Reactions over Metal Catalysts. Part II.[1] Hydrogenolysis of 3,3-Dimethylnortricyclene and Nortricyclene-3-spirocyclopropane [2]

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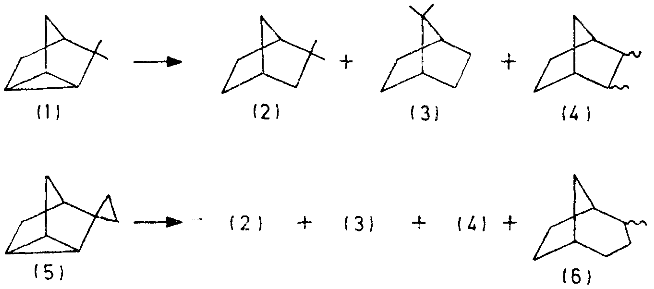
Hydrogenolysis of 3,3-dimethylnortricyclene in solution or in the vapour phase over a series of palladium and platinum catalysts gives a mixture of 2,2- and 7,7-dimethylnorbornanes with the latter predominating. Hydrogenolysis over palladium on pumice catalyst gives a mixture of products including several which arise from carbon–carbon bond breaking and formation. The formation of this latter type of product is more prevalent in reactions of nortricyclene-3-spirocyclopropane (5).

PREVIOUS studies of rearrangements of cyclic hydrocarbons [3] have led to the proposal that cyclopropane ring formation and hydrogenolysis may be important steps in such reactions. Although it has been shown that the isomerism of straight chain to branch chain hydrocarbons does not involve the formation of cyclopropanes as a major mechanistic route,[4] cyclopropane ring formation could be an important part of the isomerisation process in cyclic hydrocarbons where entropy factors are less adverse. Accordingly, the hydrogenolysis of some substituted nortricyclenes has been studied for comparison with results obtained in isomerisation reactions. In this paper we report on the hydrogenolysis of 3,3-dimethylnortricyclene (1) and the related cyclopropyl compound (5).



Reaction of (1) with hydrogen over Adams catalyst in acetic acid solution gave 2,2- (2) and 7,7-dimethylnorbornane (3) in the ratio 15 : 85. The perturbation in the product ratio from the statistical ratio of 2 : 1 can readily be explained in terms of the relative ease of approach of the C(1)–C(6) bond to the metal surface. Very similar ratios were obtained for reactions at temperatures below 200° on rhodium or platinum catalysts supported on pumice and palladium on silica (see Table 1). The proportion of 7,7-dimethylnorbornane (3) in the product is much higher than that expected on a statistical basis even at higher temperatures. Reaction over palladium on pumice however gave initial product distributions in which the rearranged products *cis-exo-*, *cis-endo-*, and *trans*-2,3-dimethylnorbornane were present in addition to the products of simple hydrogenolysis. The products of simple hydrogenolysis (2) and (3) were shown to be stable over the palladium on pumice catalyst at temperatures up to 200°. Additionally, no reaction occurred between the nortricyclene and a blank pumice catalyst at 120°. The rearranged products contained a large proportion of the di-*endo*-isomer of (4) from reactions at lower temperatures. At higher temperatures the proportion of di-*endo*-compound diminished and the *trans*-2,3-dimethyl compound predominated in the reaction mixtures. Although *trans*-2,3-dimethylnorbornane could not be separated from 2,2-dimethylnorbornane under our analytical g.l.c. conditions a sample of the product from a reaction over 2% Pd–pumice at 190° was separated by preparative g.l.c. and the relevant fraction shown to be identical with an authentic sample of *trans*-(4) by i.r. and n.m.r. comparison. No evidence for the presence of 2,2-dimethylnorbornane in the sample was found. The kinetically preferred di-*endo*-methyl isomer has previously been shown to rearrange to the thermodynamically preferred *trans*-isomer over metal catalysts at higher temperatures.[3]

