CHEMISTRY LETTERS, pp. 565-568, 1972. Published by the Chemical Society of Japan

STEREOCHEMISTRY OF THE HYDROGENATION OF ETHYL 2-METHYL-1-CYCLOHEXENYL ETHER. AN EXAMPLE OF STEREOSPECIFIC CIS ADDITION OF HYDROGEN

Shigeo NISHIMURA and Yoshio KANO
Department of Industrial Chemistry, Tokyo University of
Agriculture and Technology, Koganei, Tokyo

The hydrogenation of ethyl 2-methyl-1-cyclohexenyl ether with platinum metal catalysts yields saturated cis-ether with high stereospecificity in ethanol. Formation of the trans-ether during the course of hydrogenation arises through isomerization to ethyl 6-methyl-1-cyclohexenyl ether which yields both cis- and trans-ethers on hydrogenation.

The stereochemistry and mechanism of the hydrogenation of cycloolefins have been the subject of considerable work in recent years.[1)] An interesting example is the hydrogenation of 1,2-dimethylcyclohexene which would be expected to yield only cis-1,2-dimethylcyclohexane by simple cis addition of hydrogen. Siegel and Smith[2)] have shown, however, that both cis and trans isomers are formed from this substance in the hydrogenation with reduced platinum oxide in acetic acid. They have argued that the trans isomer arises through isomerization to 2,3-dimethylcyclohexene followed by desorption and then readsorption on both sides of the compound.[1,2)] Although some supporting evidence has been obtained for this explanation,[1,3)] objections to this have also been proposed, because the required isomerization is thermodynamically unfavorable and the isomerized olefin, even if formed on the catalyst surface, is unlikely to desorb to the required extent over a catalyst metal of such low isomerization activity as platinum.[4)] The trans isomer was even the predominant product in the palladium-catalyzed hydrogenation, but in this case an extensive isomerization prior to hydrogenation has been observed.[5)]

During the course of studies on the hydrogenation of ethyl o-tolyl ether and its tetrahydro derivatives, we have found that ethyl 2-methyl-1-cyclohexenyl ether (I) is hydrogenated to saturated cis-ether with high stereospecificity. As shown in Fig. 1, formation of the trans-ether at the initial stage of the hydrogenation as obtained by extrapolation is only 0.4 % over platinum, 1 % over ruthenium, 2 % over palladium and 3 % over rhodium in ethanol at 25°C under the atmospheric pressure of hydrogen. The hydrogenation was always accompanied by rather extensive isomerization to ethyl 6-methyl-1-cyclohexenyl ether (II). The hydrogenation was also accompanied by rapid formation of 2-methylcyclohexanone and its diethyl acetal with rhodium and palladium catalysts. The formation of the ketone and acetal took place only to a small extent with platinum, although this side reaction occurred extensively in the hydrogenation of the enol ethers derived from 3- and 4-methylcyclohexanones.[6,7)] II yields the trans-ether in varying amounts depen-

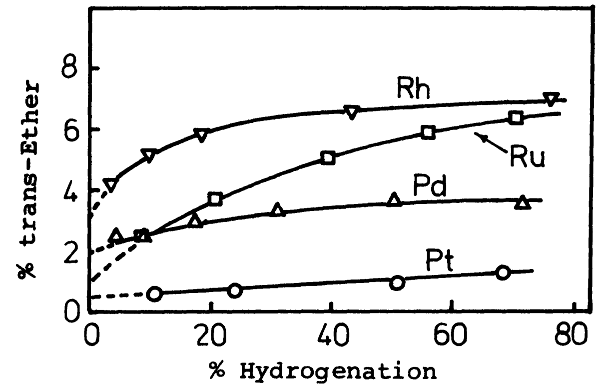


Fig. 1. Variation in the proportion of trans-ether in saturated ether as a function of the extent of hydrogenation of ethyl 2-methyl-1-cyclohexenyl ether in ethanol.

