JOURNAL OF CATALYSIS 19, 360-362 (1970)

Catalytic Hydrogenation

V. An Example of Trans Hydrogenation of an Ethylenic Double Bond*

M. PECQUE** AND R. MAUREL

Laboratoire de Catalyse Organique, Faculté des Sciences, 86-Poitiers, France

Received November 28, 1969

Liquid phase hydrogenations of (i) 2,3-dimethylbicyclo[2,2,2]oct-2-ene, (ii) 3-methyl-2-methylenebicyclo[2,2,2]octane, and several of their mixtures have been studied over Raney nickel, Adams palladium, and Adams platinum. The stereochemistry observed on the platinum catalyst cannot be explained by the Horiuti-Polanyi mechanism. Direct trans hydrogenation occurs on this catalyst.

INTRODUCTION

Stereochemical studies of hydrogenation of disubstituted cycloalkenes (*1*) have shown that hydrogenation and double-bond migration occur simultaneously on the catalytic surface.

The Horiuti and Polanyi mechanism (*2*) can account, in most cases, for the stereochemistry observed: this mechanism involves σ-$\alpha\beta$ diadsorbed species which react stepwise with adsorbed hydrogen atoms and with their face in contact with the catalyst. Accordingly, the "normal" product of hydrogenation of a disubstituted cycloalkene—for example, 1,2-dimethylcyclohexane (1,2-DMCH)—is the *cis* stereoisomer, e.g., *cis*-1,2-dimethylcyclohexane. Reversibility of the "semihydrogenation" step allows desorption of positional isomers of the initial olefin [2,3-dimethylcyclohexene (2,3-DMCH) and 2 methyl-1-methylenecyclohexane (2 M-1-MCH)]. These isomers may lead to *cis* or *trans* saturated products according as they adsorb on one or other face. It will be noted that the only way of passage between a disubstituted cycloalkene and its *trans* saturated product involves desorption and re-adsorption of a positional isomeric olefin.

However, some experimental data suggest that adsorbed species are π-bonded to active centers (*3*) so that adsorbed sp^2 carbon atoms have a planar configuration. These planar centers may be able to react with hydrogen at their upper or lower face (*4*). This is supported by experimental observations such as racemization of optically active (+) 3-methylhexane during isotopic exchange with deuterium on several metals (*5*).

Kinetic studies may be of interest in the choice between these two mechanisms, the problem being to know if desorbed positional isomers are required intermediates in *trans* hydrogenation of tetrasubstituted olefins. The problem is complex: positional isomers exhibit very large differences of reactivity according to the degree of substitution at the carbon-carbon double bond (*6*). Increase of substitution at the double bond decreases the competitive hydrogenation rate. On the other hand, the thermodynamic stability of a double bond generally follows a symmetry rule: the more symmetrical positional isomer is often the more stable one. So, in the above example of 1,2-DMCH, the order of decreasing thermodynamic stabilities is also the order of increasing reactivities:

---

* For previous papers in this series, see Ref. (7)

** Present address: Service de Chimie Générale, Bâtiment C_3, Cité Scientifique de Lille-Annappes, B.P. 36, 59-Lille, France.

Competitive reactivities:

2-M-1-MCH > 2,3-DMCH > 1,2-DMCH,

Thermodynamic stabilities:

2-M-1-MCH < 2,3-DMCH < 1,2-DMCH.

2-M-1-MCH, thermodynamically unstable, is selectively hydrogenated: it will never reach large concentrations in the reaction mixture, but only traces, perhaps, may take an important part in the hydrogenation of tetrasubstituted isomer.