The above results are consistent with a ring-opening process which is accompanied by rearrangement for reactions over palladium or palladium–silver on pumice. The stability of the products, over pumice, the lack of reactivity of the nortricyclene over a blank pumice catalyst, and the formation of rearranged products in the initial product distributions at low conversions all help to exclude the possibility that rearrangement is connected with the presence of active acidic sites on the pumice. The hydrogenolyses over palladium or palladium–silver catalysts on pumice are significantly slower than reactions over the other catalysts, *viz* the large recovery of unchanged nortricyclene (85%) from a reaction at 104°. The difference in reactivity can be attributed to the fact that the metal on the low area (*ca.* 40 $m^2 g^{-1}$) pumice is present as large crystallites, whereas it is highly dispersed on silica (600 $m^2 g^{-1}$). Perhaps on the large crystallites hydrogen atom insertion into the cyclopropane ring bonds is slow, insertion of a metal atom competing successfully. The developing metallocarbonium ion can be stabilised by a methyl migration if insertion occurs into the 1,2- or 2,6-bonds (see Scheme). Many rearrangements have now been reported involving the insertion of

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[1] Part I, M. N. Akhtar, J. J. Rooney, N. G. Samman, and W. R. Jackson, *J.S.C. Perkin II*, 1976, 595.

[2] Preliminary communication, M. N. Akhtar, W. R. Jackson, and J. J. Rooney, *J. Amer. Chem. Soc.*, 1974, **96**, 276.

[3] H. A. Quinn, W. R. Jackson, M. A. McKervey, and J. J. Rooney, *J. Amer. Chem. Soc.*, 1970, **92**, 2922; H. A. Quinn, J. H. Graham, M. A. McKervey, and J. J. Rooney, *J. Catalysis*, 1972, **26**, 333.

[4] J. R. Anderson, *Adv. Catalysis*, 1973, **23**, 1 and references therein.

TABLE 1

Product distributions from the hydrogenolysis of 3,3-dimethylnortricyclene

Catalyst	Flow rate (cm^3 min^{-1})	Temp. (°C)	Product composition (%) (2) + *trans*-(4)	(3)	*cis-exo*-(4)	*cis-endo*-(4)	Recovered (1)	Unidentified
2% Rh–pumice	10	70	7	71			22	
	10	110	9	67			24	
2% Pt–pumice	9	50	8	32			60	
	9	108	20	80				
	9	135	28	72				
	9	158	30	70				
	9	200	50	50				
2% Pd–silica	6	100	15	85 [a]				
	6	130	15	85				
	6	180	20	80				
	6	230	38	56				6
2% Pd–pumice	9	104	8	2	2	3	85	
	9	160	27	5	15	28	25	
	9	190	45 [b]	5	15	35		
	9	200	54	7	12	24		3
	9	300	60	7	12	13		8
2% Pd–Au (4 : 1)–pumice	11	108	7.5	1.5	1	2	88	
	11	150	28	4	7	14	47	
	11	195	47	5	14	33	1	
	11	301	52	7	12	16		13

[a] Identified as pure 2,2-dimethylnorbornane after preparative g.l.c. at 110°. [b] Identified as mainly *trans*-2,3-dimethylnorbornane after preparative g.l.c.

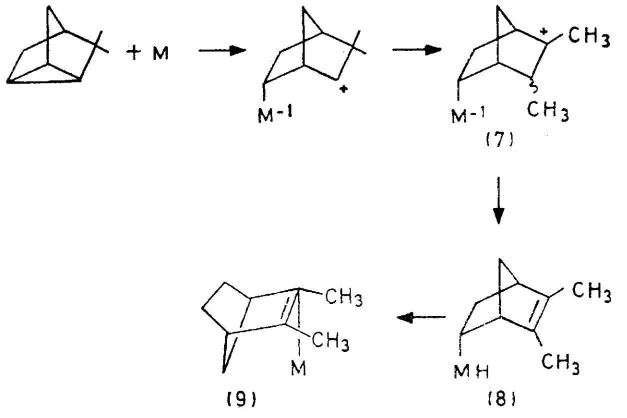
TABLE 2

Product distributions from the hydrogenolysis of the nortricyclene spirocyclopentane (5) [a]

