Cobalt(II) Tetraphenylporphyrin Catalyzed Decomposition of Bicyclic Endoperoxides[†]

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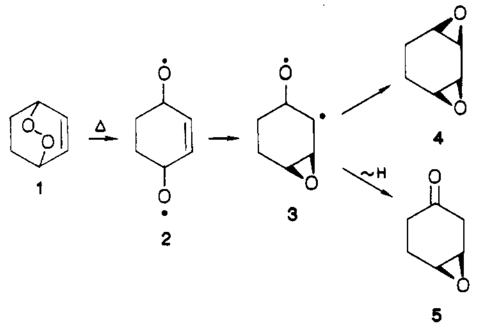
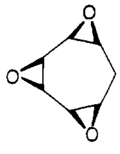
Cobalt(II) tetraphenylporphyrin (CoTPP) catalyzed decomposition of some bicyclic endoperoxides with strained and perturbed diene moieties has been studied and it has been shown that the side reactions such as formation of epoxy ketones can be suppressed. The yields for epoxide formation have been increased to 90–100%. CoTPP-catalyzed reaction of **13** has been studied in more detail. Besides the expected diepoxide **15**, two isomeric open-chain epoxy aldehydes **16** and **17** were isolated. The structures of **16** and **17** were determined by spectroscopic and chemical methods. Furthermore, it was shown that the CoTPP reaction goes through two different reaction channels to form diepoxides and open-chain epoxy aldehydes. In order to gain more insight into the reaction mechanism, bicyclic endoperoxides **31a**, **31b**, and **32** were subjected to CoTPP reaction. **31a** and **31b** gave, besides the expected diepoxides **35** and **37**, only the open-chain aldehydes **36** and **38**, respectively. However, **32** did not form any open-chain aldehyde. Reaction mechanisms and the origin of the observed stereoselectivity are discussed in terms of conformational factors.

Unsaturated bicyclic endoperoxides are readily available by reaction of singlet oxygen with conjugated dienes.[1] Such endoperoxides have proven extremly useful in synthesis, being convertible to a variety of stereospecifically oxygenated compounds.[2] One of the common reactions of unsaturated bicyclic endoperoxides is the thermal cleavage of the weak oxygen–oxygen bond followed by addition of the oxygen radicals to the adjacent double bond to give diepoxides with syn configuration. However, in strained molecules and other cases, thermolysis is always accompanied by side reactions. One of these is the formation of epoxy ketones.[3] Carless et al.[4] have shown direct evidence that β,γ-epoxy ketones are often formed as major products from thermolysis or photolysis of unsaturated bicyclic endoperoxides.



Recently, Foote et al.[5] have reported that unsaturated bicyclic endoperoxides can be conveniently converted into the corresponding diepoxides by using cobalt(II) tetraphenylporphyrin (CoTPP).[6] More recently, we successfully applied this reaction to unsaturated bicyclic endoperoxides with strained and perturbed diene moieties.[7] In a preliminary communication,[7a] we reported the formation of **6**, **7**, and **8** from the corresponding endoperoxides **9**, **10**, and **11** in nearly quantitative yield upon treatment with CoTPP at −10 °C.

These endoperoxides form **6**, **7**, and **8** also by thermolysis in yields of 39%, 44%, and 32%, respectively. From these results one can see that the CoTPP-catalyzed reaction can completely suppress the side reactions. Furthermore, we also studied the CoTPP-catalyzed decomposition of **12** and **13**. Tropon endoperoxide,[8] which undergoes a rearrangement on refluxing in xylene to give 2,5-dihydroxybenzaldehyde, has been converted to the unknown interesting diepoxide **14** in a yield of 14%. **15** has been obtained in 60% from **13**.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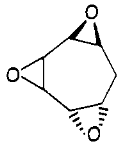
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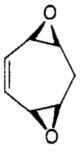
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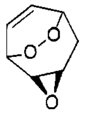
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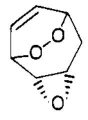
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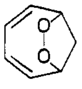
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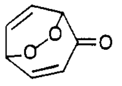
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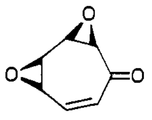
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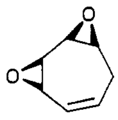
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In order to gain more insight into the reaction mechanism and to explain the lower yield in the case of **15**, the reaction mixture resulting from the CoTPP-catalyzed reaction of **13** was carefully analyzed. In addition to **15**, a

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[†] Dedicated to Professor Emanuel Vogel on the occasion of his 60th birthday.

(1) (a) *Singlet O_2, Reaction Modes and Products*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. II, Part 1; Vol. III, Part 2. (b) *The Chemistry of Functional Groups, Peroxides*; Patai, S., Ed.; Wiley: New York, 1983. (c) *Singlet Oxygen*; Wasserman, H. H., Murray, W. M., Ed.; Academic Press: New York, 1979.

(2) (a) Adam, W.; Balci, M. *Tetrahedron* **1980**, *36*, 833. (b) Balci, M. *Chem. Rev.* **1981**, *81*, 91. (c) Frimer, A. A. In *The Chemistry of Functional Groups, Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; p 201. (d) Saito, I.; Nittala, S. S., ref 2c, p 331.

(3) (a) Maheshwari, K. K.; de Mayo, P.; Wiegand, D. *Can. J. Chem.* **1970**, *48*, 3265. (b) Adam, W.; Balci, M. *J. Am. Chem. Soc.* **1980**, *102*, 1961. (c) For a case in which no diepoxide formed, see ref 8.

(4) Carless, H. A. J.; Atkins, R.; Fekarurhobo, G. K. *Tetrahedron Lett.* **1985**, *26*, 803.

