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NOTES

Unusual Feature of Catalytic Hydrogenation of Methyl 4-*t*-Butyl-1-cyclohexenyl Ether Over Platinum

An increase of reaction temperature in catalytic hydrogenation generally promotes not only hydrogenolysis (*1*, *2*), but also the formation of the stable isomer, except in a few examples (*3*, *4*). We have found the opposite trend in the hydrogenation of methyl 4-*t*-butyl-1-cyclohexenyl ether (I) over platinum.

The hydrogenation of I (5 g) was carried out in cyclohexane as solvent (20 ml) at temperatures between 40 and 295°C under 20 kg/cm^2 initial pressure of hydrogen using 20 mg of platinum (*5*) as catalyst. The reaction mixtures were analyzed directly by gas chromatography. *Cis* and *trans* isomers of methyl 4-*t*-butylcyclohexyl ether (II), *t*-butylcyclohexane (III), and 4-*t*-butylcyclohexanone dimethyl acetal (IV) were detected as reaction products.

The results are summarized in Table 1. Surprisingly, the percentage hydrogenolysis, defined as 100 × moles III/(moles II + moles III), sharply decreased with increasing reaction temperature. Compound III was formed in about 30% yield at 40°C while only about 1% was formed at 185°C. This low level of percentage hydrogenolysis was maintained through the range 135 to 245°C of reaction temperatures with a minimum around 185°C. On the other hand, the percentage of *cis* isomer in II increased with increasing temperatures. The highest

TABLE 1

HYDROGENATION OF METHYL 4-*t*-BUTYL-1-CYCLOHEXENYL ETHER OVER PLATINUM CATALYST[a]

Run	Reaction temp (°C)	Composition of reaction mixture[d] (mol%)					% *cis* isomer	% Hydrogenolysis
		I	*cis*-II	*trans*-II	III	IV		
1	40	0.1	33.7	23.5	28.7	13.4	59	33.4
2	60	0	40.7	22.0	27.1	9.2	65	29.8
3	80[b]	0	62.2	21.4	16.4	0	74	16.4
4	80[c]	36.7	38.0	13.0	5.3	6.6	75	9.4
5	100	0	73.6	16.6	8.7	1.2	82	8.5
6	135	18.9	70.6	5.8	1.7	2.4	92	2.2
7	155[b]	55.2	39.2	1.9	1.1	2.2	95	2.5
8	185	4.5	89.0	4.4	1.4	0.3	95	1.4
9	245	0	89.5	8.2	1.8	0	92	1.9
10	295	0	83.9	10.9	2.7	0	89	2.8

[a] A sample of 5 g of methyl 4-*t*-butyl-1-cyclohexenyl ether (containing 2.3% of 4-*t*-butylcyclohexanone dimethyl acetal) dissolved in 20 ml of cyclohexane, was stirred in a 100 ml autoclave at various temperatures with 20 mg of a catalyst and using an initial hydrogen pressure of 20 kg/cm^2.

[b] Deuteration.

[c] Before conducting the hydrogenation, the catalyst was treated in a stream of hydrogen (20 ml/min) at 185 to 200°C for 30 min.

[d] 4-*t*-Butylcyclohexanol and 4-*t*-butylcyclohexanone were not detected in the reaction mixtures.

TABLE 2
Isotopic Analyses of Reaction Products from Deuteration of Methyl 4-*t*-Butyl-1-cyclohexenyl Ether (80°C)

Isomer	Isotopic composition of saturated ether (%)								
	d_0	d_1	d_2	d_3	d_4	d_5	d_6	D_m[a]	D_g[b]
cis	6.4	25.3	29.6	21.9	12.3	4.4	—	2.21	92.7
trans	8.5	23.5	30.3	21.7	11.8	4.2	—	2.17	

[a] Mean number of deuterium atoms introduced into a saturated ether.

[b] Isotopic purity of the residual gas-phase deuterium.

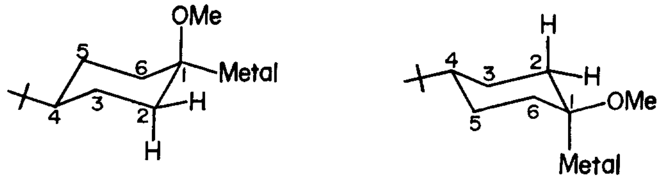
percentage (95%) of *cis* isomer was obtained at reaction temperatures between 155 and 185°C. The yield of *cis* isomer slightly decreased above 185°C. Under these conditions, no isomerization between *cis*- and *trans*-II was observed. The increase in the yield of *cis* isomer cannot be explained by thermodynamic consideration of II because the more stable isomer is the *trans* rather than the cis isomer (*6*). The very little hydrogenolysis and the high stereoselectivity for *cis* isomer at elevated reaction temperatures are surprising and unusual results since an increase in reaction temperature normally gives extensive hydrogenolysis or large amounts of more stable isomer, as mentioned above.

