Application of Nuclear Magnetic Resonance Shift Reagents to Kinetic Studies on Catalytic Deuteriation of 4-t-Butylcyclohexanone

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Summary N.m.r. shift reagents have been applied to mechanistic studies on the deuteriation of 4-t-butylcyclohexanone; a possible mechanism is discussed.

Deuterium has been extensively used in the study of catalytic hydrogenation of organic compounds, and generally the mechanisms have been discussed on the basis of the isotopic distribution of the deuteriated compounds obtained, determined by mass spectrometry. However, the actual location of deuterium in the molecule should provide more valuable mechanistic information.

Although n.m.r. spectroscopy can be used for the location of deuterium, its effectiveness is limited by low resolution. The recent advent of n.m.r. shift reagents holds promise for determination of the location of deuterium in a wide variety of catalytic hydrogenations involving organic compounds containing lone pairs.

We thus have studied the reaction of 4-t-butylcyclohexanone (I) with deuterium using palladium and platinum as catalysts.

Demarco and his co-workers[1] reported that $Eu(dpm)_3$ was a satisfactory shift reagent for *cis*-4-t-butylcyclohexanol (II); $Pr(dpm)_3$ is more satisfactory for the *trans*-isomer (III) owing to accidental chemical shift equivalences with $Eu(dpm)_3$. The assignments given in the Figure were based on the observed splitting patterns and the $1/R^3$ dependency of the pseudo-contact shift.

The deuteriation was carried out in cyclohexane solvent at 80 °C (D_2 pressure *ca.* 20 kg cm^{-2}) on palladium and platinum metal catalysts (20 mg). The products were separated into deuteriated (II) and (III) by g.l.c., and then analysed by n.m.r. and mass spectroscopy. The equatorial and axial deuterium content at each position was calculated from the integrals obtained from the shifted n.m.r. spectra (0·13M in CCl_4). This deuterium distribution is subsequently referred to as 'stereochemical distribution'.

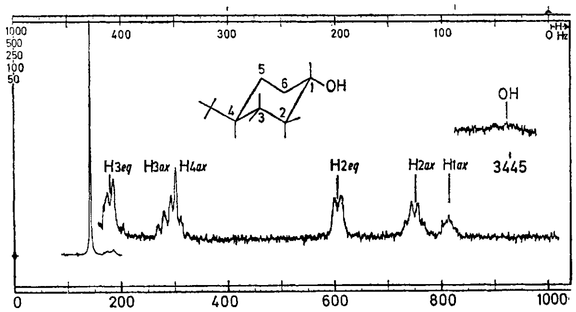


Figure. 100 *MHz* ^1H *n.m.r. spectrum of* trans-4-*t-butylcyclohexanol* (10 mg) *in* CCl_4 (0·5 ml) *containing* $Pr(dpm)_3$ (*Hz from cyclohexane*).

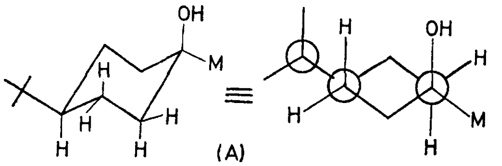
The Table shows that deuteriated (II) and (III) have a similar stereochemical distribution which is characteristic

TABLE. *Stereochemical isotopic distribution and stereoselectivity of the products from deuteriation of* (I).

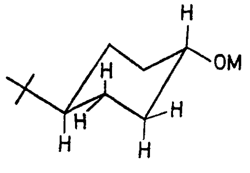
		Deuterium content							
Catalyst	Isomer	C-1	C-2,6*eq.*	C-2,6*ax.*	C-3,5*eq.*	C-3,5*ax.*	C-4	Total	D_m^a by mass spectrometry
Pd	*cis*[b]	0·40	0·64	0·64	0·0	0·0	0·0	1·68	1·56
	trans	0·34	0·68	0·68	0·0	0·0	0·0	1·70	1·70
Pt	*cis*[c]	1·0	0·0	0·0	0·0	0·0	0·0	1·0	1·02
	trans	1·0	0·0	0·0	0·0	0·0	0·0	1·0	1·03

[a] Mean overall deuterium content. [b] *cis*: *trans* = 62:38. [c] *cis*:*trans* = 30:70.

of the metal catalyst. The total deuterium content agreed with the mean deuterium content, D_m, obtained by mass spectrometry (last column). With platinum as catalyst, one deuterium atom was introduced almost quantitatively at C-1, indicating simple addition of deuterium to the carbonyl linkage. Over palladium, however, incorporation was at C-2 (or C-6) as well as C-1. Also, equatorial and axial hydrogen atoms at C-2 (or C-6) exchanged equally with deuterium. This suggests the presence of the half-hydrogenated species (A), attached to the metal by the equatorial bond at C-1. The Newman projection of (A) shows that 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* dissociation of hydrogen to form a 1,2-di-adsorbed species and addition of deuterium.



(A)



(B)

The stereochemistry of the deuteriation of (I) is also shown in the Table. More *cis*-alcohol was produced than *trans*-alcohol with palladium. Molecular models show that hydrogenation of (A) invariably leads to the *cis*-alcohol, and so the *cis*-alcohol is assumed to be formed *via* (A). Platinum, which showed less exchange, conversely gave more *trans*- than *cis*-alcohol, which suggests that the *trans*-alcohol is produced *via* another half-hydrogenated species (B) attached *via* oxygen to the metal through the equatorial carbon–oxygen bond. Although *trans*-formation occurs with no exchange, the similar stereochemical distribution of deuterium in the *cis*- and *trans*-alcohols may be the result of rapid alternation between (I) and (A).

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[1] P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, 1970, **92**, 5734.