Unusual Alkyl Group Directing Effects During Cyclopropane Ring Hydrogenolysis

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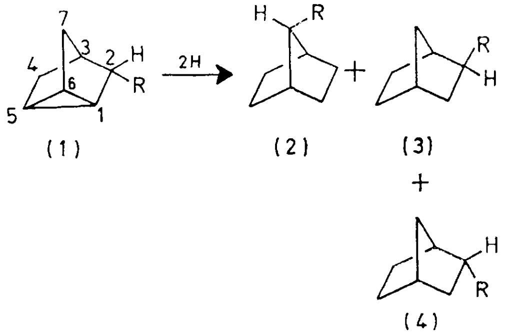
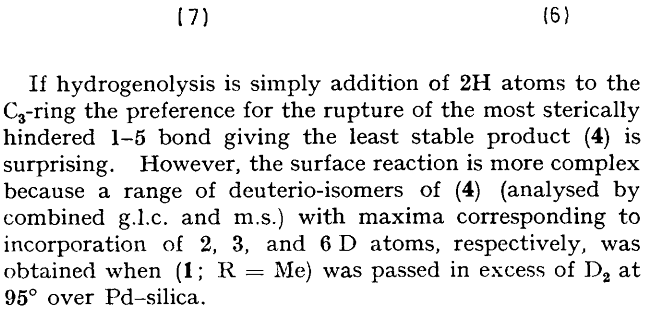
Summary 2-*endo*-Alkylnorbornanes are the kinetically preferred products of vapour phase hydrogenolysis of 2-methyl- and 2-cyclohexyl-nortricyclenes (**1**; R = Me and C_6H_{11}) over supported Pt and Pd catalysts, whereas 7-alkylnorbornanes predominate for reactions in acetic acid solutions.

Hydrogenolysis of 2-alkylnortricyclenes (**1**) over Pt catalysts in acetic acid solution gave a mixture of 7-, 2-*exo*-, and 2-*endo*-alkylnorbornanes (**2**), (**3**), and (**4**) in which the 7-isomer predominated (Table). The ratios were kinetically controlled and can be rationalized in terms of the ease of approach of the three edges of the cyclopropane ring to the catalyst surface.



In contrast reaction of vapourized (**1**; R = Me) in a large excess of H_2 over supported Pd and Pt gave predominantly (**4**), with (**2**) the least significant product. The same trend with regard to the yield of (**2**) from (**1**; R = C_6H_{11}) was also noted.



If hydrogenolysis is simply addition of 2H atoms to the C_3-ring the preference for the rupture of the most sterically hindered 1–5 bond giving the least stable product (**4**) is surprising. However, the surface reaction is more complex because a range of deuterio-isomers of (**4**) (analysed by combined g.l.c. and m.s.) with maxima corresponding to incorporation of 2, 3, and 6 D atoms, respectively, was obtained when (**1**; R = Me) was passed in excess of D_2 at 95° over Pd–silica.

The surface intermediate which best explains the results seems to be (**5**) since 2-methylnorbornene (**6**; R = Me) hydrogenates to give (**4**) (> 90%) on a Pt catalyst,[1] and (**5**) would also account for the deuteriated products. Initial attachment of the tert-C_2–H bond followed by 1–6 bond

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TABLE

Hydrogenolyses of 2-alkylnortricyclenes[a]

Catalyst	Temperature (t/°C)	Product composition %[b]		
	R = Me	(**2**)	(**3**)	(**4**)
PtO_2 in acetic acid	85	48	32	20
2% Pd on silica	128	10	15	75
	195	9	18	73
	240	14	28	64
	R = C_6H_{11}	(**2**)	(**3**+**4**)	others
PtO_2 in acetic acid	40	52	48	—
2% Pd on silica	100	31	63	6
	140	24	69	7
	213	18	71	11
2% Pt on silica	140	42	54	4
	189	34	57	9

[a] Samples of hydrocarbon (*ca.* 0·01 g) were passed over the catalyst (0·5 g in a glass tube of 6 mm i.d.) in *ca.* 0·5 h using a hydrogen flow of *ca.* 70 $cm^3 min^{-1}$ at 1 atm pressure. Hydrogenolyses in acetic acid were carried out in a conventional hydrogenator operating at 1 atm. [b] Product ratios (accuracy ±2—3%) were estimated from several g.l.c. traces using a Dupont Curve Resolver and a Perkin-Elmer F11 unit fitted with a 2 m column of Apiezon L (15% by wt) on Chromosorb W (80—100 mesh); but (**3**) and (**4**) (R = C_6H_{11}) could be resolved.

rupture can give (**5**). However *endo–exo* isomerization of (**4**) to (**3**) which also requires initial attack of a tert-C–H bond, as shown for interconversion of isomeric 2,3-dimethylnorbornanes,[2] is much slower than hydrogenolysis of (**1**), otherwise the yields of (**4**; R = Me) would not be so high. Alternatively a metallo-carbonium ion (**7**) with subsequent proton elimination would also give (**5**). Direct insertion of metal into the 1–5 bond would now be preferred because of simultaneous delocalization of the positive charge to the tert-C_2-centre.

Hydrogenolysis of 2,2-dimethylnortricyclene was examined under the same conditions but gave only 7,7-dimethyl (70—85%) and 2,2-dimethylnorbornane (30—15%) respectively over Pt in acetic acid, and over Pd or Pt on silica in the flow system, in apparent support of the first mechanism. However, using Pd on pumice, the major products were 2,3-dimethylnorbornanes which could only result from a methyl shift in the chemisorbed reactant.[3] This behaviour is good evidence that the metallo-carbonium ion suggestion is reasonable. It can also be used to explain homogeneous isomerization of strained carbocyclic compounds catalysed by Ag^+, Rh^+, and other metal cations.[4]

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[3] M. N. Akhtar, W. R. Jackson, and J. J. Rooney, *J. Amer. Chem. Soc.*, in the press.

[4] See D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Reviews*, 1973, **2**, 99.

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