The catalytic reaction of I with deuterium was carried out at 80°C. Table 2 lists the mass spectrometric data of the deuterated II. The isotopic distribution pattern of *cis*-II is closely similar to that of *trans*-II. Species with more deuterium than d_5 are absent in the isotopic composition of both isomers. No deuterium atoms were found in the methoxy and *t*-butyl groups of these isomers. An attempt to determine the stereochemical isotopic distribution (*7*) in the cyclohexyl ring failed owing to poor resolution. However, the conversion of II into the *O*-acetylated compound enabled us to determine the distribution using $Eu(fod)_3$ or $Pr(fod)_3$ as an NMR shift reagent. The stereochemical isotopic distributions for II are summarized in Table 3. The introduced deuterium atoms are located at the three positions C_1, C_2, and C_6 for *cis*- and *trans*-II, while no deuterium atom is observed at C_3 (or C_5) and C_4 positions. The axial and equatorial deuterium numbers at the C_2 (or C_6) position of the *cis*-II are equal, whereas the equatorial deuterium number at C_2 (or C_6) for the *trans*-II is greater than the axial deuterium number. The total deuterium number in the NMR data agreed with the mean deuterium number in the mass data (see Tables 2 and 3). The analyses of deuterium location suggest that the hydrogenation of I proceeds via half-hydrogenated species A and B (Fig. 1) which lead to the *cis*- and *trans*-II, respectively. The species A is at-

TABLE 3
Stereochemical Isotopic Distributions within Molecule for Deuterated Methyl 4-*t*-Butylcyclohexyl Ethers over Platinum Catalyst at 80°C[a]

Isomer	Deuterium no.						Total
	C-1	C-2,6eq.	C-2,6ax.	C-3,5eq.	C-3,5ax.	C-4	
cis	0.55	0.85	0.85	0	0	0	2.25
trans	0.55	1.05	0.80	0	0	0	2.40

[a] The stereochemical isotopic distributions were obtained from NMR spectra of *O*-acetylated-II converted from deuterated II. From the measurement with NMR spectroscopy, no deuterium atoms were found in *t*-butyl and methoxy groups of II.



Species A Species B

FIGURE 1

tached to the metal by an equatorial bond at C_1. The equatorial and axial hydrogens at C_2 (or C_6) are in equivalent positions with respect to the carbon–metal bond, and so will have an equal chance of exchanging with deuterium via 1,2-di-adsorbed species. On the other hand, the species B is connected to the metal by an axial bond at C_1. The positional equivalence of hydrogens at C_2 (or C_6) does not exist in the species B. Judging from the conformation of species B, the deuterium will exchange predominantly with the equatorial hydrogen rather than the axial hydrogen. However, the axial deuterium number at C_2 (or C_6) of the *trans*-II is large, as is also that of *cis*-II. This result suggests rapid interconversion between the species A and B through desorption–adsorption. The result may be explained by the roll-over mechanism (*8*) or the *trans* addition mechanism reported by van Rantwijk, van Vliet and van Bekkum (*9*).

The species A seems to be more stable than the species B in view of conformational considerations. The observed variation of stereoselectivity may be explained by the stability of the half-hydrogenated species A and B which depends on the reaction temperature. The variation of hydrogenolysis may be ascribed to temperature dependencies of two factors. One is the amount of ionized adsorbed hydrogen whose presence was suggested by Nishimura, Katagiri and Uramoto (*10*). The ionized hydrogen probably behaves like a proton in acidic solution which accelerates the hydrogenolysis (*11*). The other factor is the strength of the adsorption bond between C_1 and metal in the half-hydrogenated species. At lower temperatures, the adsorption bond is probably stronger, and then the half-hydrogenated species may be more subject to elimination of methanol which would be promoted by the ionized hydrogen. Accordingly, the extensive hydrogenolysis can be observed. The depression of hydrogenolysis at higher temperatures suggests that the adsorption bond becomes weak and the amount of the ionized hydrogen decreases. The remarkable decrease in percentage hydrogenolysis by the catalyst pretreated with hydrogen for 30 min near 200°C (compare Run 3 with Run 4 in Table 1) may be a result of the loss of the ionized hydrogen on the catalyst surface. The hydrogenolysis at elevated reaction temperatures more than 200°C probably proceeds by some other pathway.

The deuterium tracer studies described in this note were conducted at 80 and 155°C. We are planning to extend these tracer studies to the lower temperature region. A comparison of the deuterium distributions in the lower and higher temperature regions is expected to shed more light on the reaction mechanism, especially on possible participation of the so-called *trans* addition mechanism, since the *trans* selectivity is quite high in the lower region.

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