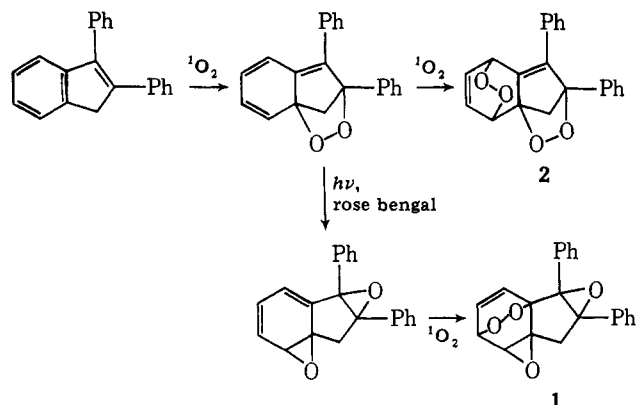


Synthesis of 1,2,3,4-Diepoxides by Catalyzed Rearrangement of 1,4-Endoperoxides¹

Sir:

We recently reported an interesting effect of sensitizer on the course of photooxygenation of indene derivatives.² With rose bengal as the sensitizer, the reaction gave the diepoxide



endoperoxide **1**, but, when *meso*-tetraphenylporphine was used, the product was the diendoperoxide **2**.

Since it was believed that the variation in product might be due to a catalytic rearrangement of the endoperoxide intermediate, the reactions of several endoperoxides (readily formed by photooxygenation of 1,3-dienes³) with potential catalysts were studied. A high-yield catalytic rearrangement of endoperoxides was found with cobalt *meso*-tetraphenylporphine.^{4,5} This sequence represents a synthetically useful route from 1,3-dienes to *syn*-1,2,3,4-diepoxides under extremely mild conditions. CoTPP was also found to decompose dioxetanes.

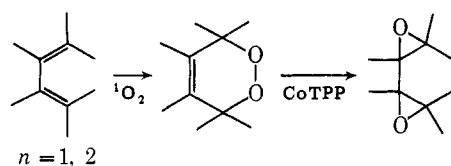


Table I lists the compounds studied and the yields of diepoxides. (Simple monocyclic endoperoxides were not studied). For comparison, the yields for conventional thermolytic or photolytic conversions are also included, where available. As can be seen, the catalyzed procedure gives much better yields with most substrates and is much more convenient and milder than any published method. Furthermore, the complicated and often inseparable reaction mixtures generally encountered with thermolytic methods are avoided.

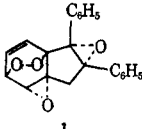
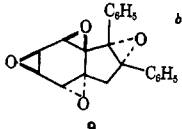
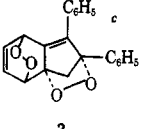
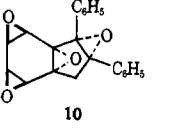
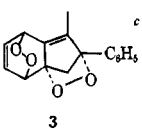
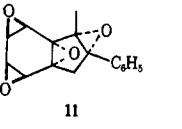
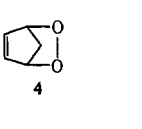
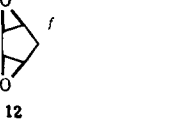
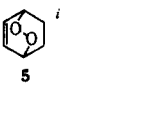
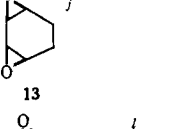
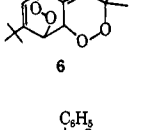
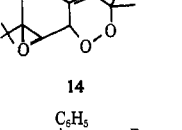
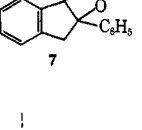
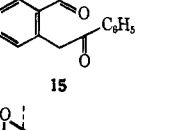
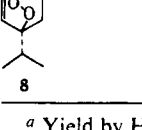
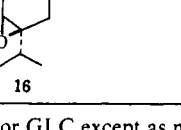
The rearrangement occurs in a stereospecific fashion. In all cases only the *syn*-diepoxides were encountered. The spectroscopic properties of compounds **9**,⁶ **12**,⁷ **13**,⁸ and **14**⁹ agreed well with the literature. Compounds **10** and **11** had IR, ¹H NMR, ¹³C NMR, and high resolution mass spectral data completely consistent with the structures shown.¹⁰ It is interesting that the *monocyclic* peroxide ring in **6** appears more resistant than the bicyclic ring.

