are shown in Table III.

Effects of Amines. The direct reactions of phosphite ozonides were always quenched before workup by the addition of either Dabco or triethylamine. During the quenching, in addition to vigorous gas evolution, a pink color was observed when Dabco was the quencher and a yellow color when triethylamine was used. The color persisted for about 1 min and then faded away. To obtain clear evidence of the involvement of electron transfer in the quenching process, we added *N,N*-tetramethyl-*p*-phenylenediamine (TMPD) to solutions containing either **1** or **3**. In both instances the solutions immediately turned the dark color of Wurster's blue. This color persisted for hours and then gradually faded. Observation by ^{31}P NMR showed that when TMPD was mixed in, the TPPO absorption (63 ppm downfield from 85% H_3PO_4) immediately disappeared and was replaced by the triphenyl phosphate absorption (17 ppm downfield from the standard). Thus upon accepting an electron from the diamine, TPPO is irreversibly decomposed to triphenyl phosphate. Superoxide anion is presumably the other product, which does not produce oxygenation of the substrates.

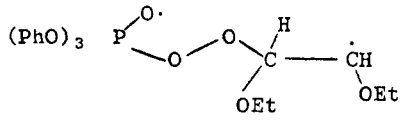
This direct change in the ^{31}P NMR signal from 63 to 17 ppm was also observed in the unquenched direct reaction with dihydropyran described above.

An attempt to observe the Wurster cation radical by ESR failed, possibly because of the oxygen present in the solution. From this observation it is possible that there is no long-lived intermediate in the direct reaction on the way from the phosphite ozonide to the product phosphate.

Discussion

If the direct reaction is initiated by attack on the double bond by the middle oxygen atom of the ozonide, it can be understood why the site selectivity on the olefin resembles that by molecular oxygen, even though the product of this step is a biradical. It also becomes understandable why biadamantylidene shows the greatest resistance to the direct reaction of any olefin yet investigated: the rest of the TPPO molecule is rigidly coupled to the reacting oxygen atom and can produce serious hindrance with the adamantane bridges even though these allow free access to an O_2 molecule.

The intermediacy of biradicals such as **18** affords opportunity for the internal rotation which makes the dioxetane formation nonstereospecific; this is true whether the formation of dioxetane **19** and phosphate is by internal displacement of phosphate from **18** or by way of the peroxy biradical **20**.



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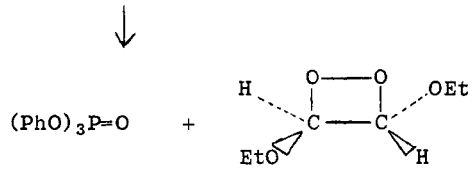

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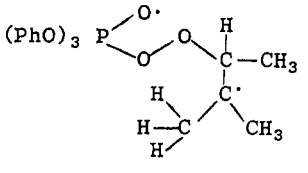

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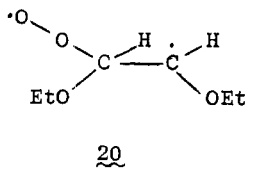

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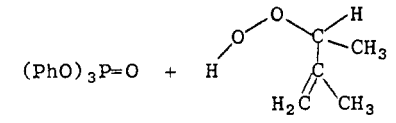
The two cases in which the product of the direct reaction differs the most from that of the singlet oxygen reaction are dihydropyran and tricyclopropylethylene, both yielding much more dioxetane addition in the direct reaction than in the singlet oxygen reaction. The difference in temperature between the two methods could contribute to this product difference, but this could not explain the great difference in polar solvent sensitivity in the case of dihydropyran between the two reactions. A true biradical should be relatively insensitive to polar effects. Tritium isotope effects indicate[11] that the transition state in singlet

(10) Foote, C. S. *Acc. Chem. Res.* **1968**, *1*, 104.

oxygen reaction with 4-methyl-Δ^2-dihydropyran resembles a perepoxide (**24**) with enough polarization to affect its



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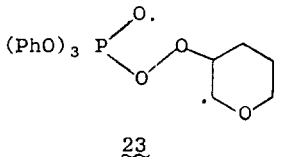

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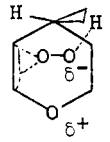

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energy profile in polar media. The essential difference between this and the biradical **23** in the direct reaction could be that in **23** the new C–O bond is localized at C-3 for best delocalization of the odd electron at C-2; this biradical cannot yield any allylic hyperperoxide, and the exclusive formation of dioxetane is to be expected.

