Chem. Pharm. Bull.
18(5)1040—1044(1970)

UDC 546.73.04 : 542.952.1

Isomerization of Epoxides to Ketones by Pentacyanocobalt Complex

JONG-YOON KIM and TAKAO KWAN

Faculty of Pharmaceutical Sciences, University of Tokyo[1]

(Received January 10, 1970)

Interaction of pentacyanocobalt hydride, $HCo(CN)_5^{3-}$, with epoxides such as propylene oxide, cyclohexene oxide, and styrene oxide has been investigated in aqueous solutions. While hydrogenation of epoxides to alcohols took place, it appeared to give way, to some extent, to isomerization to form ketones especially when excess alkali was added. This newly discovered isomerization reaction is assumed to take place *via* the interaction of epoxides with univalent pentacyanocobalt complex, $Co(CN)_5^{4-}$, that is formed in alkaline solution according to $HCo(CN)_5^{3-} + OH^- \rightarrow Co(CN)_5^{4-} + H_2O$.

The pentacyanocobalt hydride, $HCo(CN)_5^{3-}$, has been found to be an effective agent for homogeneous hydrogenation and hydrogenolysis of many organic compounds.[2] The activation mechanism of molecular hydrogen by pentacyanocobalt(II) complex to form the pentacyanocobalt hydride[3] as well as the selective hydrogenation of butadiene[4] and isoprene[5] by the latter complex was previously worked out in this laboratory.

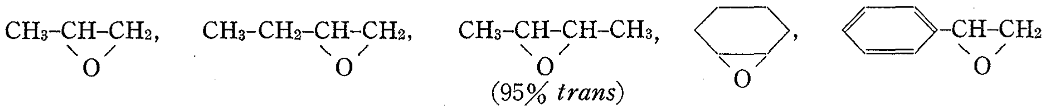
In the course of the reinvestigation of hydrogenation of epoxides by the hydride complex in a hydrogen atmosphere, carried out previously by J. Kwiatek, *et al.*,[6] we have newly found the isomerization of epoxides to ketones as well as the hydrogenation to alcohols. As no isomerization reaction has ever been reported hitherto by the hydride complex, and very few works reported on the isomerization of epoxide by metal complexes, it is of interest to have found the above isomerization reaction.

On the other hand, we already noted[3] that pentacyanocobalt deuteride, $DCo(CN)_5^{3-}$, readily exchanged its deuterium atom with hydrogen of water when excess alkali was added, and recently Vlček, *et al.* reported[7] the formation of univalent cobalt complex, $Co(CN)_5^{4-}$, by deprotonation of the $HCo(CN)_5^{3-}$ in alkaline solution.

In connection with these results it was expected that the selectivity in the reaction between the hydride complex and epoxide would vary with, on addition of alkali, the change of ratio of the two complex species, as was the case. Thus, in the present paper, we wish to report and discuss mainly the effect of alkali addition on the relative yield of alcohol and ketone.

Experimental

Materials——Following epoxides were employed in this work:



(95% *trans*)

These were either of reagent grade or of extra pure grade, all of which were supplied from Tokyo Kasei Kogyo Co. All the other chemicals used were of reagent grade and also obtained commercially.

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[1] Location: *Hongo 7-3-1, Bunkyo-ku, Tokyo.*

[2] *a*) M. Iguchi, *Nippon Kagaku Zasshi*, **63**, 634 (1942); *b*) J. Kwiatek, "Catalysis Reviews," Vol. 1, Marcel Dekker, Inc., New York, N. Y., 1968, p. 37, and references therein.

[3] T. Mizuta and T. Kwan, *Nippon Kagaku Zasshi*, **86**, 1010 (1965).

[4] T. Suzuki and T. Kwan, *Nippon Kagaku Zasshi*, **86**, 713 (1965).

[5] T. Suzuki and T. Kwan, *Nippon Kagaku Zasshi*, **86**, 1341 (1965).

[6] J. Kwiatek, I.L. Mador, and J.K. Seyler, *J. Am. Chem. Soc.*, **84**, 304 (1962).

[7] A.A. Vlček, *Pure Appl. Chem.*, **10**, 61 (1965); J. Hanzlik and A.A. Vlček, *Chem. Comm.*, **1969**, 67; *idem.*, *Inorg. Chem.*, **8**, 669 (1969).