The reaction occurs rapidly at low temperature. For example, **1** was reacted with 5 mol % CoTPP in toluene-*d*₈ at -78 °C and the ¹H NMR spectrum of the resultant mixture was immediately taken at -38 °C. The spectrum showed the rearrangement to be complete and the tetraepoxide **9** to be the only product present.

Similar catalyzed decompositions of peroxides have been reported, and both electron exchange^{16,17} and complex formation¹⁸ have been advanced as possible reaction mechanisms. Certain observations pertinent to the mechanism of our reaction can be made.

The oxidation potential of the catalyst is an important

Table 1. Substances and Products Studied

substance	product	yield of products, % ^a	
		CoTPP	thermolysis
		99	77
		86	6
		83 (51 ^d)	<i>e</i>
		52 ^g	2-3 ^h
		74	39 ^k
		50 ^d	
		100	99
		76 ⁿ	80 ^o

^a Yield by HPLC or GLC except as noted. ^b Reference 6. ^c Reference 2. ^d Isolated yield. ^e More than five major products. The exact yield was not determined. ^f Reference 7. ^g 52% overall yield based on cyclopentadiene. The photooxidation was conducted in Freon-11 with TPP at -78 °C followed by addition of 1 mol % CoTPP in THF at -78 °C and warming to room temperature behind a blast shield. ^h Reported as 10¹¹ and 7%.¹² ⁱ Reference 13. ^j Reference 8. ^k Photolysis yield, 27%.⁸ ^l Reference 9. ^m Reference 14. ⁿ Yield was determined by NMR relative to an internal standard after vacuum distillation. Several unidentified impurities were also present. Compound **16** was identified as isoascaridole by comparison of the NMR and IR with those of material prepared by thermolysis. ^o Reference 15; photolysis gave 85%.⁸ Isomerization with aqueous ferrous ion gave only hydrated product **18**.¹⁷

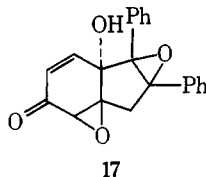
consideration, but not the only one. For example, neither zinc *meso*-tetraphenylporphine nor *meso*-tetraphenylporphine, both of which are weaker reductants than CoTPP (Table II), promoted rearrangement. However, *N,N,N',N'*-tetramethylphenylenediamine (TMPD) which is more easily oxidized than CoTPP, catalyzed the isomerization, but only very slowly. For instance, compound **1**, when treated with 4.8 mol % TMPD at -10 °C, gave a quantitative yield of tetraepoxide **9**, but the reaction took 42 h. The mechanism with TMPD is not base catalysis, since **1** was relatively stable to 57 mol % triethyl-

Table II. Reduction Potentials of Reactants

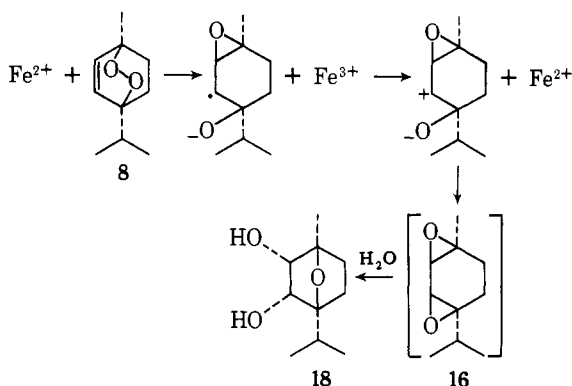
compd	$E_{1/2}$ (V vs. SCE)	compd	$E_{1/2}$ (V vs. SCE)
1/1 ⁻	-0.97 ^a	ZnTPP ⁺ /ZnTPP ^f	+0.73 ^e
TMPD ⁺ /TMPD ^b	+0.22 ^c	TPP ⁺ /TPP ^g	+0.95 ^e
CoTPP ⁺ /CoTPP ^d	+0.66 ^e		