The most probable reason for the lack of a Stephenson effect[7] with the *o*-phenylene and cage-ring phosphite ozonides is that ring opening to structures such as **5** has a higher activation energy than the bimolecular formation of **18** and plays no part in any reactions in the low-temperature range.

Since the electron-donating amines are all quenchers for the direct reactions of phosphite ozonides, it is clear that electron transfer plays no initiating role in the reaction. On the other hand, despite the frequent functioning of hindered phenols as free-radical scavengers, their function here may be that of selective electron donors rather than proton donors to the intermediates of the **23** type.[12]

The reasons which we have invoked for depressed hydroperoxide formation in the direct reaction with dihydropyran cannot apply to tricyclopropylethylene, where the preferred point of free-radical attack on the double bond is the correct one for forming the allylic hydroperoxide which results from singlet oxygen. Frimer and Roth[16] favor the view that with cyclopropylethylenes the singlet oxygen ene reaction is fully concerted. It is quite reasonable that the biradical corresponding to **21** in the case of tricyclopropylethylene or its triphenyl phosphate elimination product will lead more easily to dioxetane than to allylic hydroperoxide. The oxygen copolymerization mechanism, invoked by Frimer and Roth to explain the oxidative cleavage of 1,1-dicyclopropylethylene by $^1O_2$, is less readily adapted to explaining the direct reaction with TPPO. The present chemiluminescent experiments show that, at least in the case of tricyclopropylethylene, the cleavage products arise from a dioxetane.

Experimental Section

Solvents were all spectrograde and were either freshly distilled or taken from a freshly opened bottle. Dihydropyran, 2-methyl-2-butene, and 2,3-dimethyl-2-butene were commercial products and were redistilled before use. *N,N*-Tetramethyl-*p*-phenylenediamine was vacuum sublimed before use. Triphenyl phosphite was purified by being washed with aqueous base, dried, and fractionally vacuum distilled. 4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane was obtained from Strem Chemicals, Inc. Its purity was verified by VPC analysis. *o*-Phenylene phenyl phosphite and *o*-phenylene ethyl phosphite were kindly provided by Dr. D. R. Speth. Tricyclopropylethylene was prepared by Wittig reaction of triphenylphosphonium cyclopropylmethylide[13] and dicyclopropyl ketone. It showed the following: NMR δ 0.10–1.00 (m, 13 H), 1.40–1.84 (m, 2 H), 4.40 (d, 1 H); bp 40 °C (1 mm) [lit.[11] bp 102 °C (25 mm)]. Biadamantylidene was prepared from 2-adamantanone and McMurry reagent.[14] ^1H NMR spectra were taken on a JEOL MH-100 spectrometer. ^{31}P NMR spectra were taken on a JEOL FX-60. VPC analyses were performed on a Perkin-Elmer Sigma 3 chromatograph. Ozonolyses were done with a Welsbach ozonator.

Preparation of Phosphite Ozonides. A 50-mL, three-necked, round-bottomed flask with a stirring bar and an addition funnel with a drying tube and equipped for passage of dried gas was immersed in a bath cooled to −78 °C. The flask was first flushed with nitrogen, and then 10 mL of dichloromethane was added. Ozone was bubbled into this solvent until the solution acquired a dark blue color. A solution of the appropriate phosphite (4 mmol in 10 mL of dichloromethane) was slowly added to this ozone-saturated solution through the addition funnel at such a rate that the blue color was always present in the solution. After the addition of phosphite solution was complete, the phosphite ozonide solution was flushed with nitrogen for 1 h at −78 °C to remove the excess ozone. Such ozonide solutions can also be prepared in the same way in acetone or *n*-butyronitrile and, at temperatures as high as −55 °C, in chloroform.

