Solvent Participation in Catalytic *trans*-Hydrogenation of an Olefinic Double Bond

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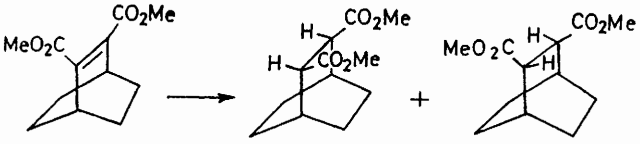
Summary *trans*-Addition in the palladium-catalysed hydrogenation of dimethyl bicyclo[2,2,2]oct-2-ene-2,3-dicarboxylate (**1**) increased from 1 to over 60% if traces of strong acid were present; as shown by deuteriation experiments, the solvent participates in the formation of the *trans*-isomer.

THE mechanism of *trans*-addition of hydrogen to an olefinic double bond has been under discussion for several years.[1,2] We have studied (**1**) as an example of an olefinic compound in which double bond migration does not occur.



(1) (2) (3)

Palladium-catalysed hydrogenation of (**1**) in methanol at ambient conditions gave dimethyl *cis*-bicyclo[2,2,2]octane-2,3-dicarboxylate (**2**) (98·6%). In the presence of acid (0·02M) more substantial amounts of the *trans*-isomer (**3**) were formed, *e.g.* with acetic acid 3·4%, trifluoroacetic acid 35·5%, and perchloric acid 61·8%. It should be noted that treatment of (**2**) under the above conditions did not lead to any formation of (**3**).

Deuteriation of (**1**) was performed in MeOD–CF_3CO_2D (0·012M); (**2**) and (**3**) were separated by means of preparative g.l.c. and analysed by m.s. Both compounds had an average deuterium content of 1·92 atoms, whilst the amount of trideuteriated products was less than 0·1%, showing that migration of the double bond to the 1,2-position is not involved in *trans*-addition.

TABLE. *Hydrogenation of* (**1**) *in* MeOD[a]

	Isotopic content (%)					
Product	D_0	D_1	D_2	D_3	D_4	D
(2)	38·8	44·9	16·2	0·1	—	0·78
(3)	6·9	51·5	40·4	0·8	0·4	1·37

[a] (1), 1·2 g; Pd (10% on C), 0·2 g; MeOD, 25 ml CF_3CO_2D, 0·34 mmol; 1 atm, 25°.

The results of the hydrogenation of (**1**) in monodeuteriomethanol are given in the Table. The incorporation of deuterium into (**2**) is due to exchange of chemisorbed hydrogen with active deuterium of the solvent. The difference in deuterium incorporation in (**2**) and (**3**) shows that the solvent participates in the formation of (**3**).

Reaction *via* a desorbed enolic tautomer is considered unlikely since *trans*-addition requires the presence of acid. We propose that *trans*-addition involves top-side attack of an adsorbed species by the protonated solvent. As to the stage of proton transfer several possibilities are open: chemisorbed alkene, or the half hydrogenated (alkyl) state may be attacked, the latter sequence is similar to the mechanism proposed for homogeneously platinum–tin catalysed *trans*-hydrogenation.[2] Simultaneous transfer of hydride from the catalyst and a proton from the solvent should also be considered. In all cases expulsion of a proton from the catalyst surface[3] should accompany transfer of a proton from the solvent.

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[1] For a review see: S. Siegel, *Adv. Catalysis*, 1966, **16**, 123; J. Erkelens, Ph.D. Thesis, Queens University of Belfast, 1961, p. 68, 97; F. G. Gault, J. J. Rooney, and C. Kemball, *J. Catalysis*, 1962, **1**, 255; J. J. Rooney, *ibid.*, 1963, **2**, 53; J. Erkelens, *ibid.*, 1967, **8**, 212; G. C. Bond, in 'Proceedings of the Fourth International Congress on Catalysis,' Akademiai Kiadó, Budapest, 1971, part II, p. 266; M. Pecque and R. Maurel, *J. Catalysis*, 1970, **19**, 360.

[2] H. van Bekkum, F. van Rantwijk, G. van Minnen-Pathuis, J. D. Remijnse, and A. van Veen, *Rec. Trav. chim.*, 1969, **88**, 911.

[3] *Cf.* A. P. G. Kieboom, J. F. de Kreuk, and H. van Bekkum, *J. Catalysis*, 1971, **20**, 58