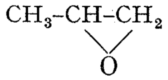
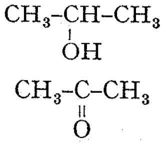
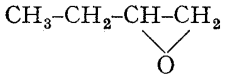
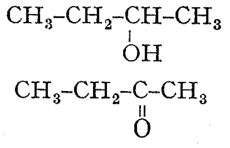
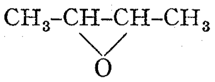
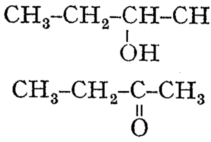
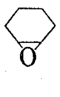
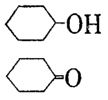
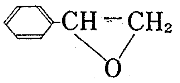
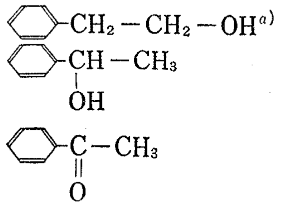
Preparation of Pentacyanocobalt Complex——To an aqueous solution containing 10 mmoles $CoCl_2 \cdot 6H_2O$, an appropriate amount of KCN (51—70 mmoles, namely, CN/Co 5.1—7.0 according to the runs) solution was added, the whole solution totalling to *ca.* 50 ml, at 0—5° with vigorous bubbling with H_2. The resulted cobalt complex system was allowed to absorb H_2 for about 15 min. In one case, N_2 was used in place of H_2. In the case of alkali addition, an appropriate amount of KOH (15—180 mmoles, namely, OH/Co 1.5—18 according to the runs) was added soon after the addition of KCN solution.

Reaction of Epoxides with the Cobalt Complex System——After sufficient absorption of H_2 by the complex system as mentioned above, temperature was set usually at 30° and 2 mmoles of a given epoxide were injected into the system by means of hypodermic syringe and then subjected to reaction usually for 1 hr in the presence of 1 atm of H_2 with magnetic stirring.

Extraction of Products——The aqueous solution of reaction mixture from each run was salted out with a proper amount of KCl and allowed to cool to *ca.* 10° and then the solution was transferred to a separatory funnel to which 10 ml of purified ether or chloroform was added. After separating the organic solvent layer containing reaction products, 5 ml of the solution was pipetted out and a definite amount of a proper material was added as an internal standard. Extraction efficiency tests were carried out for each product whereby the yield of each product was corrected.

Analysis by Gas-Liquid Chromatography——The apparatus used for the analyses of the products was Shimadzu Gas Chromatograph Model GC-2B equipped with T.C.D. and copper columns (3 m × ϕ3 mm) packed with 25% PEG 6000 on Shimalite (30—60 mesh) or 25% Silicone DC 550 on Shimalite (30—60 mesh) (the latter for acetophenone only). The temperatures of the columns and injection chamber were set suitably for each set of products. Helium was used as the carrier gas.

Table I. Reaction Products between Epoxides and Pentacyanocobalt Complex System

Epoxide	Products	Molar ratio of ketone to alcohol + ketone S	Total yields Y mole %
	 $CH_3\text{-}CH(OH)\text{-}CH_3$ $CH_3\text{-}C(=O)\text{-}CH_3$	0.16	68
	 $CH_3\text{-}CH_2\text{-}CH(OH)\text{-}CH_3$ $CH_3\text{-}CH_2\text{-}C(=O)\text{-}CH_3$	0.17	63
	 $CH_3\text{-}CH_2\text{-}CH(OH)\text{-}CH_3$ $CH_3\text{-}CH_2\text{-}C(=O)\text{-}CH_3$	0.18	9
		0.15	63
	 [a]	~0.03	~67

reaction temperature: 30° (20° for propylene oxide)
reaction time: 1 hr
hydrogen pressure: 1 atm CN/Co: 6.0
a) Primary alcohol 89%, secondary alcohol 11%.

Results and Discussion

Reaction Products

The reaction products from individual epoxide are listed in Table I.