^a Reference 19. ^b *N,N,N',N'*-tetramethylphenylenediamine. ^c E° : S. N. Frank and A. J. Bard, *J. Am. Chem. Soc.*, **97**, 7427 (1975). ^d Cobalt *meso*-tetraphenylporphine. ^e A. Wolberg, *Isr. J. Chem.*, **12**, 1031 (1974). ^f Zinc *meso*-tetraphenylporphine. ^g *meso*-tetraphenylporphine.

amine in acetone at -10°C . Furthermore, the major product of the reaction with triethylamine was not **9** but the hydroxy ketone **17**.⁶



An electron-exchange mechanism for the rearrangement can be written, and such a mechanism has been suggested for the ferrous ion catalyzed rearrangement of ascaridole (**8**) to compound **18**.¹⁷ However, it seems unlikely that such a mechanism would give diepoxide **16** in even moderate yield, as rearrangements might be expected.



If the catalyzed rearrangement of endoperoxides proceeded by pure outer sphere electron exchange in our case, the more easily oxidized TMPD should have promoted more rapid rearrangement than CoTPP; however, as was noted above, the reaction was actually much slower. Furthermore, since the reduction potential of peroxide **1** was found to be -0.97 V vs. SCE ,¹⁹ complete electron transfer with either CoTPP or TMPD is endothermic by $>1\text{ V}$. Instead, a mechanism involving complex formation between the oxidizing peroxide and the reducing catalyst without separation of ion pairs is proposed.

The facile, low temperature, and high yield rearrangement by CoTPP strongly suggests that a similar catalytic reaction (possibly with excited dye as the donor) can account for the rearrangements which occur readily under some conditions during the photooxidation of indenes.²

When coupled with singlet oxygen oxidation of the diene to give the endoperoxide, this procedure provides a mild, high yield, "one-pot" method of converting conjugated dienes to *syn*-diepoxides. Similar oxidations of dienes with *m*-chloroperbenzoic acid give *anti*-diepoxides and require forcing conditions for complete reaction. However, epoxidation with *tert*-butyl peroxide catalyzed by $\text{VO}(\text{acac})_2$ gave a *syn*-diepoxide,²⁰ but the scope of this reaction has not been investigated.

Studies on the mechanism and scope of this rearrangement are being conducted.

Acknowledgment. We thank Dr. Pauline M. Allen for her suggestions on the electrochemical sections.

