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Stereochemistry and the Mechanism of Catalytic Hydrogenation of Cycloalkenes

VI. The Isomerization of 1,2-Dimethylcycloalkenes as a Route to Both *cis*- and *trans*-1,2-Dimethylcycloalkanes

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The reduced-platinum-oxide–catalyzed hydrogenation of 1,2-dimethylcyclohexene or 1,2-dimethylcyclopentene is accompanied by isomerization to the corresponding 2,3-dimethylcycloalkene. These isomers are reduced more rapidly than their precursors and the products are mixtures of *cis*- and *trans*-1,2-dimethylcycloalkanes whose ratio is apparently independent of the fraction of the original cycloalkene which has reacted. Clearly, the majority of the *trans* isomers arise from the reduction of the 2,3-dimethylcycloalkenes but some appear to be formed directly from the 1,2-dimethylcycloalkene.

Several alternative explanations for this result are considered.

INTRODUCTION

The hydrogenation of 1,2-dimethylcyclohexene (*1*) or 1,2-dimethylcyclopentene (*2*) catalyzed by reduced platinum oxide yields mixtures of *cis*- and *trans*-dimethylcycloalkanes. The proportion of the *cis* isomer increases as the pressure of hydrogen is raised and below 1 atm the ratio is about that obtained from the isomeric 2,3-dimethylcycloalkene. Although the formation of *cis* isomers from compounds such as these was explained in somewhat different ways by the theories of Farkas and Farkas (*3*) and Horiuti and Polanyi (*4*), present discussions are concerned with accounting for the *trans* isomers (*5, 6*).

The now classical Horiuti-Polanyi mechanism will accommodate the result providing a sufficient fraction of the 1,2-dimethylcycloalkene is isomerized to the 2,3-dimethylcycloalkene which can form either the *cis* or the *trans* saturated product by the addition of two hydrogen atoms from one or the other side of the molecule (*1, 2*). However, the required intermediate compounds were not detected and similar results led others to postulate more complex changes than appear in the classical theory (*5*).

The availability of improved analytical techniques prompted a re-examination of the above reaction and the postulated isomeric alkenes were observed.

EXPERIMENTAL

Both 1,2-dimethylcyclohexene and 1,2-dimethylcyclopentene were obtained free of impurities (less than 0.01 mole % as judged by a gas chromatographic analysis; see below) by chromatography of the products obtained from conventional preparative procedures for these cycloalkenes (*1, 2*). The separations were accomplished with a Wilkens Aerograph, Model A-700 "Autoprep" which contained a 22-ft by ⅜-inch aluminum column packed with polyethylene glycol 1000 distearate (25% by weight) on 60–80-mesh firebrick.

The hydrogenations were performed in the constant pressure apparatus described previously (*2*), except that in some experiments with 1,2-dimethylcyclopentene, five times the usual quantities of reagents were used in a flask modified by the addition of a side tube through which samples could be removed. In this flask, 30 ml of glacial acetic acid and 10 mg of platinum oxide were shaken under 1 atm of hydrogen to reduce the catalyst before 1.0 ml of the cycloalkene was added. The reduction was interrupted at intervals by stopping the shaker and samples were withdrawn for analysis. Results from these experiments were concordant with those obtained by the batch method.

A gas chromatograph equipped with a hydrogen flame detector (Wilkens Instrument Co., Aerograph Hy-Fi, Model 600) and fitted with a 200-ft by 0.01-inch polyethylene glycol 1000 distearate coated capillary column was used for the analysis of the hydrocarbon mixtures. This column was operated at 70–80° for the analysis of mixtures of cyclohexenes and cyclohexanes and at 35–45° for the cyclopentenes and cyclopentanes. The separations which were achieved are indicated by the relative retention times at 72° of 1.00, 1.16, 1.36, 1.62, and 2.92 for *trans*-1,2-dimethylcyclohexane, *cis*-1,2-dimethylcyclohexane, 2,3-dimethylcyclohexene, 1,2-dimethylcyclohexene, and *o*-xylene. At 45°, the relative retention times were 1.00, 1.14, 1.19, and 1.52 for *trans*-1,2-dimethylcyclopentane, *cis*-1,2-dimethylcyclopentane, 2,3-dimethylcyclopentene, and 1,2-dimethylcyclopentene.