Catalyst	Temp. (°C)	Product composition (%) (2) + *trans*-(4)	(3)	*cis-exo*-(4)	*cis-endo*-(4)	*endo*-(6)	*exo*-(6)	Un-identified	Recovered (5)
PtO$_2$ in acetic acid	30 (2 mol uptake)	15	85						
	30 (1 mol uptake)	>98% of (1)							
2% Pd–pumice	115			1	4				95
	140			2.5	12	0.5			85
	195	7	0.5	7.5	4.5	56	16	8.5	
	210	10.5		7.5	3.5	56	14	8.5	
	250	6.5		8.5	10.5	50.5	16	9	
2% Pt–silica	82	43.5	23.5	13.5	8.5	5.5	5.5		
	102	20.5	1	22	11	18.5	15.5		
	140	8	1.5	11.5	15	39	14	12	
	160	7	1	10	18	38	11	15 [b]	
	242	1	1	15.5	10.5	38	7.5	26.5	

[a] Using hydrogen flow rates of 9—10 cm^3 min^{-1}. [b] Including *ca.* 8% dimeric material.

low valent metallic species into strained hydrocarbons containing cyclopropane rings.[5] Methyl group migration has also been reported in the silver ion-catalysed rearrangements of a tricyclo[3.2.0.0^{2,4}]heptane.[6]



SCHEME

The stereochemistry of the product 2,3-dimethylnorbornanes is not easily explained. If transfer of hydrogen from the metal surface to the carbonium ion species (7) is possible, product stereochemistry would be determined by the stereochemistry of the methyl group rearrangement giving either *cis*-di-*exo*-, or *trans*-products. *cis*-Hydrogen transfer to the surface bonded alkene species (8) would give the di-*exo*-compound. The large amounts of di-*endo*-compound could possibly arise from the intervention of the π-bonded species (9). Such a species could be involved in hydrogenation of 2,3-dimethylbicyclo[2.2.1]hept-2-ene which has been shown to give predominantly the di-*endo*-methyl compound on hydrogenation in solution.[7] Thus, no one species readily accounts for the observed stereochemistry.

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

[6] L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, 1972, **94**, 3653.

[7] K. Alder and W. Roth, *Chem. Ber.*, 1955, **88**, 407.

The nortricyclene spirocyclopropane (5) on reaction with hydrogen over platinum on silica or palladium on pumice catalyst gave a complex mixture of products in contrast to reaction over platinum oxide in solution where simple cleavage of the most exposed cyclopropyl bond led to the formation of 3,3-dimethylnortricyclene. The complex mixture (Table 2) contained in addition to the 2,3-dimethylnorbornanes, ring enlarged products (2-methylbicyclo[3.2.1]octanes), and dimeric product from reactions at higher temperatures. The more ready formation of rearranged product from the cyclopropyl compound (5) as opposed to dimethylnortricyclene (1) could be connected with the greater strain in the former compound. A further possibility is that the presence of two cyclopropane rings leads to a deficiency of available hydrogen on the surface. Thus, metal insertion is preferred after an initial hydrogen insertion into one ring, leading to a high proportion of rearranged products.