It is apparent from Table I that all epoxides employed give rise to both alcohols and ketones. As the dehydrogenation of alcohol to ketone or its reverse reaction was confirmed not to occur under the reaction conditions, the data of Table I indicate that epoxides undergo mainly hydrogenation, but accompanied simultaneously by isomerization to a minor extent.

Further inspection of the data reveals that (1) the external epoxides react more readily than the internal epoxides (except cyclohexene oxide); (2) the aliphatic epoxides afford only secondary alcohols while styrene oxide does mainly primary alcohol along with a small amount of secondary alcohol (the formation of the latter alcohol also is new discovery); (3) even terminal epoxides give not aldehydes but ketones only.

The result (1) implies that it is difficult for the cobalt complex to cleave internal epoxide ring overcoming the steric hindrance exerted by the epoxide. In the case of cyclohexene oxide, it seems that less steric hindrance is exerted compared with acyclic internal epoxides. This might be supported by the fact that cyclohexene oxide formed an adduct with bis(dimethylglyoximato) cobalt(1) complex,[8] whereas 2,3-butylene oxide could not, as the latter reaction was carried out by us. The result (2) is on the whole in accord with those of the reaction by general nucleophiles[9] (see Mechanism of the Reaction in later part). The result (3) was also observed with some other metal complex systems,[10] which forms a striking contrast compared with the reaction by some Lewis acids which always give aldehydes only.[9]

Effect of Alkali Addition on the Molar Ratio

Ketone/Alcohol Formed——The effect of alkali addition on the relative yield of alcohol and ketone will be considered using cyclohexene oxide as an example. When KOH was added to the reaction system, following changes in the selectivity (denoted as *S*) and the total yields (denoted as *Y*) were observed as shown in Fig. 1.

It is apparent from Fig. 1 that the formation of ketone is enhanced about three times while the total yields of alcohol and ketone remain unchanged or are not suppressed appreci-

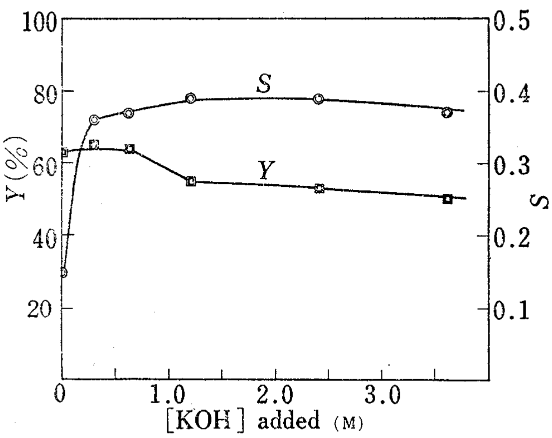


Fig. 1. Effect of Alkali Addition on Y and *S* in the Reaction between Cyclohexene Oxide and Pentacyanocobalt Complex System at 30° for 1 hr

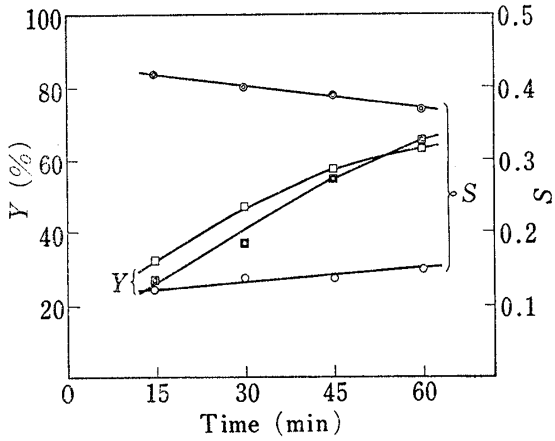


Fig. 2. Formation of Cyclohexenol and Cyclohexanone in the Course of Reaction at 30°

▣, ◎ : KOH added (0.6M)
□, ○ : No KOH added

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8) G.N. Schrauzer and R.J. Windgassen, *J. Am. Chem. Soc.*, **89**, 143 (1967).
9) R.E. Parker and N.S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).
10) J.Y. Kim, unpublished work.

ably. As a similar tendency was observed with propylene oxide, it is considered that the effect is operative in all the cases studied.

Time Dependence of *S* and *Y*

In the reaction of cyclohexene oxide with the complex system, *S* as well as *Y* was examined at regular intervals. The results are shown in Fig. 2 where *S* and *Y* were determined with or without KOH.

