Tetrahedron Letters,Vol.24,No.38,pp 4135-4138,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

CoTPP-CATALYZED REACTION MECHANISM OF THE CYCLOHEPTATRIENE 1.4-ENDOPEROXIDE

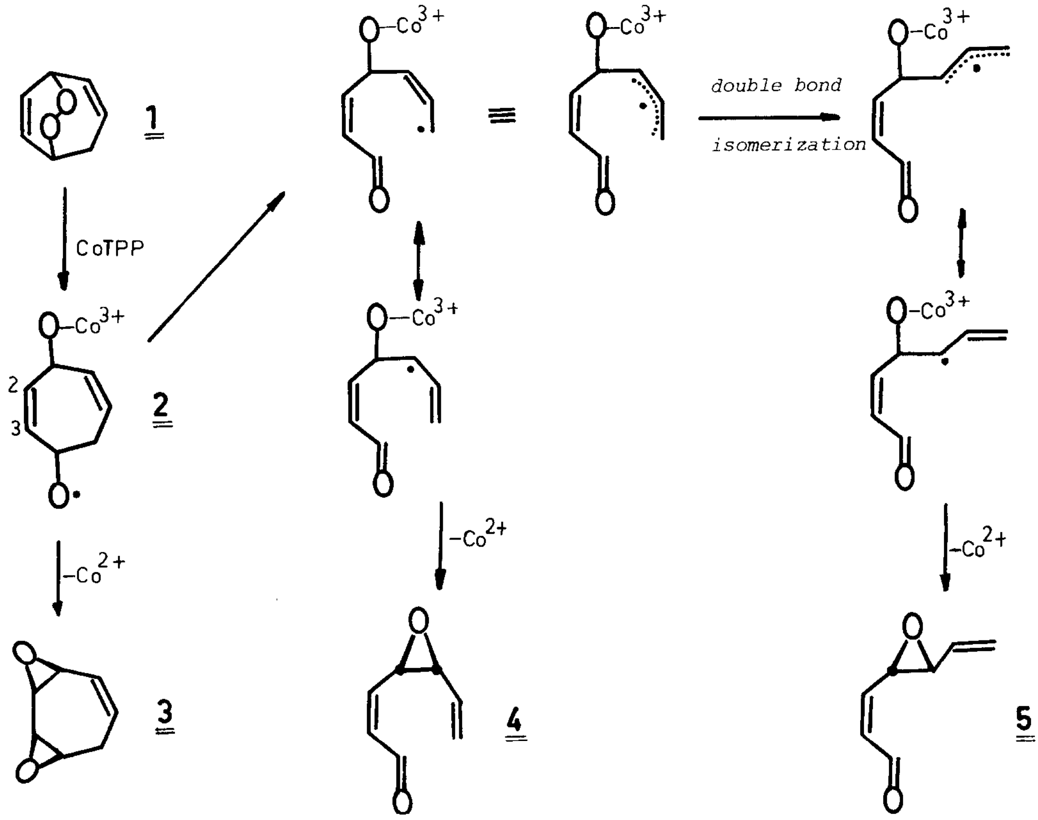
Metin Balcı*, Yaşar Sütbeyaz

Faculty of Science, Department of Chemistry,
Atatürk University, Erzurum/TURKEY

Summary : CoTPP-catalyzed reaction mechanism of the cycloheptatriene 1.4-endoperoxide is studied. Beside the expected bisepoxide, two isomeric open-chain aldehydes are isolated. The mechanism for the formation of the aldehydes are discussed in terms of radical intermediates.

Unsaturated [n.2.2] bicyclic endoperoxides upon thermolysis form bisepoxides with syn-configuration.[1] Recently, Foote et al.[2] introduced cobalt meso-tetraphenylporphine (CoTPP) catalyzed rearrangement of endoperoxides at low temperature to give bis-epoxides in high yield. We succesfully applied this rearrangement to endoperoxides with strained and perturbed diene moiety and suppressed side reactions like formation of epoxyenone.[3] In most cases the syn-epoxides were encountered. Only in the case of 1 and tropone endoperoxide were yields relatively lower (60 and 40%, respectively) compared with the other studied endoperoxides.

In order to gain more insight into the reaction mechanism and to explain the lower yield, we analyzed carefully the reaction mixture resulting from the CoTPP-catalyzed rearrangement of the 1.4-bicyclicendoperoxide 1. Beside the expected bisepoxide 3, we isolated a mixture of two aldehydes in a yield ca. 30 % which contained olefinic and epoxide protons. After repeated column chromatography at low temperature (-10 °C, Silica gel, eluiting with petroleum ether/ether 9:2) this mixture was separated in two aldehydes 4 and 5. Pure isomeric aldehydes for structural determination and further studies were obtained by preparative TLC separation. Control experiments showed that the isolated products were stable under the reaction conditions.