(5) Boyd, J. D.; Foote, C. S.; Imagawa, D. K. *J. Am. Chem. Soc.* **1980**, *102*, 3641.

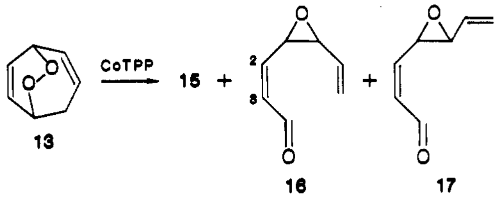
(6) (a) Balci, M.; Akbulut, N. *Tetrahedron* **1985**, *41*, 1315. (b) Menzek, A.; Akbulut, N.; Balci, M. *Doga Bilim Dergisi A* **1985**, *9*, 28. (c) Also other metalloporphyrines are known to catalyze the decomposition of some peroxides: Ho, Y.; Tone, M.; Yokoya, H.; Matsuura, T.; Schuster, G. B. *J. Org. Chem.* **1986**, *51*, 2240.

(7) (a) Balci, M.; Sütbeyaz, Y. *Tetrahedron Lett.* **1983**, *24*, 311. (b) Balci, M.; Sütbeyaz, Y. *Tetrahedron Lett.* **1983**, *24*, 4135. (c) Akbulut, M.; Menzek, A.; Balci, M. *Tetrahedron Lett.* **1987**, *28*, 555.

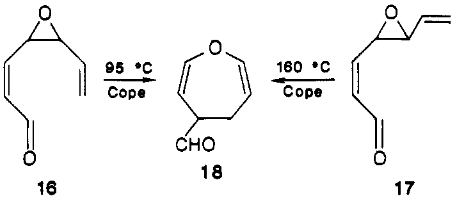
(8) Oda, M.; Kitahara, Y. *Tetrahedron Lett.* **1965**, 3295.

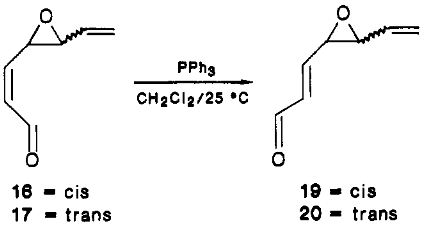
0022-3263/88/1953-2312$01.50/0

mixture of two aldehydes was isolated in a yield of 30%. After repeated column chromatography at low temperature (-15 °C, silica gel), two open-chain aldehydes **16** and **17** were isolated. Pure isomeric aldehydes for structural determination were obtained by preparative TLC separation. The structural assignment of these aldehydes was made on the basis of spectroscopic data. Unequivocal configurational evidence, especially at the epoxide ring and the C_2–C_3 double bond was made by means of chemical reactions. The cis isomer contains a 1,2-divinylethylene oxide unit that is a suitable species for the Cope rearrangement.[9] This epoxide **16** was heated in a sealed tube for 2 h at 95 °C. The cyclization of **16** into the 4,5-dihydrooxepine[10] **18** was complete. Under identical conditions the trans epoxide was recovered unchanged. A higher temperature was required for conversion of **17**.

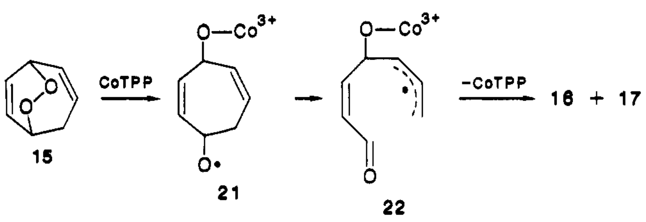


After heating **17** at 160 °C for 1 h, it was completely decomposed. From the ^1H NMR spectra of this mixture we could establish the formation of **18** in a yield of 11%. After determination of the configuration at the epoxide ring, we were interested in determining the correct configuration of the conjugated double bond C_2–C_3. To obtain experimental evidence for this, pure samples of **16** and **17** were reacted with triphenylphosphine in CH_2Cl_2. This converted them into the corresponding more stable trans aldehydes **19** and **20** in nearly quantitative yield. With this experiment it was established that the configuration at the C_2–C_3 double bond has remained intact during the rearrangement.



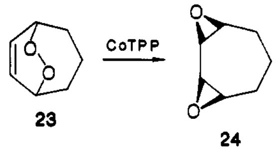


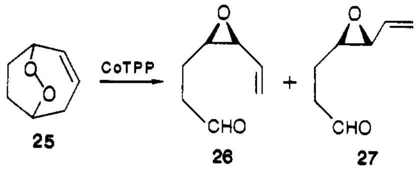
At this stage, we postulated a radical mechanism for the formation of **16** and **17**. We assumed that the radical **21** resulting from the electron-transfer reaction between Co^{2+} species and endoperoxide **13** serves as a key intermediate as shown below. Cleavage of the C–C bond can form the allyl radical **22**. Consequently, this intermediate appears to be capable of rotation about the interconnective double bond, ring closure occurring ultimately to deliver cis and trans aldehydes **16** and **17**.



In order to shed light on the reaction mechanism of this interesting decomposition, we studied simple alkylated and reduced derivatives of **13** like **23** and **25**. We have shown that the decomposition reaction of **13** probably goes through two different channels, leading to diepoxide **15** and open-chain aldehydes. In order to answer the question of whether one can control these two different reaction modes, we synthesized **23** and **25** derived from **13**.