Enhanced formation of cyclohexanone in the alkali-added system is again obvious from Fig. 2 during the progress of the reaction. However, *S* appeared to decrease gradually in the case of alkali addition. The phenomenon may be explained as due to aldol condensation that can be accelerated by excess alkali. Indeed, it was shown by reference runs that cyclohexanone decreased gradually in the presence of excess alkali under otherwise the same reaction conditions. So the amount of cyclohexanone formed would actually be more than that shown in Fig. 2.

Mechanism of the Reaction

Possible reaction mechanisms are to be speculated, which will be preceded by the consideration on the nature of the hydride complex, $HCo(CN)_5^{3-}$.

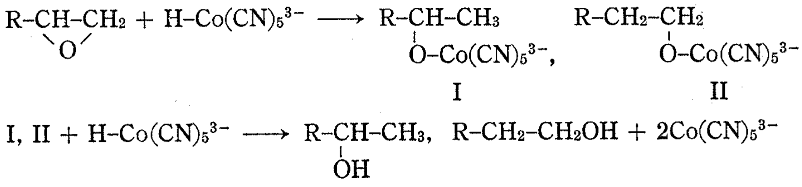
From several physical or chemical experimental data, it was recognized that the hydrogen atom of the hydride complex was either hydridic or almost covalent.[2b,3,11] As reported previously, the absorption of D_2 by $Co(CN)_5^{3-}$ in an aqueous solution was followed by the more rapid appearance of HD than H_2 in the gas phase while, on addition of KOH to the solution, molecular species that appeared initially was H_2 rather than HD.[3]

Together with the above-mentioned results of our present work, it can be assumed therefore that a common alkali effect is operative in the two sorts of reactions, involving the following equilibrium reaction as confirmed by Vlček, *et al.*[7]

$$\mathrm{HCo(CN)_5^{3-} + OH^- \rightleftharpoons Co(CN)_5^{4-} + H_2O} \qquad (1)$$

From many hydrogenation reactions by the $HCo(CN)_5^{3-}$ complex, sometimes with alkali addition, it has been shown to act sometimes *via* addition mechanism involving "hydrogen" transfer. On the other hand, the $Co(CN)_5^{4-}$ complex is expected to act, besides as a proton acceptor, *via* redox addition mechanism involving "two-electron" transfer. In this connection reference will be made to the behaviour of the above-mentioned, univalent bis(dimethylglyoximato)cobalt complex which seems also to be a "two-electron" donor. It can be formed only in an alkaline solution in equilibrium with divalent species *via* hydride species and reacts with epoxides to form isolable *β*-hydroxy-*n*-alkyl complexes that are degraded in an alkaline solution, without alcohol formation, probably *via* deprotonation of the hydroxyl group to give ketones.[8]

Thus, although attempted isolation of intermediate complexes was unsuccessful, the probable difference in the reactivity between the two complexes would lead to the assumption that alcohols are formed by the action of $HCo(CN)_5^{3-}$ whereas ketones by $Co(CN)_5^{4-}$. Thereby following mechanisms are suggested in connection with the nature of the epoxides studied, acyclic external epoxide being represented as typical one:



$$\underset{\diagdown O \diagup}{\mathrm{R{-}CH{-}CH_2}} + \mathrm{H{-}Co(CN)_5^{3-}} \longrightarrow \underset{\mathrm{I}}{\underset{\mathrm{O{-}Co(CN)_5^{3-}}}{\mathrm{R{-}CH{-}CH_3}}},\quad \underset{\mathrm{II}}{\underset{\mathrm{O{-}Co(CN)_5^{3-}}}{\mathrm{R{-}CH_2{-}CH_2}}}$$

$$\mathrm{I, II} + \mathrm{H{-}Co(CN)_5^{3-}} \longrightarrow \underset{\mathrm{OH}}{\mathrm{R{-}CH{-}CH_3}},\ \mathrm{R{-}CH_2{-}CH_2OH} + 2\mathrm{Co(CN)_5^{3-}}$$

Chart 1. Alcohol Formation

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[11] K. Tarama, T. Yonezawa, and M. Sahara, Abstracts of Papers, 16th Symposium on Coordination Chemistry, Tokyo, Japan, Oct. 1966, p. 160.