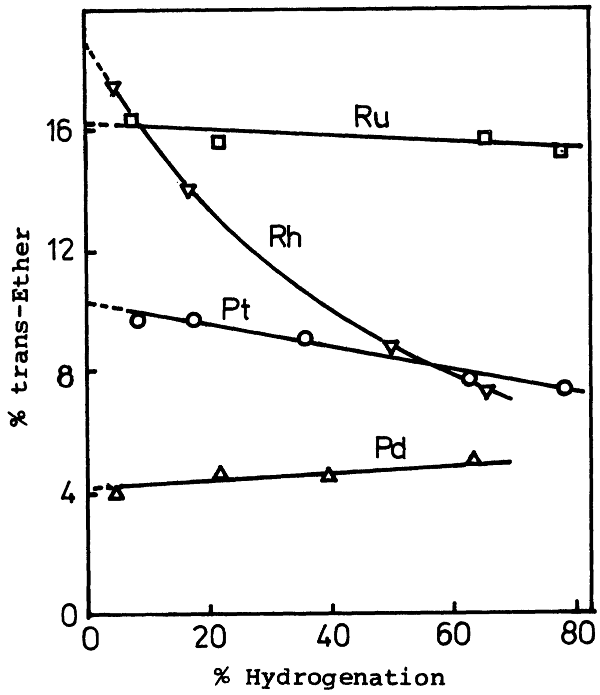


Fig. 2. Variation in the proportion of trans-ether in saturated ether as a function of the extent of hydrogenation of ethyl 6-methyl-1-cyclohexenyl ether in ethanol.

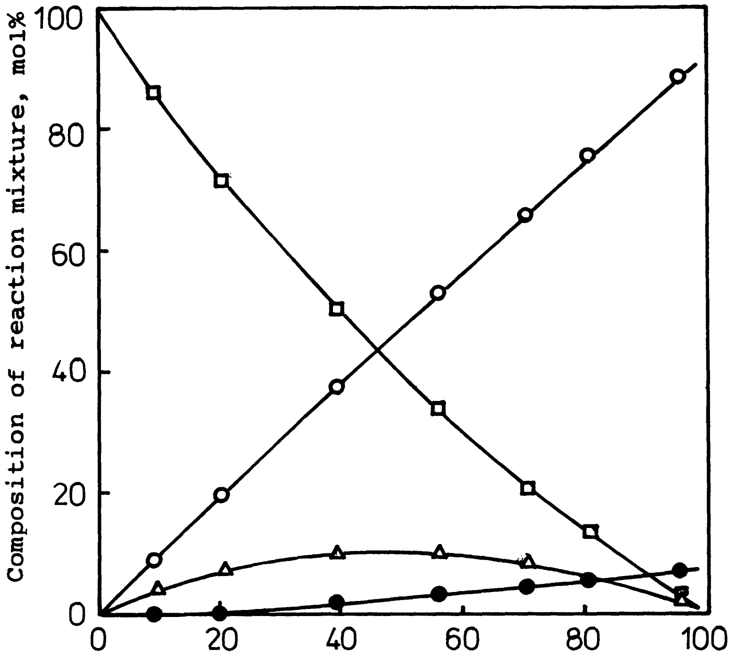
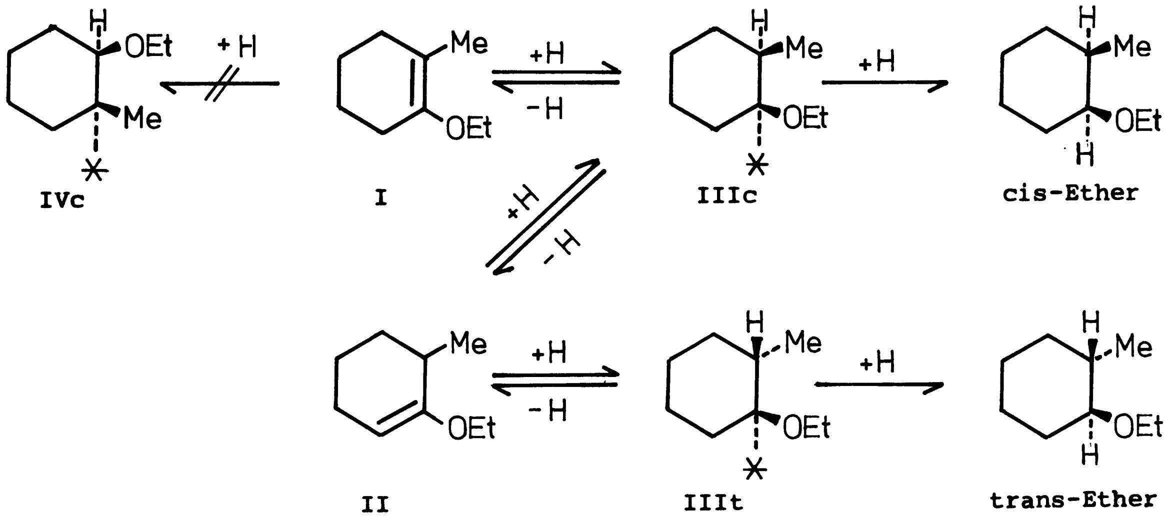