The above example is too complex and furnishes experimental data which cannot be easily computed for quantitative kinetics, because of the number of positional isomers to be taken in account. Our purpose was to study the hydrogenation of a "simple" ethylenic system limited to two positional isomers and leading by hydrogenation to *cis* and *trans* saturated products. Kinetics of such a system may be studied by a method (*7*) which we have previously used to account for hydrogenation with isomerization of pairs of positional isomeric olefins. We have chosen the case of 2,3-dimethylbicyclo[2,2,2]octenes (Fig. 1), attempting to solve the question of the direct passage (a) between tetrasubstituted olefin and its *trans* saturated product.[1]

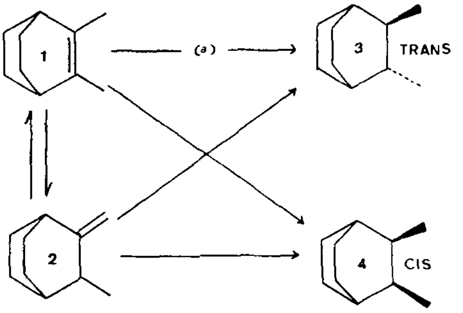

Fig. 1. Reaction paths in the hydrogenation of 2,3-dimethylbicyclo[2,2,2]oct-2-ene.

Results

Pure 2,3-dimethylbicyclo[2,2,2]oct-2-ene (**1**), 3-methyl-2-methylenebicyclo[2,2,2]octane (**2**), and several of their mixtures have been hydrogenated in liquid phase (20% in ethyl alcohol) at 25°C on different catalysts, namely Raney nickel, Adams palladium and platinum.

TABLE 1

Hydrogenation of 3-Methyl-2-methylenebicyclo[2,2,2]octane

Maximum percentage of positional isomer observed; [2,3-dimethylbicyclo[2,2,2]octane, *trans* (**3**), *cis* (**4**)].

Catalyst	Maximum (**1**)(%)	Remaining (**2**)(%)	(**3**) + (**4**) (%)
Raney Ni	15	≃0	≃85
Adams Pd	93	3	4
Adams Pt	1.5	≃0	98.5

On these three catalysts, hydrogenation is accompanied by positional isomerization of the double bond. The importance of this isomerization greatly depends on the nature of the catalyst. Table 1 summarizes the maximum percentages of isomer observed during hydrogenation of pure (**2**).

Reverse isomerization from tetrasubstituted to methylenic isomer is more difficult to observe because of the very low stability (0.6% at thermodynamic equilibrium at

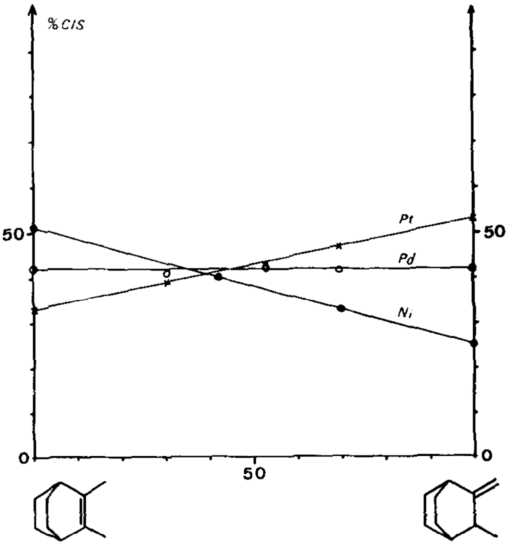

Fig. 2. Hydrogenation of mixtures of 2,3-dimethylbicyclo[2,2,2]oct-2-ene and 3-methyl-2-methylenebicyclo[2,2,2]octane: % *cis* stereoisomer in final products.

---

[1] We have already described (*8*) the organic chemistry part of this work, viz, the synthesis and characterization of the two ethylenic isomers and the *cis* saturated hydrocarbon.

room temperature) and the great reactivity of the latter.

For each mixture and catalyst studied, Fig. 2 shows the percentage of *cis*-2,3-dimethylbicyclo[2,2,2]octane (4) in the products of complete hydrogenation as a function of initial ethylenic mixture composition.

DISCUSSION

The low stability of the methylenic isomer is very unfavorable for an accurate determination of relative rate constants.