Reactions of Δ^2-Dihydropyran and TPPO. A solution containing 4 mmol of dihydropyran in 10 mL of dichloromethane cooled to −78 °C was added to 20 mL of freshly prepared 0.2 M TPPO solution in dichloromethane at −78 °C. The mixture was stirred at −78 °C for 5 h and then quenched by the addition of a small amount of Dabco (1,4-diazabicyclo[2.2.2]octane) in dichloromethane. The mixture was analyzed by VPC (6-ft column of Carbowax 20-M, 120 °C). The reaction was about 50% complete. The two oxygenation products on VPC yielded 4-formoxybutyraldehyde and Δ^3-dihydropyran-2-one in a 10:1 ratio which were identified by comparison of their NMR spectra with those of authentic samples prepared from singlet oxygen and by the known spectral data.[15] The reactions performed in acetone and in *n*-butyronitrile gave the same composition, in contrast to photooxygenation.[2b]

Reactions of Tricyclopropylethylene and TPPO. A solution containing 444 mg (3 mmol) of tricyclopropylethylene in 5 mL of dichloromethane cooled to −78 °C was added to 15 mL of a 0.2 M TPPO solution in dichloromethane at −78 °C. The mixture was then stirred at −60 °C for 24 h. The mixture was quenched by the addition of a small amount of Dabco. The NMR spectrum showed a small doublet at δ 8.64, indicating cyclopropyl carboxaldehyde. Except for aromatic protons and the vinylic proton (δ 4.42), no other proton signals appeared below 2 ppm. VPC (10 ft, 5% Se-30, 120 °C) showed cyclopropylcarboxaldehyde and dicyclopropyl ketone formed in equimolar amounts. The reaction was 50% complete. Preparative TLC (silica gel, hexane) separated 68.5 mg of dicyclopropyl ketone (21%).

Reaction of Tricyclopropylethylene with Singlet Oxygen. In contrast to the TPPO direct reaction, the reaction of tricyclopropylethylene with singlet oxygen under methylene blue sensitization with a 500-W projection lamp resulted in exclusive formation of 1,2-dicyclopropyl-1-cyclopropylidene-2-(hydroperoxy)ethane (**12**) which was identified by a doublet in the NMR spectrum (δ 3.81, methine proton). Upon treatment of the reaction mixture with triphenylphosphine, the doublet was shifted upfield to δ 3.57 (J = 8 Hz), and a new broad peak appeared at δ 2.85 (OH). VPC analysis of this mixture showed neither dicyclopropyl ketone nor cyclopropylcarboxaldehyde.

Reactions of Biadamantylidene with TPPO. A solution containing 10 mg (0.04 mmol) of biadamantylidene in 10 mL of

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acetone, cooled to -78 °C, was added to 10 mL of a 0.1 M solution of TPPO in acetone at -78 °C. The reaction mixture was stirred at -60 °C for 24 h and then quenched by triethylamine. VPC analysis showed that no biadamantylidene dioxetane or epoxide had been formed. A control experiment in which the mixture was warmed from -78 °C to room temperature in a period of 30 min gave 79% dioxetane and 21% epoxide by VPC analysis (6 ft, 5% SE-30; 150 °C for 5 min, linear programming with the temperature rising at 20 °C/min to 220 °C, and then held constant). The reaction gave the same results in dichloromethane.

Molecular Weight of TPPO. It was found that freezing point depressions in chloroform could be determined within the precision shown in Table I by using the apparatus already set up for the low-temperature experiments and a low-temperature thermometer with 1 °C graduations. For each solution 3-5 cooling curves were run, each with about ten points, and extrapolated to yield a freezing point reading. The freezing point of pure chloroform was thus determined by averaging the values -61.1, -61.1, -61.0, -60.9, and -60.8 °C (average -60.98, mean deviation 0.104 °C). A solution of TPPO prepared from 3.72 g (12.0 mmol) of triphenyl phosphite in 30.00 g of chloroform at -55 °C, with the usual precautions to avoid any momentary excess of phosphite, yielded from five cooling curves the freezing points -63.8, -63.5, -63.7, -63.6, and -63.0 °C (average -63.52, mean deviation 0.216 °C). If the deviant last point is excluded, the average of the other four is -63.65 °C, and the mean deviation is 0.10, making the deviation of the last point 6.5 times the mean of the others. Both averages are shown in Table I.