RESULTS

Displayed in Figs. 1 and 2 are the results obtained upon reducing, respectively, 1,2-dimethylcyclohexene and 1,2-dimethylcyclopentene under the conditions stated above. The reductions are too fast to permit an accurate measure of their rates during the first few per cent of the change but previous studies showed the rate to be independent of the concentration of the substrate and consequently the per cent reduction is a measure of the reaction time.

Both compounds studied isomerize rapidly to the 2,3-dimethylcycloalkene which reduces faster than its progenitor. The latter result had been demonstrated before by experiments in which the pairs of isomers were reduced competitively (*1*, *2*). Furthermore, the steady state ratio of 2,3- to 1,2-dimethylcyclohexene attained in the

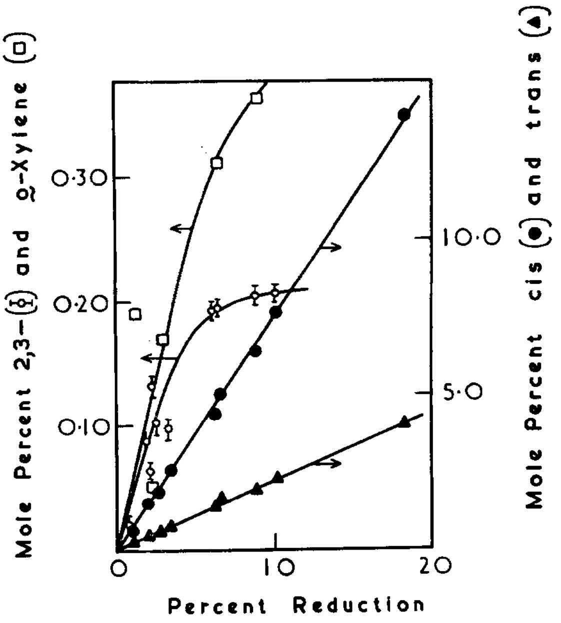

FIG. 1. The hydrogenation of 1,2-dimethylcyclohexene (PtO_2).

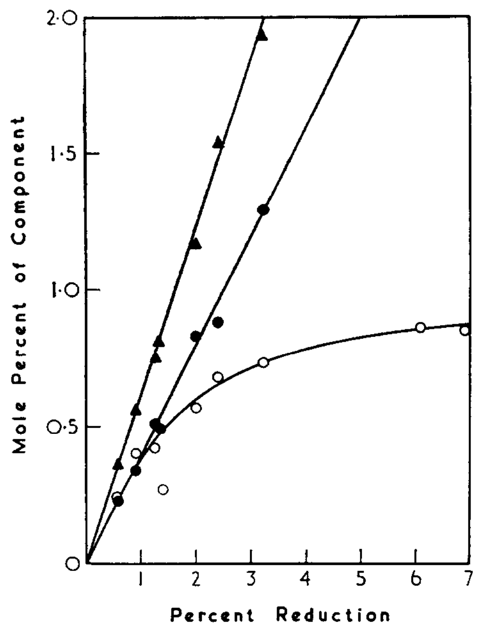

FIG. 2. Hydrogenation of 1,2-dimethylcyclopentene (PtO_2); 2,3-dimethylcyclopentene (○), *cis* (●), and *trans* (▲) 1,2-dimethylcyclopentane.

present experiment (approximately 0.003) is much less than the equilibrium ratio of 0.18 ± 0.05 (*7*, *8*). Therefore, under these conditions the specific rate of reduction of the 2,3 isomer is greater than the specific rate of its formation. The same comparison for the cyclopentene analog cannot be made until the equilibrium ratio has been measured; however the conclusions are likely to be the same. 1,2-Dimethylcyclopentene yields a larger value for the steady state ratio of 2,3- to 1,2-dimethylcycloalkene (0.01), a result consistent with the finding that the relative rate of migration of a double bond within the cycle to the rate of reduction of the 2,3 isomer is greater in the five- than in the six-membered cycloalkene (*2*).