Reaction of **23**, obtained by photooxygenation of 1,3-cycloheptadiene,[11] with CoTPP provided the diepoxide **24** as a single product as expected. **25** was synthesized by submitting **13** to selective diimide[12] reduction. The more strained double bond incorporated into the six-membered ring was readily reduced.[13] Achieving the complete reduction causes some difficulties, since the double bond in **25** is incorporated into the seven-membered ring and the strain in the molecule was reduced due to the reduction of the first double bond. Therefore, **25** was isolated in high purity. Reaction of **25** with CoTPP gave a mixture of **26** and **27** in a ratio of 2:1. Attempts to separate this mixture failed. Analysis of the NMR spectra, especially the ^{13}C NMR spectrum, indicated the existence of stereoisomers. The ^1H NMR spectrum of this mixture exhibited the characteristic resonances of the aldehyde group at δ 9.55, olefinic protons at δ 4.9–5.6, and epoxide-methylene protons at δ 1.4–3.4. The ^{13}C NMR spectrum was more informative for the presence of diastereomers **26** and **27**. The spectrum consisted of two sets of signals in a ratio of 2:1 which belong to one aldehydic, two olefinic, two epoxide, and two methylenic carbon atoms. The IR spectrum showed carbonyl absorption at 1730 cm^{-1}. This is also strong supporting evidence for the saturated aldehyde group.





Furthermore, we reacted the endoperoxide **28**[14] derived from 5*H*-benzocycloheptene with CoTPP and obtained the epoxide **29** in quantitative yield. In this instance, the double bond C_6–C_7, which is necessary for the formation of an open-chain aldehyde such as **30**, is incorporated into a benzene ring. The formation of **30** would cause the loss of the resonance energy of the annelated benzene ring. These observations indicate that the CoTPP reaction goes

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[9] Roads, S. J.; Rawlins, R. N. *Org. React.* (*N.Y.*) **1975**, *22*, 1.

[10] For conversion of the *cis*- and *trans*-1,2-divinylethylene oxide to 4,5-dihydrooxepine, see: (a) Braun, R. A. *J. Org. Chem.* **1963**, *28*, 1383. (b) Stogryn, E. L.; Gianni, M. H.; Passannte, A. J. *J. Org. Chem.* **1964**, *29*, 1275.

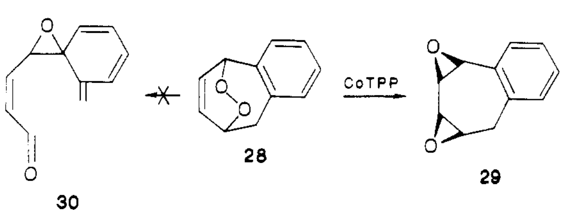
[11] Cope, A. C.; Liss, T. A.; Wood, G. W. *J. Am. Chem. Soc.* **1957**, *79*, 6287.

[12] (a) Coughlin, D. J.; Brown, R. S.; Salomon, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 1537. (b) Adam, W.; Eggelte, H. J. *J. Org. Chem.* **1977**, *42*, 3987.

[13] Adam, W.; Balci, M. *Angew. Chem.* **1978**, *90*, 1014.

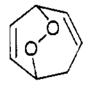
[14] (a) Balci, M.; Atasoy, B. *Tetrahedron Lett.* **1984**, *25*, 4033. (b) Atasoy, B.; Balci, M. *Tetrahedron* **1986**, *42*, 1461.

through two different channels as suggested.



30 28 29

If the decomposition mechanism of **13** goes through allylic radical **22** as suggested before, one should be able to stabilize this intermediate by introduction of simple alkyl groups like CH_3 at the methylene group in **13**. In this case, the formation of an open-chain aldehyde should be favored at the expense of diepoxide formation. To test for this behavior of **31a**, **31b**, and **32** upon treatment with CoTPP, we synthesized these endoperoxides as described in the literature. **31a** and **31b** were synthesized by photooxygenation of 7-methylcycloheptatriene.[15] The reaction mixture consisting of **31a**, **31b**, a norcaradiene-type adduct, and two aromatic aldehydes was separated by repeated low-temperature column chromatography, so that the samples **31a** and **31b** were isolated in high purity.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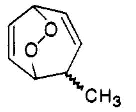
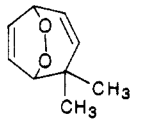


31a endo
31b exo



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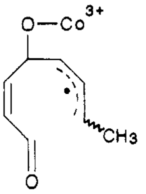
22



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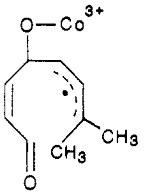

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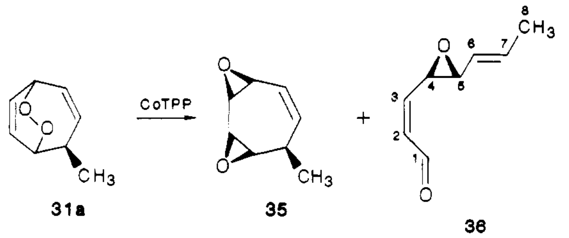
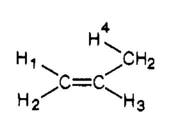
31a was subjected to CoTPP under the same reaction conditions as described for **13**. The *endo*-methylcycloheptatriene endoperoxide (**31a**) behaves in a similar manner as **13**. The resulting reaction mixture was analyzed very carefully by ^1H and ^{13}C NMR spectroscopy. Especially, the 75-MHz ^{13}C NMR spectrum indicated clearly the formation of two products **35** and **36** in a ratio of 2:1.

