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CATALYTIC HYDROGENATION OF CYCLOPROPYL ALKENES. II. NATURE OF THE INTERMEDIATES IN THE HETEROGENEOUS HYDROGENOLYSIS REACTION

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In the preceding communication (3), we showed that a series of alkylated vinylcyclopropanes suffer almost exclusive ring hydrogenolysis when reduced over palladium, that the degree of hydrogenolysis varies only slightly with the degree of alkylation, and that hydrogenolysis must precede or occur concomitantly with double bond saturation. Over platinum or rhodium, the major pathway is simple double bond reduction, and the degree of hydrogenolysis observed is somewhat related to the position and degree of alkylation. We now wish to report results which bear on the question of the intermediates formed in the hydrogenolysis reaction.

Figs. I, II, and III show graphically the composition of the reaction mixtures at various stages in the reduction of isopropenylcyclopropane over Pd-C, Pt-C, and Rh-C. In the reduction over palladium (Fig. I), an initial mixture of all possible 2-methyl pentenes is produced in a non-thermodynamic ratio, which remains constant until approximately 80% of the isopropenylcyclopropane has reacted. At this point, the olefin composition undergoes adjustment, finally reaching a new ratio (after 1.1 equiv. of hydrogen has been absorbed), which is maintained for the duration of the reaction. Table I shows the composition of the olefin mixture in these two regions, along with the calculated equilibrium ratios for the relevant compounds in the ideal gaseous state. The observed steady state ratio of olefins after 1.1 equiv. of hydrogen has reacted agrees well with the observed equilibrium composition in dimethylsulfoxide, corrected to 25° (4).

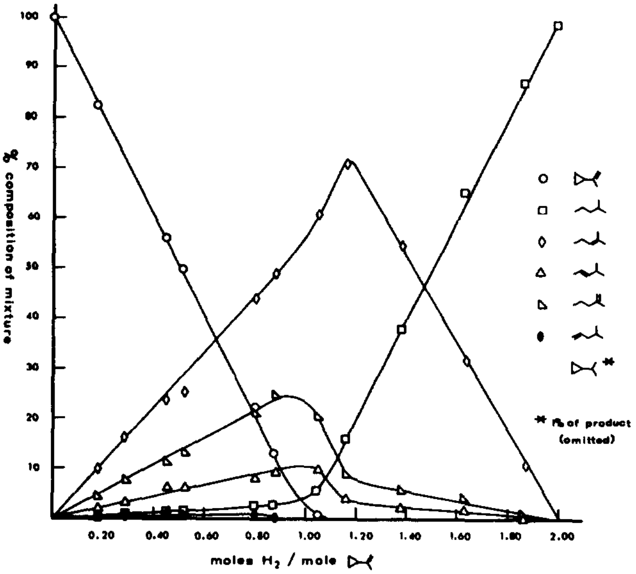
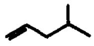
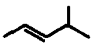
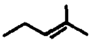
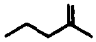


FIG. I Hydrogenation of Isopropenylcyclopropane with Pd/C

TABLE I

Composition of 2-Methylpentene Mixtures

				
Initial Mixture	2%	14%	57%	27%
After 1 equiv. H_2	0	4	86	10
Equilibrium, meas.[a]	0.18	3.1	86.8	10.0
Equilibrium, calc.[b]	0.2	9.5	78.8	11.5

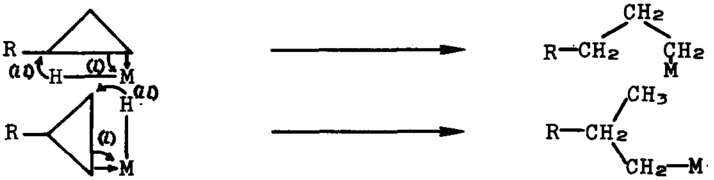
[a] Measured equilibrium ratios in dimethylsulfoxide at 55°C; extrapolated to 25°C.

[b] Calculated for the ideal gaseous state at 25°, using ΔF_f^0 [J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Res. Nat. Bur. Standards*, **36**, 559 (1946)].

From these results, it appears that in the presence of palladium, isopropenylcyclopropane is much more tightly adsorbed to the metal surface than any of the methylpentenes. Similar selectivity has also been observed in the reduction of 1,3-dienes, acetylenes and allenes (5,6). The initial methylpentene mixture must be a kinetically-produced ratio. After the isopropenylcyclopropane has reacted, the olefins are isomerized and hydrogenated. The ratio of isomerization to hydrogenation of simple olefins over palladium is known to be high (7); measurements of k_I/k_H in these laboratories gave values ranging from 0.68 for cis-4-methyl-2-pentene to 9.6 for 2-methyl-1-pentene. Therefore, the olefin composition in the later stages of the reaction reflects the thermodynamic stabilities of the isomers, although it may be biased slightly in favor of the less reactive compounds.

In the reduction of isopropenylcyclopropane over platinum (Fig. II) or rhodium (Fig. III), much different behavior is observed. Here, the major process is simple reduction of the double bond. Both the thermodynamic selectivity (exclusion of alkene by cyclopropylalkene) and the mechanistic selectivity (amount of completely saturated product in initial product mixture) are lower with these catalysts than with palladium, again in analogy to the behavior of 1,3-dienes, acetylenes and allenes (5,6).