The formation of *o*-xylene from 1,2-dimethylcyclohexene again illustrates the existence of a reaction path which joins the aromatic hydrocarbon and its saturated product via the desorbed cyclohexene (*9*).

The analyses were not sufficiently accurate to permit one to conclude with complete assurance whether the ratio of *cis*- to *trans*-dimethylcycloalkane is or is not a function of the extent of the reaction. The values for this ratio obtained from 1,2-dimethylcyclohexene range from 2.72 to 3.56 (average value 3.26 ± 0.22), and from 1,2-dimethylcyclopentene the range was 0.51 to 0.72 with an average of 0.62 ± 0.07. Unfortunately the ratio is most uncertain near the beginning of the reaction where a larger fraction of the saturated product might be expected to be formed directly from the 1,2-dimethylcycloalkene. That there is little or no trend in this ratio is suggested by Figs. 1 and 2, which contain all of the data obtained up to the per cent reduction shown. The reduction of the cyclohexene was carried to 15% and the cyclopentene to 25% and the results are included in the limits given above.

DISCUSSION OF RESULTS

The results in general support the Horiuti-Polanyi mechanism for the hydrogenation of olefins in that most, if not all, of the *trans*-1,2-dimethylcycloalkane arises via the isomerization of the 1,2- to the 2,3-dimethylcycloalkene. A similar conclusion followed from a recent study of the mechanism of formation of racemic alkanes in the hydrogenation of optically active alkenes (*10*). However, the initial rate of formation of the 2,3-dimethylcycloalkene is less than the initial rate of reduction; and there is little if any more of the *cis* isomer formed at the beginning of the reduction than after the 2,3-dimethylcycloalkene has reached its steady state concentration. Apparently a part of the 1,2-dimethylcycloalkene is converted directly to the *trans* saturated product.

A number of alternative hypotheses have been offered to account for such a result. Gault, Rooney, and Kemball (*6*) [see also discussion by Rooney (*11*)] suggest that a 1,2-dimethylcycloalkene forms with the catalyst a π complex which can not only combine with hydrogen adsorbed on the surface but also with hydrogen molecules from the gas phase. Accordingly both *cis*- and *trans*-dimethylcycloalkanes could be formed without the prior isomerization of the 1,2- to the 2,3-dimethylcycloalkene.

Others have postulated that the 1,2 isomer is transformed on the surface to a hydrogen-deficient species which is able to combine with adsorbed hydrogen to yield the requisite mixture of stereoisomeric dimethylcycloalkanes (*5*), but this suggestion seems unattractive for reasons we have previously cited (*12*).

The problem may be resolved in quite a different manner. The reduction of an olefin, particularly on platinum catalysts, is a fast reaction and because much of the surface resides within the porous structure, the apparent ratio of isomerization to reduction may be distorted by intraparticle diffusional effects. For example a reaction sequence $A \rightleftarrows B \rightarrow C$ can appear to be (*13, 14*).

$$\begin{tikzcd} A \arrow[r, shift left] \arrow[dr] & B \arrow[l, shift left] \arrow[d] \\ & C \end{tikzcd}$$

Ciola and Burwell (*15*) have provided experimental evidence that this phenomenon is of some importance in the reduction of 3,3-dimethyl-1,4-pentadiene on a nickel catalyst and the effect should be more pronounced in the present situation because the intrinsic rates of reduction are faster in the present instance by a factor of at least 10 (compare the rate constants per mg of catalyst in refs. *2* and *15*).

We plan to examine these hypotheses further by appropriate experimentation.

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