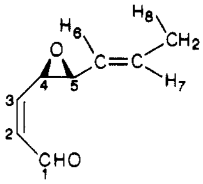


31a 35 36

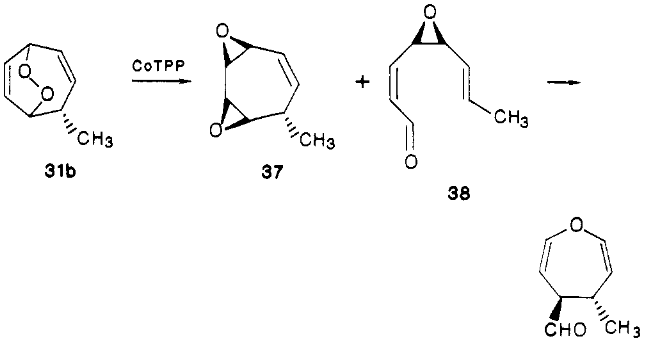
Diepoxide **35** has been isolated by chromatography of the resulting mixture on a silica gel column and its structure was confirmed from spectroscopic data as well as elemental analysis. All efforts to isolate **36** failed due to the instability of **36** on silica gel. Therefore, spectroscopic data of **36** was extracted from the NMR spectra of the mixture. All the signals in the ^1H NMR and ^{13}C NMR spectra were well-resolved. The ^{13}C NMR spectrum of **36** consisted of four sp^2 carbons (147.11, 133.17, 132.60, and 126.85), two epoxide carbons (60.44, 55.18), one methyl group (17.78), and one aldehyde carbon (190.07). The extracted ^1H NMR data of **36** were also in complete agreement with the proposed structure. In contrast to the reaction of **13** with CoTPP, there was no indication for the formation of another isomeric epoxy aldehyde. We assumed that the stereochemistry at the C_2–C_3 carbon atoms is cis by comparison with **16** and **17**. The configuration at the epoxide ring was determined by the thermal behavior of **36**. Epoxy aldehyde **36** was still stable upon heating to 130 °C in a sealed NMR tube. On the basis of this thermal behavior, we assume that the configuration at the epoxide ring is trans (see thermal behavior of **38**). Furthermore, we have established the configuration at the C_6–C_7 double bond by using the allylic coupling constant J_{68}. The methyl group resonance appears in the ^1H NMR spectrum at δ 1.7 as a doublet of doublets (J_{78} = 6.5 Hz, J_{68} = 1.31 Hz). Despite the complexity of allylic coupling,[16] both theoretical and emprical results established some general correlation between the magnitude of allylic coupling constants and structural parameters which are sufficiently well-defined to be useful for structural studies. In the propene, ^4J values have been observed which experimentally confirm the relation discussed above. The measured value of the allylic coupling constant in **36** is ^4J = 1.31 Hz and this value is in accordance with cisoid coupling in propene. Therefore, we conclude that the configuration of the double bond C_6–C_7 is trans.



$^4J_{14}$ = 1.33 Hz cisoid
$^4J_{24}$ = 1.75 Hz transoid



$^4J_{68}$ = 1.31 Hz



31b 37 38 39

Exo isomer **31b** was treated under the same reaction conditions with CoTPP. The reaction mixture was again analyzed by ^1H and ^{13}C NMR spectroscopy. The expected diepoxide **37** was formed as the major product in addition to the open-chain epoxy aldehyde **38** in a ratio of 4:1. We have already noted that the configuration of the conjugated double bond remains intact during the reaction. Since there are two further isomerization centers in **38** (epoxide ring and C_6–C_7 double bond), a total of four isomeric products could be formed. As matters turned out, again only one isomer could be detected by spectroscopic studies. It proved possible to separate diepoxide **37** which was characterized by means of spectral data and elemental analysis. Again, **38** was decomposed by attempted separation on column material. The product distribution (4:1) was ascertained by integration of the methyl doublet of

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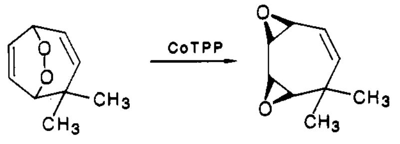
(15) Adam, W.; Balci, M.; Pietrzak, B.; Rebollo, H. *Synthesis* **1980**, 820.

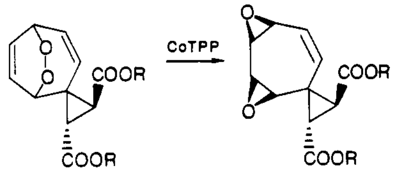
(16) Barfield, M.; Spear, R. J.; Sternhell, S. Chem. *Rev.* **1976**, *76*, 593.

37 at δ 1.2 and methyl doublet of doublets of **38** at δ 1.85. The allylic coupling constant was determined to be $^4J_{68}$ = 1.34 Hz, which is again in good agreement with cis orientation of the CH_3 group and vinylic hydrogen. Upon heating a mixture consisting of **37** and **38** at 100 °C, the aldehyde resonance at δ 9.95 and methyl signal at δ 1.85 were shifted to 9.4 ppm and 1.2 ppm, respectively. This observation is consistent only with the formation of dihydrooxepine derivative **39** so that we have been able to secure the stereochemistry of **38**.

Interestingly, **32**[17] also reacted with CoTPP to produce a single product in nearly quantitatively yield. This substance was identified as **40** by spectroscopic methods. Contrary to our expectation, there was not any indication of formation of any open-chain aldehyde. Also spirocyclopropanannulation did not change the product distribution. In this instance, again diepoxide **42** was formed exclusively.[18]



32 40



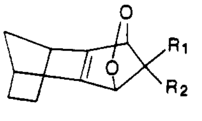
41 42

Discussion

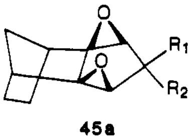
Thermal and photochemical rearrangements of bicyclic endoperoxides normally lead to stereospecific formation of syn diepoxides. In most cases, these reactions are accompanied by the formation of β,γ-epoxy ketones. The first step in this reaction is the formation of oxygen–oxygen diradicals **2**, assuming that diepoxides and epoxy ketones are both formed from this diradical. Ring closures of the later to give diepoxide are in competition with the 1,2-hydrogen shift required to yield an epoxy ketone. We assume that the activation energy for 1,2-hydrogen shift is higher than that for the epoxide formation. CoTPP is capable of cleaving the oxygen–oxygen bond at lower temperature by an electron-transfer mechanism. At this temperature (−10 °C) a hydrogen shift cannot occur. Therefore, the formation of the epoxy ketone has been suppressed completely and the yield of diepoxides has been increased, in many cases up to 95–100% at the expense of epoxy ketone formation.