SCHEME 1

The structural assignment was made on the basis of the spectroscopic data.[4] Selected spectroscopic data are given in Table 1. We ascribed them trans-cis and cis-cis structures. As these compounds contain 1.2-divinylethylene oxide units, they are suitable species for the Cope-rearrangement. Herewith, we obtained unequivocal evidence for the structures by thermal isomerization. Both epoxides were converted into the 4.5-dihydrooxepin derivative 8.[5] The cyclization of the cis-isomer was completed at 95 °C in two hours with high yield. However, the trans-isomer needed higher temperature for conversion and yield was lower. Dihydrooxepin resulted from the [3.3] -Cope-rearrangement.[6]

Obviously such reactions, decomposition of endoperoxides, proceed via radical pathways. The formation of the products are reasonably understood

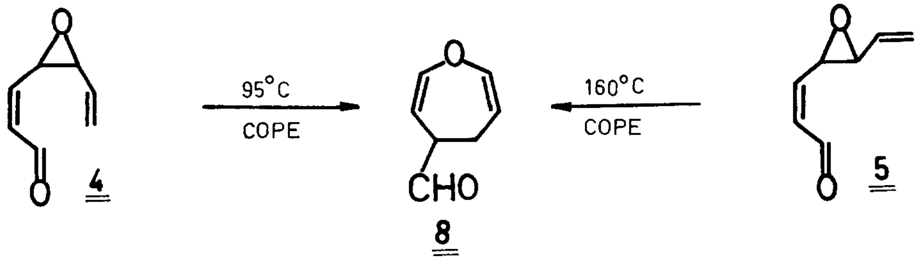
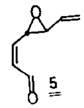
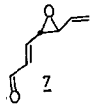
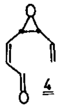
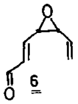
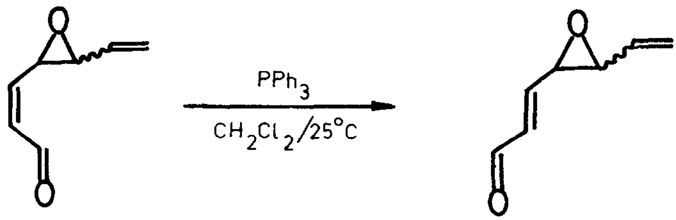


TABLE 1 : Selected physical data of the epoxyaldehydes

	^{1}H-NMR (CCl_4) ppm	IR (CCl_4) cm^{-1}
 5	*10.15 m, 1H aldehydic, 5.9-6.3 m, 2H olefinic, 5.15-5.75 m, 3H vinylic protons, 4.00 m, 1H epoxide, 3.25 m, 1H epoxide*	*3090, 3020, 2980, 2845 2740, 1685, 1640, 1605, 1440, 1140, 980, 925, 870*
 7	*9.4 m, 1H aldehydic, 6.45-6.2 m, 2H olefinic, 5.7-5.1 m, 3H vinylic protons, 3.4-3.1 m, 2H epoxide*	*3090, 2980, 2810, 2720, 1695, 1640, 1440, 1155, 1120, 1090, 965, 925, 870*
 4	*10.1 m, 1H aldehydic, 6.2 m, 2H olefinic, 5.8-5.2 m, 3H vinylic protons, 4.3 m, 1H epoxide, 3.75 m, 1H epoxide*	*3080, 3020, 2980, 2850, 2735, 1690, 1600, 1040, 920*
 6	*9.5 m, 1H aldehydic, 6.45 m, 2H olefinic, 5.7-5.1 m, 3H vinylic protons, 3.6 m, 2H epoxides*	*2810, 2710, 1695, 1640, 1220, 1120, 1105, 965, 930*

in terms of the mechanism outlined in Scheme 1. The radical, depicted as 2 resulting from the electron transfer reection between Co^{2+} species and endoperoxide, serves as a key intermediate. This radical undergoes various transformations. The radical collapses into diepoxide and fragments into allylic radical. The allylic radical can cause double bond isomerization which is responsible for the formation of the two epoxides isomers.

The conjugated C=C double bond in 4 and 5 has cis-configuration. In order to have an experimental evidence for this, we reacted pure samples of the aldehydes 4 and 5 with PPh_3 in CH_2Cl_2 and obtained the corresponding trans-aldehydes 6 and 7 nearly in quantitative yield. With this experiment we have furtheremore established that the configuration of the C_2-C_3 double bond was intact during the reaarangement as expected. 6 and 7 were also converted into the dihydrooxepin derivative 8 by heating at 95 °C and 160 °C, respectively.



4 or 5

6 or 7

ACKNOWLEDGEMENT : The authors are indepted to the Department of Chemistry, Atatürk University for financial support of this work and appreciate the technical assistance by Mr. Şahmettin Yıldız.

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3) M. Balcı, Y. Sütbeyaz, Tetrahedron Lett., 24, 311, (1983).
4) More details about the spectroscopic data will be reported in a full-paper.
5) **8** : Colourless liquid, ^{1}H-NMR (CCl_4) λ : 9.45 d, aldehydic proton, 6.4-6.05 m, 2H olefinic protons (α), 5.1-4.65 m, 2H olefinic protons (β), 3.25 m, 1H methine proton, 2.5 m, 2H methylene protons, IR (CCl_4) shows bands at 2950, 2920, 2850, 2820, 2720, 1730, 1700, 1640, 1350, 1325, 1215, 1130, 860 cm^{-1}.
6) For conversion of the cis- and trans 1,2-divinylethylene oxide to 4,5-dihydrooxepine see:
   a) R. A. Brauen, J. Org. Chem., 28, 1383, (1963).
   b) E. L. Stogryn, M. H. Gianni, A. J. Passannante, J. Org. Chem., 29, 1275, (1964).

(Received in UK 18 July 1983)