When the TPPO solution was warmed, gas evolution was observed at -30 °C, which became very vigorous at -10 °C. After the gas evolution had ceased, the solution was again cooled, and three more cooling curves were determined, leading to mp -63.5, -63.8, and -63.7 °C (average -63.67 °C, mean deviation 0.11 °C). Thus the freezing point depression produced by TPPO was 94% of that produced by the product phosphate, or 99% if the final point for TPPO is rejected.

The freezing point depression by the product of the TPPO decomposition was checked with a solution of triphenyl phosphate (1.30 g, 4.0 mmol) in 10 g of chloroform. The five cooling curves gave freezing points of -63.8, -64.1, -64.2, -64.0, and -63.8 °C (average -63.98 °C, mean deviation 0.14 °C). The depressions produced by equimolar amounts of triphenyl phosphate with these two histories were within 6% of each other.

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Registry No. 1, 29833-83-8; 3, 58594-17-5; 4a, 41850-90-2; 4b, 41850-89-9; 6, 110-87-2; 9, 24350-41-2; 10, 3393-45-1; 11, 23603-63-6; 12, 73789-90-9; 13, 1489-69-6; 14, 1121-37-5; 15, 30541-56-1; 16, 35544-39-9; 17, 29186-07-0; 1,2-dimethylcyclohexene, 1674-10-8; 2-methyl-2-butene, 513-35-9; 1-methyl-2-methylenecyclohexyl hydroperoxide, 54683-51-1; 1,2-dimethyl-2-cyclohexen-1-yl hydroperoxide, 54683-52-2; 2,3-dimethyl-2-cyclohexen-1-yl hydroperoxide, 56201-42-4; 1,2-dimethyl-2-propenyl hydroperoxide, 15315-29-4; 1,1-dimethyl-2-propenyl hydroperoxide, 15315-30-7; O_2, 7782-44-7.

Direct Epoxy Alcohol Synthesis from Cyclic Olefins Using O_2 and $VO(acac)_2$-AIBN Catalyst System

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The vanadium-catalyzed oxidation of cyclic olefins with molecular oxygen is examined. The $VO(acac)_2$-AIBN system is an efficient catalyst for epoxy alcohol synthesis. Chloro hydrocarbons such as 1,2-dichloroethane and 1,1,2-trichloroethane are suitable solvents for the epoxidation reaction. Cyclohexene (1), methylcyclohexene (2), and cyclododecene (5) give the corresponding epoxy alcohols in good yields; in the case of 2 with the $VO(acac)_2$-AIBN system, the selectivity to epoxy alcohol reaches over 70%. 1,4-Cyclooctadiene (7) is oxidized to give 9-oxabicyclo[3.3.1]non-3-en-*exo*-2-ol (6a) via the rearrangement of *cis*-2,3-epoxycyclooct-4-en-1-ol. Exceptional is cyclooctene (4), which gives exclusively cyclooctene oxide (4b).

Olefins with hydrogen on the α-carbon undergo autoxidation to give allylic hydroperoxides. Soluble transition metals decompose catalytically the hydroperoxides.[1] Iron, cobalt, and manganese compounds accelerate the autoxidation and the homolytic cleavage of the hydroperoxide forms allylic alcohol and α,β-unsaturated ketone (path A, Scheme I). With molybdenum and tungsten compounds, the oxygen transfer from the hydroperoxide to the starting olefin occurs by the heterolytic cleavage of the hydroperoxide and then both epoxide and allylic alcohol are formed (path B).[2] Furthermore, vanadium compounds are prone to the formation of epoxy alcohol because they epoxidized the allylic alcohol much faster than the parent olefin (path C).[3]

To our knowledge, three groups, Allison,[4] Lyons,[5] and Noels,[6] have reported the epoxy alcohol formation from olefins. For example, Lyons has succeeded in 65% selective formation of epoxycyclohexanol (1a) from the reaction of cyclohexene (1) using $CpV(CO)_4$ (Cp = cyclopentadienyl) catalyst. In these reactions, 1 has been often used as a representative reactant. Because of the potential significance of epoxy alcohols in general,[7] it is important to examine the scope and limitation of their formation from various olefins with molecular oxygen.

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