Bicyclic endoperoxides derived from cycloheptatriene and its derivatives behave differently by reacting with CoTPP. The corresponding diepoxides are major products. In these instances, the formation of epoxy ketones was not observed. However, open-chain aldehydes were encountered by CoTPP-catalyzed decomposition of these endoperoxides. The striking feature of these epoxy aldehydes is their configurations. In the case of **13**, two epoxy aldehydes **16** and **17** whose configurations differ at the epoxide ring were formed. However, methyl derivatives **31a** and **31b** produced only single aldehydes with different configurations at the epoxide ring. Contrary to our expectation, **32** and **41** did not form any trace of C–C ring cleavage product. On the basis of this observation we can conclude that the intermediate formed by opening of the oxygen–oxygen bond followed by cleavage of the C–C bond upon treatment with CoTPP cannot be a radical or ionic species as in **22**, **33**, and **34**. Otherwise, the formation of open-chain aldehydes should be favored by reaction of **32** and **41** with CoTPP.

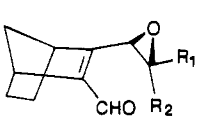
Recently, Paquette et al.[19] have studied the photooxygenation of simple alkylated systems derived from isodicyclopentadienes. They observed that the thermolysis of unsubstituted endoperoxide **44a** led to formation of epoxy aldehyde **46a** and the corresponding diepoxide **45a**. However, in the case of dimethyl derivative **44c**, the epoxy aldehyde **46c** was the only characterizable product isolated in this experiment. This observation was taken as an indication that cleavage of a ring C–C bond is kinetically preferred to intramolecular double-bond capture. The tertiary nature of the carbon-centered radical in **48** is undoubtedly responsible for this exclusivity. This conclusion was supported by the reactivity profile exhibited by monomethyl derivative **44b**. In this case C–C bond cleavage is slowed because of the secondary nature of the carbon radical. The diepoxide production dominated by a factor of 1.6:1.



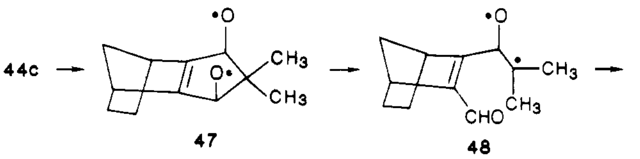
$R_1 = R_2 = H$ 44a
$R_2 = CH_3$ 44b
$R_1 = R_2 = CH_3$ 44c



45a
45b
45c



46a
46b
46c



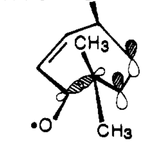
47 48

46c

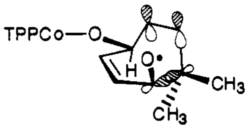
On the basis of our observation and the above-mentioned results, a similar mechanism cannot operate in the cases of alkyl-substituted cycloheptatriene endoperoxides.

Recently, Carless et al.[4] have shown that conformational factors control the product distribution resulting from heating bicyclic endoperoxides.

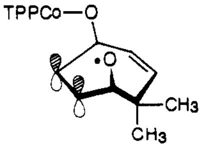
Therefore, we assume that the conformational factors in the seven-membered ring, formed after cleavage of the oxygen–oxygen bond in the endoperoxides by an electron-transfer mechanism, play an important role in determining the product distribution. Inspection of Dreiding models indicates that the intermediate formed by cleavage of the peroxide linkage in **32** can adopt three different conformations as shown below. In the first conformation,



49A



49B



49C

49A, there is a steric interaction between the axial CH_3 group and axial oxygen atom which is probably bonded to CoTPP. In the second conformation, **49B**, there is also

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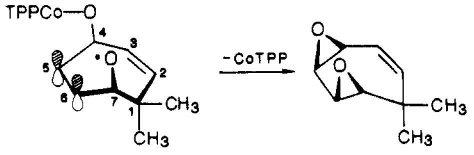
[17] Adam, W.; Adamsky, F.; Klärner, F. G.; Peters, K.; Rebollo, H.; Rüngeler, W.; Peters, E. M.; Schnering, H. G. *Chem. Ber.* 1983, *116*, 1848.

[18] Balci, M.; Atasoy, B. *Chim. Acta Turcica* 1984, *12*, 158.

[19] (a) Hathaway, S. H.; Paquette, L. A. *Tetrahedron* 1985, *41*, 2037. (b) Paquette, L. A.; Carr, R. V. C.; Arnold, E.; Clardy, J. *J. Org. Chem.* 1980, *45*, 4907.

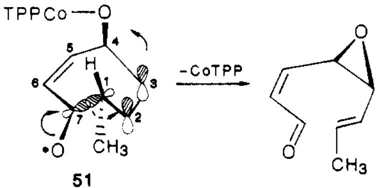
steric interaction between the second methyl group and axial hydrogen atoms as shown in **49B**. In contrast, **49C** does not reveal any steric repulsion between the methyl and other groups. On the other hand, the nearly parallel arrangement of the C–O bonds with the adjacent *p* orbital lobes which is necessary for epoxide formation facilitates the formation of the diepoxide **40**.