Positional isomerization of the double bond during hydrogenation decreases in the order:

$$\mathrm{Pd} > \mathrm{Ni} > \mathrm{Pt}$$

as noted by Gostunskaya *et al.* (*9*) in the hydrogenation of several hexenes. It is very fast on the palladium catalyst, on which positional isomers reach the equilibrium. Accordingly, the stereochemistry of the products does not depend on the composition of the initial ethylenic mixture.

For the tetrasubstituted isomer the extent of *trans* hydrogenation increases in the order:

$$\mathrm{Ni} < \mathrm{Pd} < \mathrm{Pt}$$

as noted by Van Bekkum *et al.* (*10*) in hydrogenation of tetrasubstituted olefins and diene with very similar structural features. However, this order is reversed in hydrogenation of methylenic isomer.

The Horiuti and Polanyi mechanism is sufficient to account for the stereochemistry observed on Raney nickel: tetrasubstituted olefin gives more *cis* saturated product than its methylenic isomer, as is usually observed with other hydrocarbons (dimethylcyclopentene,dimethylcyclohexene . . .) on each catalyst. Methylenic isomer leads principally to *trans* saturated compound; it is not forbidden to think that the whole *trans* saturated hydrocarbon given by hydrogenation of tetrasubstituted olefin is produced via the methylenic isomer (rate constant of path $a = 0$). Only accurate determination of rate constants, which is lacking in this example, will permit the verification of this hypothesis.

On the other hand, the Horiuti and Polanyi mechanism is unable to explain the results obtained on Adams platinum catalyst. As far as we know, it is the only example of a catalyst on which hydrogenation of a tetrasubstituted olefin gives more *trans* product than hydrogenation of the methylenic isomer. Obviously, this stereochemistry cannot be explained without a direct passage between tetrasubstituted olefin and its *trans* saturated product. This result, in spite of the lack of accurate determination of rate constants, allows us to conclude that, at least on platinum, direct *trans* hydrogenation occurs.

We do not attempt to explain here this direct *trans* hydrogenation, but only to point out the observed stereoselectivity, which is very poor in comparison with the results of Van Bekkum *et al.* (*10*) about hexamethyl Dewar benzene. *Plane* π-adsorbed *allylic* species, which are currently postulated as intermediates in this reaction (*11, 12*), are unlikely in this structure because of the bulk of the bicyclic skeleton.

REFERENCES

1. SIEGEL, S., THOMAS, P. A., AND HOLT, J. T., *J. Catal.* **4,** 73 (1965).
2. HORIUTI, J., AND POLANYI, M., *Trans. Faraday Soc.* **30,** 1164 (1934).
3. ROONEY, J. J., GAULT, F. G., AND KEMBALL, C., *Proc. Chem. Soc. London* **1960,** 407.
4. ROONEY, J. J., AND WEBB, G., *J. Catal.* **3,** 488 (1964).
5. BURWELL, R. L., JR., SHIM, B. K. S., AND ROWLINSON, H. C., *J. Amer. Chem. Soc.* **79,** 5142 (1957).
6. MAUREL, R., AND TELLIER, J., *Bull. Soc. Chim. Fr.* **1968,** 4191.
7. PECQUE, M., AND MAUREL, R., *Bull. Soc. Chim. Fr.* **1969,** 1878–1887.
8. PECQUE, M., thesis, Poitiers, 1969.
9. GOSTUNSKAYA, V., PETROVA, V. S., LEONOVA, A. I., MIRONOVA, V. A., ABUBAKER, M., AND KAZANSKII, B. A., *Neftekhimiya* **7** (1), 3–8 (1967).
10. VAN BEKKUM, H., VAN RANTWIJK, F., VAN MINNEN-PATHUIS, G., REMIJNSE, J. D., AND VAN VEEN, A., *Rec. Trav. Chim. Pays-Bas* **88,** 911, (1969).
11. GAULT, F. G., ROONEY, J. J., AND KEMBALL, C., *J. Catal.* **1,** 255 (1962).
12. BURWELL, R. L., JR., *Accounts Chem. Res.* **2,** 289 (1969).