Fig. 3. Variation in the composition of products as a function of the extent of hydrogenation of ethyl 2-methyl-1-cyclohexenyl ether (□) over ruthenium in ethanol. ○ : cis-ether; ● : trans-ether; △ : ethyl 6-methyl-1-cyclohexenyl ether.

ding on the catalyst metals as indicated in Fig. 2 by extrapolation to the initiation of hydrogenation. As in the case of I, extensive isomerization to I and, with rhodium and palladium, rapid formation of the ketone and acetal accompanied the hydrogenation. The variations in the proportion of the trans-ether show characteristic features according to the catalyst metals. These might be due to the differences in the extent of isomerization as well as in the relative reactivity of I and II which both appear to depend on the nature of the catalyst metals. The situation is further complicated by the concurrent formation of the ketone and acetal in the cases of rhodium and palladium catalysts.

Evidence for that the trans-ether formed during the hydrogenation of I would arise through isomerized II can be seen in the ruthenium-catalyzed hydrogenation, as shown in Fig. 3, where the isomerization to II is not so much extensive (ca. 36 %) and the II formed by isomerization affords a significant amount of the trans-ether (see Fig. 2). In all cases the formation of ethyl 2-methyl-2-cyclohexenyl ether could not be detected during hydrogenation.

The stereospecific formation of the cis-ether from I may be explained by the reaction scheme shown below:



Addition of a hydrogen atom(or proton) to I leads to the half-hydrogenated state IIIc, the preferential formation of which would be directed by the electron-releasing ethoxyl group. IIIc is either hydrogenated to give the cis-ether or isomerized to II through which both cis- and trans-ethers are produced. It is to be noted that over palladium both I and II afford the cis-ether in high yields. These results are in contrast to those with 1,2- and 2,3-dimethylcyclohexenes which were reported to give the trans isomer predominantly on hydrogenation with palladium.[5] The results with palladium can be explained also by the reaction scheme described above on the assumption that the stereochemistry-controlling step is the hydrogenation of the half-hydrogenated states IIIc and IIIt that are almost equilibrated on the catalyst surface.

The directive effect of the ethoxyl group in the formation of half-hydrogenated state has been postulated previously for the explanation of the stereochemistry of hydrogenation of ethyl 4-methyl-1-cyclohexenyl ether,[6] but in this ether the direction of the double bond migration could not be demonstrated. The present results obtained on the stereochemistry of hydrogenation and the isomerization of I and II thus strongly support the postulation made previously.

Recently, Pecque and Maurel[8)] have reported that the trans isomer is formed in considerable amounts in the hydrogenation of 2,3-dimethylbicyclo[2,2,2]oct-2-ene which can isomerize only to 3-methyl-2-methylenebicyclo[2,2,2]octane. Formation of only the cis-ether from I is very probably related to the circumstance that IVc (see the reaction scheme) is not involved among the half-hydrogenated species derived from I. This result, together with those by Pecque and Maurel, suggest that the presence of the methyl groups attached to unsaturated carbons would be responsible for the formation of the trans isomers in 1,2-dimethylcyclohexene and 2,3-dimethylbicyclo[2,2,2]oct-2-ene, via desorbed or not desorbed intermediates. The catalysts used in this study are unsupported metals prepared by the methods described previously.[6)] Further studies on the hydrogenation with other metals and in other solvents are in progress.

REFERENCES

1) S. Siegel, Advan. Catal., 16, 123 (1966).
2) S. Siegel and G. V. Smith, J. Amer. Chem. Soc., 82, 6082 (1960).
3) A. W. Weitkamp, Advan. Catal., 18, 1 (1968).
4) G. C. Bond and P. B. Wells, ibid., 15, 91 (1964).
5) S. Siegel and G. V. Smith, J. Amer. Chem. Soc., 82, 6087 (1960).
6) S. Nishimura, M. Katagiri, T. Watanabe, and M. Uramoto, Bull. Chem. Soc. Japan, 44, 166 (1971).
7) S. Nishimura, T. Saigo, and Y. Kano, unpublished results.
8) M. Pecque and R. Maurel, J. Catal., 19, 360 (1970).

(Received April 4, 1972)