49C **40**

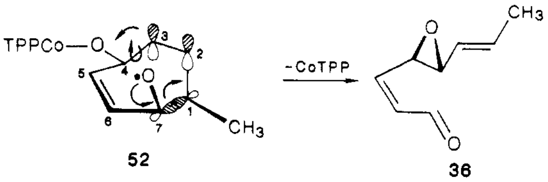
We have already discussed that the ring C_1–C_7 bond cleavage during epoxy aldehyde formation is neither radical nor ionic. For a synchronous cleavage of this C_1–C_7 bond, the parallel orientation of this with the p orbital at the adjacent C_2 carbon is necessary. This suitable orientation for a synchronous C–C bond breaking is only possible in of **49A** and **49B**. In view of the steric interactions we showed that the intermediate **49** cannot adopt the conformations A and B. That is the reason why dimethyl intermediate **49** is not prone to form any open-chain aldehyde.

If the axial methyl group in **49A** is substituted by a hydrogen as in the case of **51** (derived from CoTPP reaction of **31b**), the steric interaction is eliminated so that the intermediate can now adopt two conformations as in A and C. The latter one can form diepoxide **37** as discussed above. A synchronous cleavage of the ring C–C bond can now take place. This conformation holds at the same time the desired alignment of the C–O bond and p orbital for the formation of the epoxide ring in **38**. From this synchronous cleavage one can also see the observed stereochemistry at the epoxide ring and the double bond.



51 **38**

Substitution of the axial methyl group in **49B** by a hydrogen should eliminate the steric interaction between CH_3 group and the axial hydrogen as in **52**. This intermediate **52** is formed by CoTPP reaction of **31a** and can adopt two different conformations as in **49B** and **49C** from which two products, epoxy aldehyde **36** and diepoxide **35** can be



52 **36**

formed. But, the orientation of C_4–O bond and the adjacent p orbital of the double bond is perpendicular which is not suitable for a ring closure to form the epoxide ring. Therefore, a rotation around the C_3–C_4 σ-bond is necessary in order to complete the ring closure. This rotation leads exclusively to the formation of the trans epoxy aldehyde **36**.

In conclusion, the origin of the observed stereoselectivity of the CoTPP-catalyzed reactions of alkylated cycloheptatriene endoperoxides and the product distribution are controlled completely by conformational rather than electronic factors.

Experimental Section

General. Melting points were determined in open capillary tubes and are uncorrected. Infrared spectra were obtained from films on NaCl plates for liquids or from solutions in 0.1-mm cells or KBr pellet for solids on a Perkin-Elmer 337 infrared recording spectrophotometer. The NMR spectra were recorded with EM 360 Varian spectrometer and Nicolet NT-300 spectrometer. Mass spectra were recorded on a Finnigan-MAT MS Model 4000 mass spectrometer at an ionizing voltage of 70 eV. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} plates. Column chromatography was done on silica gel (60–200 mesh) from Merck Chemical Company.

General Procedure for CoTPP. To a magnetically stirred solution of 3 mmol of endoperoxide in 30 mL of CH_2Cl_2 was added a solution of 20 mg (0.04 mmol) of cobalt *meso*-tetraphenylporphyrin[20] in 5 mL of CH_2Cl_2 at 0 °C. After complete addition (15 min) the mixture was stirred for 1 h at room temperature. The solvent was rotoevaporated (15 mmHg, 25 °C). The residue was chromatographed on silica gel eluting with the appropriate solvent.

6:[3b] residue was passed through 10 g of silica gel eluting with CH_2Cl_2/petroleum ether (2:1); yield 95%.

7:[3b] residue was passed through 10 g of silica gel eluting with $CHCl_3$/*n*-pentane (1:1); yield 98%.

8:[21] residue was passed through 10 g of silica gel eluting with CH_2Cl_2/*n*-pentane (1:1); yield quantitative.

6,9-Dioxabicyclo[5.1.0.0^{5,7}]non-3-en-2-one (14). The reaction was carried out as described above. Chromatography of the residue on 25 g of silica gel eluting with $CHCl_3$/*n*-pentane (2:1) gave tropon diepoxide (**14**): yield 60%; light-yellow crystal; mp 82–83 °C (subl at 60 °C and 0.1 mmHg); ^{1}H NMR ($CDCl_3$, TMS) δ 6.4 (dd, *J* = 11.0, 2.6 Hz, 1 H), 5.8 (dd, *J* = 11.0, 0.9 Hz, 1 H), 3.8 (m, 1 H), 3.75–3.10 (m, 3 H); ^{13}C NMR ($CDCl_3$, TMS) δ 198.8, 131.05, 130.68, 60.06, 53.35, 52.72, 52.30; IR ($CHCl_3$) 2980, 2920, 1695, 990, 965, 905, 865 cm^{-1}; MS, *m/e* 138 (M^+). Anal. Calcd for $C_7H_6O_3$: C, 60.87; H, 4.35. Found: C, 60.65; H, 4.48.

CoTPP Reaction of Cycloheptatriene Endoperoxide (13): Cycloheptatriene Diepoxide (15), 4,5-*trans*-Epoxy-2(*Z*),6-heptadienal (16), and 4,5-*cis*-Epoxy-2(*Z*),6-heptadienal (17). The resulting reaction mixture from the CoTPP reaction of **13** was subjected to low-temperature (−10 °C) column chromatography (30 g, silica gel) using ether/*n*-hexane (2:9) to give **15** as the first fraction in a yield of 60%. **15** was characterized by comparison of physical data with those reported in the literature.[21]

The mixture of **16** and **17** (in a ratio of 1:1) was isolated as a second fraction: yield 30%. Low-temperature column chromatography of this mixture (−20 °C), eluting with ether/*n*-hexane (2:11), afforded **16** and **17** in order of elution. Pure analytical samples were obtained by preparative TLC separation. **17**: ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 190.14, 146.67, 133.62, 132.90, 120.88, 60.49, 55.41; MS, *m/e* 124 (M^+). **16**: *m/e* 124 (M^+). For further physical data of **16** and **17**, see ref 7b.