References and Notes

- (1) Supported by National Science Foundation Grant No. CHE77-21560.
- (2) J. D. Boyd and C. S. Foote, *J. Am. Chem. Soc.*, **101**, 6758 (1979).
- (3) R. W. Denny and A. Nickon, *Org. React.*, **20**, 133 (1973).
- (4) P. Rothenmund and A. R. Menotti, *J. Am. Chem. Soc.*, **70**, 1808 (1948).
- (5) Although the manipulation of peroxides can be done safely, precautions against explosion are recommended. The procedure usually consisted of the addition of a solution of CoTPP in THF or chloroform to a solution of the peroxide in THF or acetone. Although in most instances 1–2 mol % CoTPP (relative to substrate) is sufficient for the reaction, 5% was usually employed. If the endoperoxide was suspected of being unstable, the addition was done at low temperature. **Preparation of 11 (3-methyl-2-phenyl-2,3,4,5,6,7,8,9-tetraepoxyoctahydroindene)**. A solution of 2.2 mg of CoTPP, 2.5 mL of dichloromethane, and 100 mL of acetone was cooled to -10°C . To this solution 93.8 mg of **3** (3-methyl-2-phenyl-2,8,4,7-diperoxy- $\Delta^{3,9}\Delta^{5,6}$ -tetrahydroindene)² was added in one portion and the resulting mixture was allowed to stand in the freezer for $\sim 2\text{ h}$. An additional 7.8 mg of CoTPP in 3 mL of chloroform was added to the reaction mixture and stirred at -10°C . The reaction was immediately complete by TLC (silica gel, CHCl_3). The solvent was removed in vacuo and the residue separated by column chromatography on silica gel (Merck) to give 47.8 mg (51%) of compound **9** (3-methyl-2-phenyl-2,3,4,5,6,7,8,9-tetraepoxyoctahydroindene): white granules; mp (sintered at 180°C), $184.0\text{--}185.0^\circ\text{C}$; IR (CDCl_3) 3003, 1602, 1495, 1445, 1263, 1153, 951, 860 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.33 (br s, 5 H), 3.6–3.3 (m, 4 H), 2.50 (s, 2 H), 1.39 (s, 3 H); ^{13}C NMR (50 MHz, CDCl_3) δ 134.8 (s), 128.7 (d), 128.5 (d), 127.0 (d), 77.2 (s), 70.9 (s), 66.6 (s), 63.3 (s), 49.6 (d), 48.8 (d), 48.4 (d), 48.0 (d), 33.8 (t), 11.7 (q).
- (6) P. A. Burns, C. S. Foote, and S. Mazur, *J. Org. Chem.*, **41**, 889 (1976).
- (7) B. Tolbert, R. Steyn, J. A. Franks, Jr., and H. Z. Sable, *Carbohydr. Res.*, **5**, 62 (1967).
- (8) K. K. Maheshwari, P. de Mayo, and D. Wiegand, *Can. J. Chem.*, **48**, 3265 (1970).
- (9) M. Matsumoto, S. Dobashi, and K. Kuroda, *Tetrahedron Lett.*, 3361 (1977).
- (10) N. R. Easton, Jr., F. A. L. Anet, P. A. Burns, and C. S. Foote, *J. Am. Chem. Soc.*, **96**, 3945 (1974).
- (11) W. R. Adams and D. J. Trecker, *Tetrahedron*, **27**, 2631 (1971).
- (12) K. H. Schulte-Elte, B. Willhalm, and G. Ohloff, *Angew. Chem., Int. Ed. Engl.*, **8**, 985 (1969).
- (13) G. O. Schenck and W. Willmund, reported by R. Criegee in Houben-Weyl, "Methoden der Organischen Chemie", Vol. VIII, E. Müller, Ed., 4th ed., Georg Thieme Verlag, Stuttgart, 1952, p 16.
- (14) P. A. Burns and C. S. Foote, *J. Am. Chem. Soc.*, **96**, 4339 (1974).
- (15) J. Boche and O. Runquist, *J. Org. Chem.*, **33**, 4285 (1968).
- (16) B. G. Dixon and G. B. Schuster, *J. Am. Chem. Soc.*, **101**, 3116 (1979); J.-y. Koo and G. B. Schuster, *ibid.*, **100**, 4496 (1978); S. P. Schmidt and G. B. Schuster, *ibid.*, **100**, 1966 (1978).
- (17) J. A. Turner and W. Herz, *J. Org. Chem.*, **42**, 1895 (1977). In some cases diepoxides were isolated by the ferrous ion catalyzed procedure.
- (18) P. D. Bartlett, A. L. Baumstark, and M. E. Landis, *J. Am. Chem. Soc.*, **96**, 5557 (1974); P. D. Bartlett and J. S. McKennis, *ibid.*, **99**, 5334 (1977).
- (19) P. M. Allen and C. S. Foote, unpublished work.
- (20) M. R. Demuth, P. E. Garrett, and J. D. White, *J. Am. Chem. Soc.*, **98**, 634 (1976).
- (21) Summer Research Fellow, Associated Western Universities.

Jack D. Boyd, Christopher S. Foote,* David K. Imagawa²¹

Department of Chemistry, University of California
Los Angeles, California 90024
Received November 30, 1979

Carbon-Carbon Bond Formation Catalyzed by Vitamin B₁₂ and a Vitamin B₁₂ Model Compound. Electrosynthesis of Bicyclic Ketones by 1,4 Addition¹

Sir:

Vitamin B₁₂ derivatives and vitamin B₁₂ model compounds have recently been found to catalyze the electrochemical reduction of alkyl halides² as well as the zinc-acetic acid promoted reduction of nitriles,^{3a} α,β -unsaturated nitriles,^{3b} α,β -unsaturated carbonyl derivatives,^{3c} olefins,^{3d} alkyl halides,^{3d} and alcohols.^{3d} Evidence was presented^{2,3d} that the above-mentioned reactions proceed through intermediates containing a Co–C bond, which is reductively cleaved and transformed into a C–H bond. It seemed of interest to investigate the potential of such intermediates for the formation of C–C bonds.