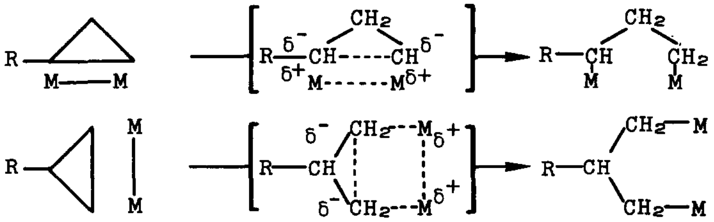
It has recently been proposed that substituted cyclopropanes undergo hydrogenolysis via a mechanism involving an electrophilic polarization step, consequent on chemisorption, followed by hydrogen transfer (eq. 1 or 2), with the


(1)

(2)

course of the reaction being determined by the electronic nature of the substituent (8).

In the case of hydrogenolysis over platinum and rhodium, we favor an alternative mechanism (eq. 3 and 4) in which polar and steric effects in the transi-


(3)

(4)

tion state, rather than in the ground state, are important. For alkylcyclopropanes, path 3 is disfavored by the -I effect and the unfavorable steric effect of the alkyl group, resulting in preferential cleavage of the C_2-C_3 bond (2,9). For vinyl (3), phenyl (7), and acylcyclopropanes, path 3 is selected by the ability of the substituent group to delocalize the partial negative charge in the transi-

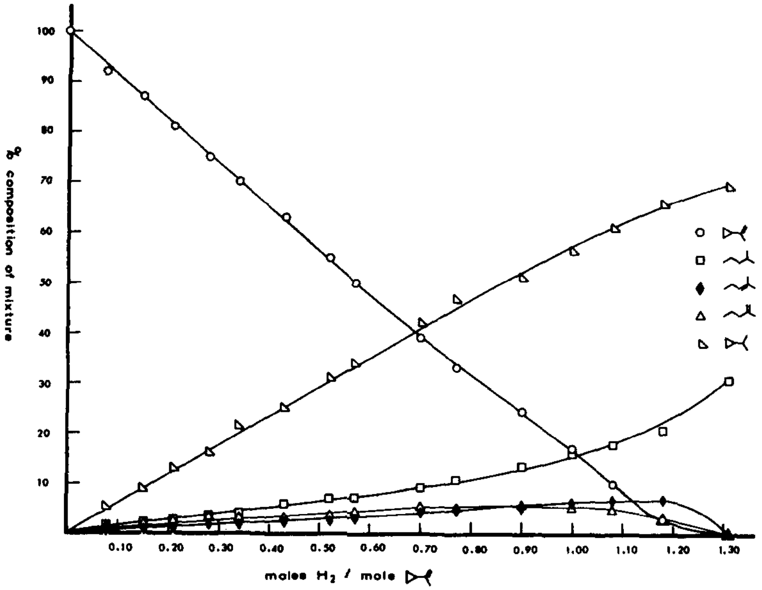


FIG. II Hydrogenation of Isopropenylcyclopropane with Pt/C

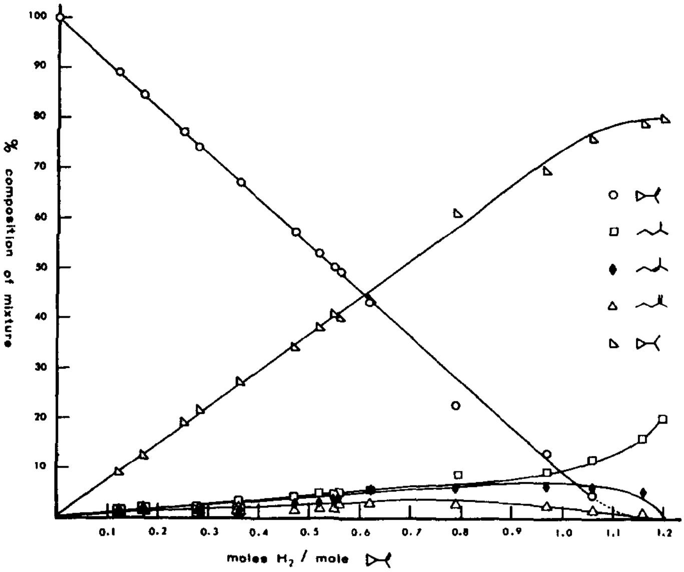
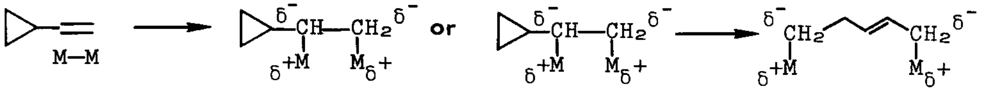


FIG. III Hydrogenation of Isopropenylcyclopropane with Rh/C tion state, even though a deleterious steric effect is also operating.

Over these metals, simple alkene saturation would then result from chemisorption at the alkene linkage, followed by reduction in the normal manner, although some hydrogenolysis may result from rearrangement of one of the intermediate monosorbed alkanes (eq. 5). This interpretation is in agreement with the observed effect of double bond substitution on the ratio of hydrogenolysis to double bond reduction, since more highly alkylated olefins are hydrogenolyzed to a greater degree (3), and has previously been suggested (9) as an explanation for results obtained over barium-promoted copper chromite (10).



(5)

The high degree of thermodynamic selectivity observed over palladium indicates that chemisorption on this metal is not due solely to the cyclopropane ring, as has been implied (8), but that the alkene linkage must also be important in the adsorption phenomenon. The adsorbed molecule may resemble the π-complex suggested by Burwell (6) for butadiene (eq. 6). The observed kinetic mixture of olefin isomers in the palladium reduction could then result from equilibration of the half-hydrogenated states on the catalyst surface prior to desorption.

(6)

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