Here the hydride complex is considered to behave as $H^{\delta-}$—$Co^{\delta+}$, forming two sorts of intermediates I or/and II according to attack by hydridic moiety at either the α- or the β-carbon atom of the epoxide ring. Further reaction of these intermediates with another hydride complex would yield secondary or/and primary alcohols as shown in the above scheme. The formation of only secondary alcohols from the saturated aliphatic epoxides and that of mainly primary alcohol from styrene oxide as shown in Table I seem to be explicable on the basis of predominant steric effect by alkyl group on the nucleophilic hydridic moiety, thus causing sole attack at the β-carbon in the former cases, whereas greater steric effect by phenyl group on the electrophilic cyanocobalt moiety together with electronic effect inducing increased positive charge on the α-carbon in the latter case.

Possible participation of $H^{\delta+}$—$Co^{\delta-}$ species, if formed, is hardly considered for steric reasons, as supported by the main formation of primary alcohol from styrene oxide.

On the other hand, the univalent $Co(CN)_5^{4-}$ complex would react with epoxide like analogous bis(dimethylglyoximato)cobalt(I) complex as a "two-electron" donor to form the activated complexes of deprotonated forms of β-hydroxyalkyl complexes of the type, III or/and IV, which would lead to the formation of ketone or/and aldehyde *via* intramolecular hydride shift. The mechanism would be given by the scheme:

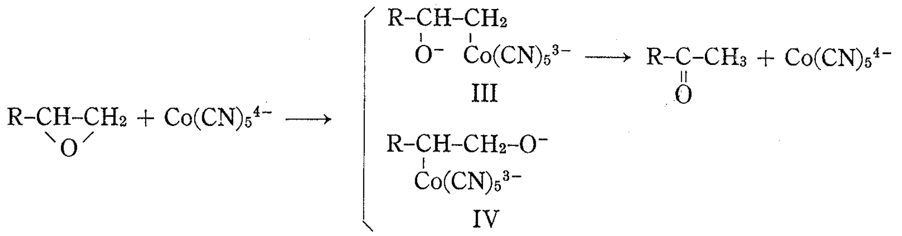

Chart 2. Ketone Formation

Since no aldehydes were formed in the reaction of all epoxides studied, IV should be excluded, this postulate is in accord with the steric effect and the degradation of the adducts, β-hydroxy-*n*-alkyl complexes, formed by the reaction between the analogous cobalt(I) complex and epoxides only to ketones as mentioned above.

The latter result, in turn, supports the elimination of alternative possibility that the Co-$(CN)_5^{4-}$ species may function as a proton acceptor from epoxide, aside from unlikeliness of such function under the reaction conditions.

Possible isomerization of epoxides to ketones by the interaction with $Co(CN)_5^{3-}$ species was excluded by the result of a run carried out in a nitrogen atmosphere where the species was present predominantly. Furthermore, possible formation of either alcohols by hydrogenation of the ketones produced[2b)] or of ketones by dehydrogenation of the alcohols produced[12)] was also precluded by reference runs.

Finally some comments should be made on the effect of alkali addition on *S*. As shown in Fig. 1, *S* appeared to be little dependent on [KOH] at higher concentrations. The selectivity, *S*, should depend upon the [KOH] if ketones are formed only by the action of the $Co(CN)_5^{4-}$ complex and alcohols by $HCo(CN)_5^{3-}$. However, it is not quite deniable that OH^- may take part in the reaction routes especially at higher [KOH] concentrations. The suggested mechanisms together with the effect of alkali on the reaction system are under further study.

Acknowledgement We wish to express our gratitude to Drs. Haruhiko Yamamoto and Taiichi Mizuta for their kind assistance in this work.

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12) It was reported that alcohol was dehydrogenated to aldehyde or ketone by hydrogenation catalysts such as Pt or Pd complexes even under high hydrogen pressure. Ref: J. Chatt and B.L. Shaw, *J. Chem. Soc.*, **1962**, 5075; H. Itatani and J.C. Bailar, Jr., *J. Am. Oil Chem. Soc.*, **44**, 147 (1967).