Triphenylphosphine Reaction of 16 and 17: 4,5-*trans*-Epoxy-2(*E*),6-heptadienal (19) and 4,5-*cis*-Epoxy-2(*E*),6-heptadienal (20). To a solution of **16** (62 mg, 0.5 mmol) in CD_2Cl_2 (2 mL) at room temperature was added slowly triphenylphosphine (66 mg, 0.25 mmol). The progress of the reaction was monitored by ^{1}H NMR. After 2 h the reaction was complete and **19** was formed quantitatively. For isolation of **19** the solvent was evaporated. Chromatography on silica gel (10 g) eluted with CH_2Cl_2/*n*-hexane (1:1) afforded **19** as a colorless liquid in a yield of 73%. **20** was obtained as described above. For physical data of **19** and **20**, see ref 7b.

CoTPP Reaction of 6,7-Dioxabicyclo[3.2.2]non-2-ene (25): *cis*- and *trans*-4,5-Epoxy-2-heptenal (26 and 27). The resulting reaction mixture (4 mmol of endoperoxide **25**) from CoTPP reaction of **25** was subjected to low-temperature (0 °C) column chromatography (30 g, silica gel), eluting with petroleum ether/ether (9:2), and gave an oil which consisted of **26** and **27** in

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[20] Rothemund, P.; Menotti, A. R. *J. Am. Chem. Soc.* **1948**, *70*, 1808.

[21] Adam, W.; Balci, M. *J. Am. Chem. Soc.* **1979**, *101*, 7537.

a ratio of 2:1: yield 65%. Attempts to separate this mixture failed. ^{1}H NMR spectrum of the mixture ($CDCl_3$, TMS): δ 9.55 (br s, 1 H), 4.9–5.6 (m, 3 H), 1.4–3.4 (m, 6 H); IR (CCl_4) 3050, 2970, 2930, 2820, 2720, 1730, 1640, 1445, 1410, 1390, 925 cm^{-1}; ^{13}C NMR of the major isomer ($CDCl_3$, TMS) δ 201.11, 135.16, 119.45, 59.09, 58.72, 39.77, 24.29; minor isomer 201.11, 131.84, 120.84, 57.52, 57.34, 40.50, 20.51; MS, *m/e* (relative intensity) 126 (13, M$^+$), 125 (21), 109 (20), 85 (100), 83 (20), 81 (43), 79 (26), 70 (40), 69 (43), 57 (69), 55 (42).

Thermolysis of 16 and 17: 4,5-Dihydrooxepine-4-aldehyde (18). A solution of **16** (62 mg, 0.5 mmol) in CCl_4 (1 mL) was placed into a NMR tube, sealed under vacuum, and heated in an oil bath at 95 °C. The reaction was monitored by ^{1}H NMR and was complete after 2.5 h. The conversion of the cis aldehyde **16** into the oxepinealdehyde **18** was in quantitative yield. Evaporation of the solvent gave **18**: colorless liquid, unstable at room temperature; ^{1}H NMR (CCl_4, TMS) δ 9.45 (d, 1 H), 6.05–6.40 (m, 2 H), 4.65–5.10 (m, 2 H), 3.25 (m, 1 H), 2.5 (m, 2 H); IR (CCl_4) 2950, 2920, 2850, 2820, 2720, 1730, 1700, 1640, 1350, 1325, 1215, 1130, 860 cm^{-1}.

A solution of **17** (62 mg, 0.5 mmol) in CCl_4 (1 mL) was thermolyzed at 160 °C for 1 h as described above. **18** was formed in a yield of 11%.

***endo*-[22] and *exo*-2-Methyl-6,7-dioxabicyclo[3.2.2]-3,8-nonadienes (31a and 31b).**[15] **31a** and **31b** were synthesized as described in the literature. Samples in high purity of **31a** and **31b** were obtained by repeated low-temperature (0 °C) column chromatography on silica gel (55 g), eluting with petroleum ether/CH_2Cl_2 (65:35). As the first fraction endo isomer was eluted. **31a**: colorless liquid; ^{13}C NMR ($CDCl_3$, TMS) 137.02, 134.07, 127.19, 126.01, 80.77, 73.25, 40.05, 18.63. Second eluate **31b**: colorless liquid; ^{13}C NMR ($CDCl_3$, TMS) δ 137.32, 135.88, 127.06, 124.44, 80.49, 73.56, 41.16, 14.32. For further physical data of **31a** and **31b**, see ref 15.

CoTPP Reaction of 31b. **31b** (276 mg, 2 mmol) was reacted with CoTPP as described. Evaporation of the solvent gave a mixture of **37** and **38** in a ratio of 4:1. The residue was subjected to column chromatography (silica gel, 20 g, CH_2Cl_2/petroleum ether 1:4) to give 172 mg (78%) of diepoxide **37** as a colorless oil: ^{1}H NMR (CCl_4, TMS) δ 5.15–5.7 (AB system, 2 H), 3.4 (dd, J = 4.8 and 2.2 Hz, 1 H), 3.1–3.3 (m, 2 H), 2.95 (dd, J = 4.4 and 2.2 Hz, 1 H), 2.45 (dd, J = 6.0 and 4.4 Hz, 1 H), 1.2 (d, J = 7.9 Hz, 3 H); IR (CCl_4) 3020, 2985, 2928, 2875, 1455, 1380, 1275, 1072, 1042, 935, 890 cm^{-1}; ^{13}C NMR ($CDCl_3$, TMS) δ 138.48, 122.47, 55.98, 53.66, 51.32, 51.18, 30.82, 19.75; MS, *m/e* (relative intensity) 138 (13, M$^+$), 121 (29), 109 (34), 97 (39), 91 (56), 81 (61), 71 (51), 57 (78). Anal. Calcd for $C_8H_{10}O_2$: C, 69.56; H, 7.52; O, 23.19. Found: C, 69.28; H, 7.09.