EXPERIMENTAL

General directions and apparatus were as reported previously.[1]

Materials.—3,3-Dimethylnortricyclene was prepared by the method of Nickon *et al.*[8] as a waxy solid, m.p. 33—34° (lit.,[9] 42—43°). 2,2-Dimethylnorbornane was prepared as an oil, b.p. 84—86° at 15 mm Hg (lit.,[10] 143.5° at 760 mmHg) and further purified by preparative g.l.c. at 110°. 7,7-Dimethylnorbornane was prepared *via* 7,7-dimethylnorbornene from camphenilone by the method of Hintikka and Komppa [11] as crystals, m.p. 88—89.5° (lit.,[12] 89.5—90.5°). *cis-endo-* and *trans*-2,3-Dimethylnorbornanes were available from previous work.[3] 2-Methylenebicyclo[3.2.1]octane, b.p. 102—104° at 25 mmHg (lit.,[13] 156—157°) was prepared by a Wittig reaction of bicyclo[3.2.1]octan-2-one and hydrogenated over palladium on carbon in methanol to give the isomeric 2-methylbicyclo[3.2.1]octanes, b.p. 155—157° (lit.,[13] 156—157°), which were purified by preparative g.l.c. using an Apiezon L column at 90° and characterised as described previously.[14]

Nortricyclene-3-*spirocyclopropane* (5). 3-Methylenenortricyclene (5.0 g), prepared as described previously,[1] and diiodomethane (15.8 g) were added to a rapidly stirred suspension of a zinc–copper couple (3.9 g) in ether (25 cm^3). The mixture was stirred and heated under reflux for 10 h. The ether solution was decanted off and the residue washed with ether (3 × 20 cm^3). The combined ether layers were washed successively with saturated ammonium chloride solution (2 × 20 cm^3), sodium hydrogen carbonate (2 × 20 cm^3), and water (20 cm^3). The solution was dried ($MgSO_4$), the ether removed through a short Fensky column and the residue distilled to give the *cyclopropyl compound* (5) (1.8 g, 32%), *m/e* 120 (M^+, 40%) 105 (100), 92 (55), 91 (65), 79 (45), 78 (25), 77 (25), 67 (25), and 66 (25), δ 0.3 (d, cyclopropyl H), 0.6, and 1.1—1.7 (7 H, m); ^{13}C n.m.r. δ, 5.07 (cyclopropyl C), 12.26 (C-1), 17.29 (C-2), 32.8 (C-3), 33.19 (C-5,-7), and 37.68 (C-4) (Found: C, 89.85; H, 10.1. C_9H_{12} requires C, 89.95; H, 10.05%).

Hydrogenolyses.—Solution reactions. The nortricyclenes (1.0 g) were reacted with hydrogen in acetic acid (10 cm^3) at 80—85° in the presence of platinum oxide (0.1 g) until uptake of hydrogen ceased. The product was isolated in ether and analysed by g.l.c.

Catalyst preparation. Metals were supplied as hydrated chloroplatinic acid, palladium(II) chloride, and rhodium(III) chloride by Johnson, Matthey. The supports used were silica 60—85 mesh (B.S.S.), Whatman SG 40, and pumice stone 22—60 mesh (B.S.S.) from Hopkins and Williams. The appropriate support was impregnated with a solution of the metal at the required concentration. In a typical preparation, 2% palladium on pumice was made up in the following manner. Palladium(II) chloride (0.33 g) was added to a 1 : 1 solution of AnalaR hydrochloric acid and distilled water (10 cm^3). The mixture was heated with stirring until all the palladium salts dissolved. Pumice stone (9.67 g) was then added and the resultant slurry heated gently to dryness with continuous stirring. The almost dry mixture was then dried at 100° for 4 h, allowed to cool, and stored in a desiccator. Hydrogen was then passed over the catalyst while the temperature was raised to 320—340° and maintained at this temperature for 12—15 h.

Blank catalysts were prepared by submitting the supports to the above treatment but without adding the transition metal.

Reactions were carried out in a flow system in which the compound was introduced in an open ended capillary into a stream of hydrogen at *ca* 35° and swept over the supported catalyst over *ca.* 1 h. The hydrogen flow was *ca.* 70 cm^3 min^{-1} at 1 atm. pressure. The catalyst (0.5 g) was contained by two glass wool plugs in a tube of internal diameter 7 mm; *ca.* 3 cm of tube were filled by catalyst. Products were trapped at −78°.

Attempted isomerisations of the products were carried out under similar conditions.

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