

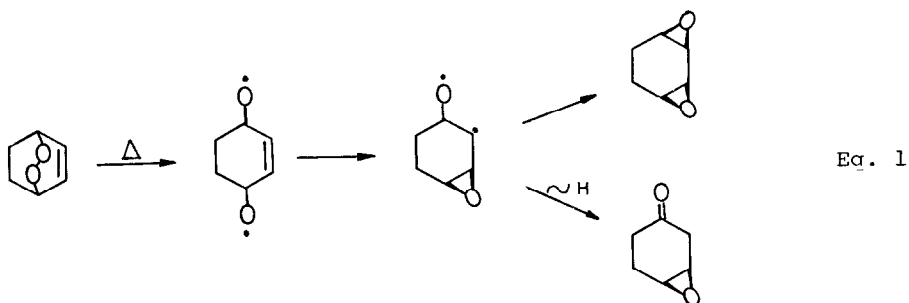
COTPP-CATALYZED REARRANGEMENT OF 1.4-ENDOPEROXIDES

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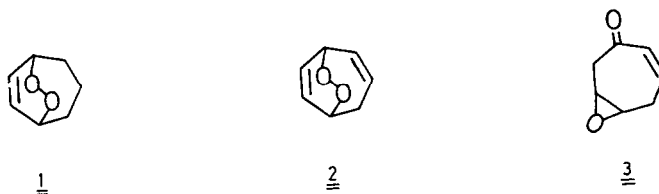
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Summary: Bicyclic endoperoxides with strained and perturbed diene moiety have been submitted to CoTPP-catalyzed rearrangement. Side reaction, like formation of epoxyenone, has been suppressed and yield of the formation of bisepoxides highly increased.

One of the common reactions of unsaturated [n.2.2] 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 bisepoxides with syn configuration. However, in strained molecules like [2.2.1] systems thermolysis is always accompanied by side reactions. One of these side reactions is the formation of epoxy ketones¹ (Eq. 1). Such side reactions have been observed



recently also in cycloheptatriene systems. For example, the thermolysis of 1,3-cycloheptadiene endoperoxide (1) gives a quantitative yield of bisepoxide². In contrast, (2) which differs from (1) by an additional double bond, forms bisepoxide only in 11% yield. The major product of this reaction is the epoxyenone³ (3). The intermediate-formed diradical either transposes an alkoxy α -hydrogen by β -scission, affording epoxyenone, or cycloadds into ene bisepoxide.



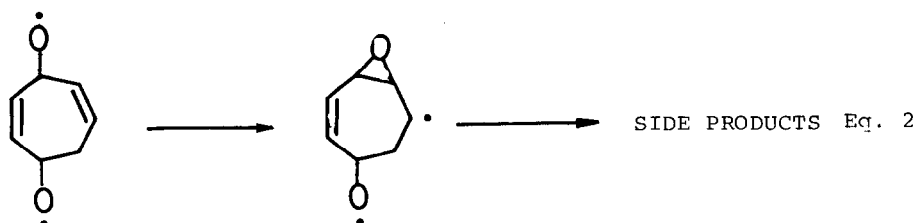
The driving force of this rearrangement is not the formation of α - β unsaturated ketones, since blocking of the double bond in (2) by epoxidation does not prevent the rearrangement to form epoxyenone⁴.