4,5-*cis*-Epoxy-2(*Z*),3(*E*)-octadienal (38): yield 20%; ^{1}H NMR (CCl_4, TMS) δ 9.95 (dd, 1 H), 5.2–6.2 (m, 4 H), 2.8–3.1 (m, 2 H), 1.85 (dd, J = 6.3 and 1.34 Hz, 3 H.

CoTPP Reaction of 31a. **31a** (200 mg, 1.45 mmol) was reacted with CoTPP as described above. Removal of the solvent gave a mixture of **35** and **36** in a ratio of 2:1. The residue was subjected to column chromatography (silica gel, 15 g, ether/petroleum ether 9:1) to give 102 mg (51%) of diepoxide **35** as a colorless oil: ^{1}H NMR (CCl_4, TMS) δ 4.95–5.9 (AB system, 2 H), 3.2 (m, 3 H), 2.9 (m, 1 H) 2.85 (d, 2 H), 1.25 (d, J = 7.8 Hz, 3 H); IR (CCl_4) 3060, 3000, 2960, 2910, 1470, 1400, 1080, 918, cm^{-1}. ^{13}C NMR ($CDCl_3$, TMS) δ 134.61, 123.45, 57.49, 53.29, 52.71, 49.64, 30.31, 20.90; MS, *m/e* 128. Anal. Calcd for $C_8H_{10}O_2$: C, 69.56; H, 7.25; O, 23.19. Found: C, 69.38; H, 7.17.

4,5-*trans*-Epoxy-2(*Z*),6(*E*)-octadienal (36): ^{1}H NMR (CCl_4, TMS) δ 10.1 (dd, 1 H), 6.2 (dd, 2 H), 6.6–6.9 (m, 1 H), 5.2 (m, 1 H), 3.9 (m, 1 H), 3.2 (m, 1 H), 1.7 (dd, J = 6.5 and 1.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, TMS) δ 190.07, 147.11, 133.17, 132.60, 126.85, 60.44, 55.18, 17.78.

Thermolysis of 38. A solution containing a mixture (62 mg) of **37** and **38** (4:1) in CCl_4 (0.7 mL) was placed into NMR tube, sealed under vacuum, and heated in an oil bath at 95 °C. The reaction was monitored by ^{1}H NMR and was complete after 3.5 h. All signals which belong to **38** disappeared and all signals which belong to **37** remained unchanged. Analysis of the spectrum showed the formation of oxepine derivative **39**: ^{1}H NMR (CCl_4, TMS) δ 9.4 (d, 1 H), 6.4 (d, 1 H), 6.1 (d, 1 H), 4.8–5.0 (m, 2 H), 1.2 (d, 3 H). Thermolysis of **36**: A mixture of **35** and **36** was thermolyzed as above. **36** was decomposed at 130 °C. **35** remained unchanged.

7,7-Dimethylcycloheptatriene (2 + 4) endoperoxide 32[17] was synthesized by photooxygenation of 7,7-dimethylcycloheptatriene as described in the literature.[23]

CoTPP Reaction of 32. **32** (154 mg, 1.0 mmol) was reacted in 40 mL of CH_2Cl_2 as described. After removal of the solvent the residue was analyzed by ^{1}H NMR. Diepoxide **32** was formed as the sole product. There was no indication of formation of open-chain aldehydes. A pure sample was obtained by sublimation (40 °C, 2 mmHg): colorless wax; ^{1}H NMR (CCl_4, TMS) δ 5.05–5.75 (AB system, J = 11.0 Hz, 2 H), 3.15 (m, 3 H), 2.75 (m, 1 H), 1.30 (s, 3 H), 1.23 (s, 3 H); IR (CCl_4) 3020, 2965, 1460, 1388, 1364, 1080, 942 cm^{-1}; MS, *m/e* 152 (M$^+$). Anal. Calcd $C_9H_{12}O_2$: C, 71.05; H, 7.79; O, 21.05. Found: C, 71.13; H, 7.98.

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Registry No. **6**, 59992-00-6; **7**, 61687-82-9; **8**, 61606-41-5; **9**, 72390-44-4; **10**, 72441-84-0; **11**, 68525-34-8; **12**, 24141-96-6; **13**, 67963-09-1; **14**, 85920-90-7; **15**, 61606-40-4; **16**, 88491-98-9; **17**, 88547-32-4; **18**, 113627-72-8; **19**, 88547-34-6; **20**, 88547-33-5; **25**, 68525-36-0; **26**, 113627-74-0; **27**, 113627-75-1; **31a**, 76821-93-7; **31b**, 76778-59-1; **32**, 86318-24-3; **35**, 113667-61-1; **36**, 113667-62-2; **37**, 113627-70-6; **38**, 113627-71-7; **39**, 113627-73-9; **40**, 113627-76-2; CoTPP, 59888-73-2.

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(22) Endo and Exo refer to the CH_3 group with respect to peroxide bridge.

(23) Hoffmann, R. W.; Friekel, F. *Synthesis* 1975, 444.