# Catalytic Hydrogenation of Aromatic and Cyclo-olefinic Hydrocarbons Consistent with the Rideal Mechanism

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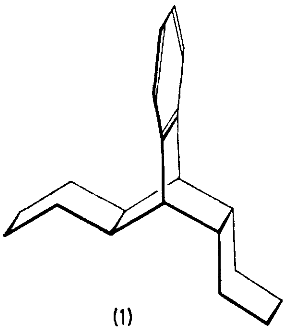
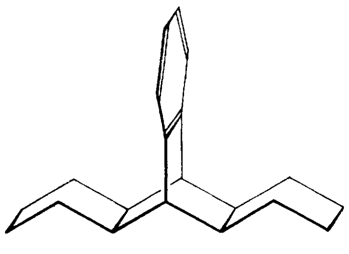
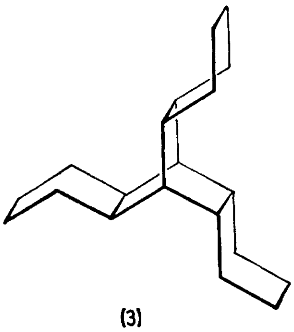
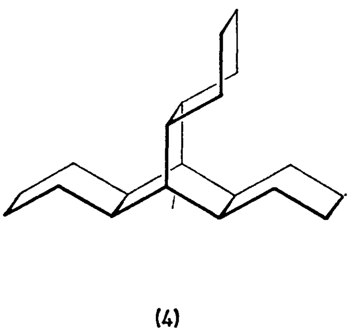
*Summary* Hydrogenation over palladium of certain aromatic and cyclo-olefinic hydrocarbons proceeds with addition of hydrogen from the side of the molecule opposite to the catalyst; this result supports the Rideal mechanism.

IN the heterogeneous hydrogenation of unsaturated hydrocarbons in the gas phase or in non-polar solvents it is generally assumed that both hydrogen atoms add from the same side (*cis* addition) and that they appear to add from the side of the original double bond that faces the catalyst (bottomside addition).[1] This mechanism has been proposed also for the hydrogenation of aromatic hydrocarbons[2] and is related to a kinetic scheme where both hydrogen and substrate are adsorbed on the surface of the catalyst (Langmuir–Hinshelwood mechanism).[3a,b]


(1)


(2)

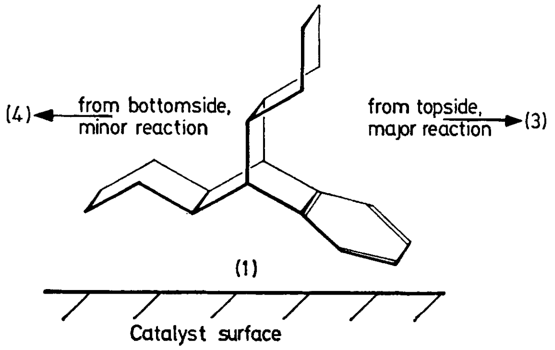

(3)


(4)

A different mechanism proposed by Rideal[3b,c] implies that only the substrate is chemisorbed on the catalyst and that hydrogen comes from the gas phase. This mechanism is consistent with *cis*-addition and with the approach of hydrogen from the side of the molecule opposite to the catalyst.

In a study of the hydrogenation of aromatic hydrocarbons with bulky side groups, we have obtained stereochemical evidence which appears to support the Rideal mechanism.

The aromatic compounds (1) and (2), obtained by catalytic hydrogenation of triptycene, were heated at 150 °C in heptane solution under $H_2$ (60 atm) in the presence of Pd–C.



Compound (1) was easily converted into a mixture of saturated hydrocarbons (3) and (4) in the ratio of *ca.* 10 : 1. After disappearance of (1) the concentration of (3) and (4) remained constant for several hours. On this basis we exclude the possibility that (**3**) is derived in a considerable amount from epimerization of (**4**).†

The formation of both (**3**) and (**4**) indicates the presence of two different mechanisms (topside and bottomside addition, the former being largely predominant), because (**1**) can be adsorbed on the catalyst in one way only (see Scheme). The opposite disposition is forbidden, owing to the shielding effect of one of the outer cyclohexane rings, placed in an unfavourable arrangement. Compound (**2**), in which such a shielding effect occurs on both sides, does not react when subjected to hydrogenation under the same conditions.

The same conclusions were obtained from stereochemical analysis of the hydrogenation of olefinic compounds related to (**1**) and (**2**), in which the aromatic ring is replaced by a cyclohexene ring having a tetrasubstituted double bond.

This effect has been observed only in the case of palladium. Hydrogenation of (**1**) over ruthenium on charcoal gave (**3**) and (**4**), the latter being the major product. In this case, however, compound (**2**) shows some reactivity and the interpretation of the results is ambiguous.

An independent proof of our stereochemical results might be obtained from kinetic studies. However, the complexity of the reaction, which does not allow a simple expression of the rate law, and the difficulty of obtaining large amounts of such products, hinders this possibility.

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† The structures of compounds (**1**)—(**4**) were determined by mass, i.r., and $^1$H and $^{13}$C n.m.r. spectroscopy. A detailed discussion of the catalytic hydrogenation of triptycene will be reported elsewhere.

[1] R. L. Burwell, Jr., *Accounts Chem. Res.*, 1969, **2**, 289.

[2] R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine, and R. R. Whetstone, *J. Amer. Chem. Soc.*, 1942, **64**, 1985.

[3] (a) K. J. Laidler in 'Catalysis,' ed. P. H. Emmett, vol. I, ch. **4**, pp. 128—151; (b) H. A. Smith, *ibid.*, vol. V, ch. **4**, p. **183**; (c) ref. (a), pp. **130**, **154**.