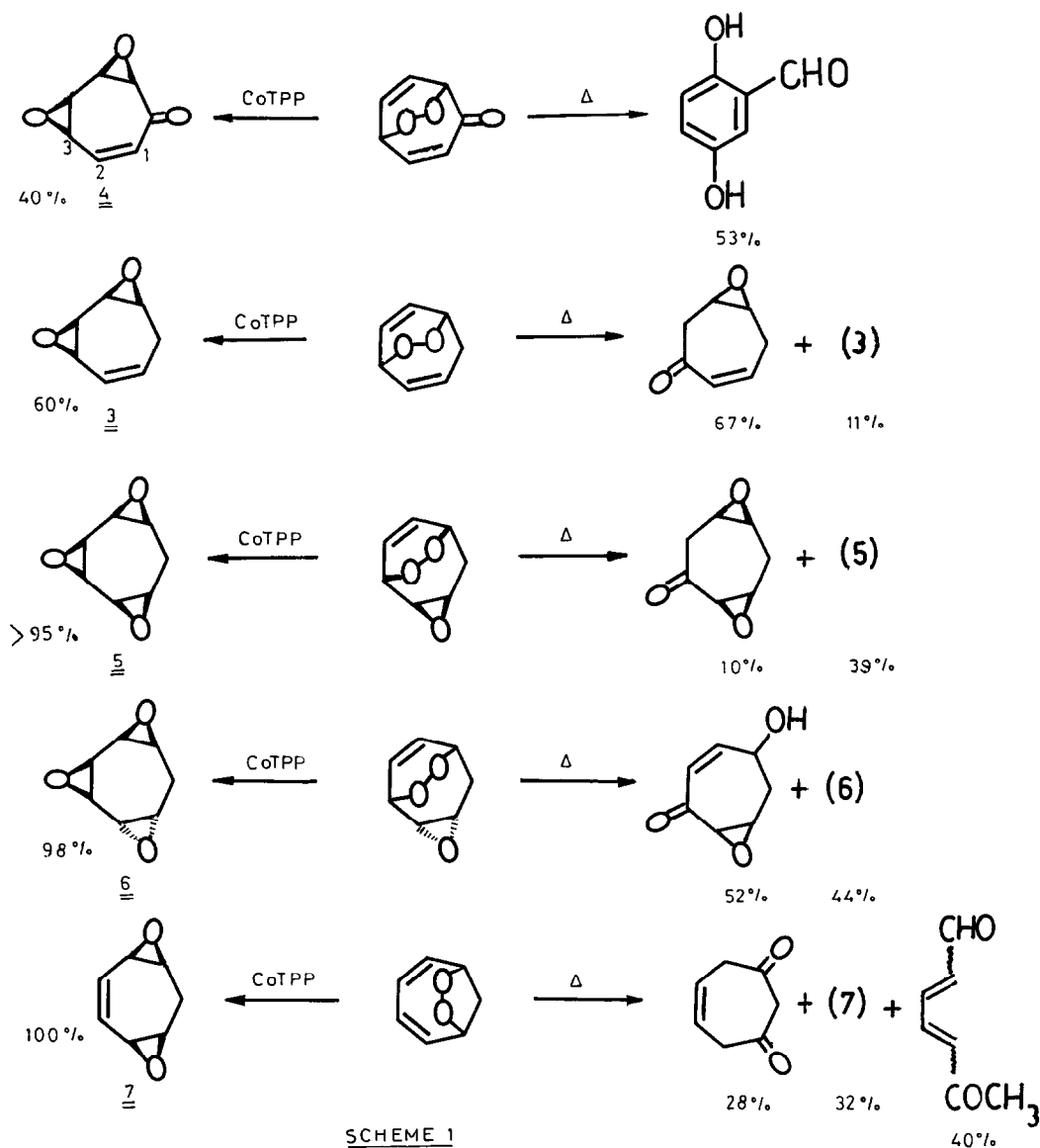
In summary, bisepoxides can not be formed in high yield from bicyclic endoperoxides, if molecules are highly strained or diene moiety perturbed by double bonds or epoxides. In these cases side reactions become important.

Recently, Foote et al.⁵ have shown that cobalt meso-tetraphenylporphine catalyzes the rearrangement of endoperoxides at low temperature to form bisepoxides with syn configuration. The catalyzed procedure gives much better yields with most substrates and is much more convenient.

Since the activation energy for H-shift to form epoxyenone will be higher than that for the epoxide formation, CoTPP-catalyzed rearrangement can suppress this side reaction and increase the yield of the epoxide formation.

Herewith, we describe our results obtained by application of CoTPP-catalyzed rearrangement to endoperoxides with strained and perturbed diene moiety. We have submitted the following endoperoxides (see Scheme 1), derived from cycloheptatriene and tropone, to CoTPP-catalyzed rearrangement and obtained the desired epoxides⁶ in some cases nearly in quantitative yield. Tropon endoperoxide, which undergoes a rearrangement on refluxing in xylene to give 2,5-dihydroxybenzaldehyde⁷, could be converted to the unknown interesting bisepoxide⁸ in a 40% yield. The rearrangements occur in a stereospecific fashion.





In all cases only the syn epoxides were encountered. The spectroscopic properties of compounds 3^3 , 5^4 , 6^4 , and 7^3 agreed well with the literature. In the cases of (3) and (4), yields are relatively lower compared to the other endoperoxides. This can be explained in terms of the intermediate formed oxygen-diradicals which can add to two different double bonds as shown in Eq.2. Consequently, side reactions will occur and decrease the yield for the formation of bisepoxides.

Studies on the mechanism and scope of this kind of addition are being conducted and will be reported in the near future.

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- 6) The procedure usually consists of the addition of a solution of CoTPP in CH_2Cl_2 to a solution of the peroxide in CH_2Cl_2 at 0°C . 5% of CoTPP⁹ (relative to substrate) was sufficient for the reactions.
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