

## Skeletal Rearrangement of Some Cyclic Hydrocarbons Catalyzed by Palladium

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Isomerizations of *endo*, *endo*-2,3-trimethylene(I), *exo*, *exo*-2,3-tetramethylene(IV), *endo*, *endo*-2,3-dimethyl(VI), *exo*, *exo*-2,3-dimethyl(VII), *trans*-2,3-dimethyl(VIII), *endo*-2-methyl-3,3-dimethyl(IX), *exo*-2-methyl-3,3-dimethyl(X), and 1,7,7-trimethylbicyclo[2.2.1]heptanes(XI), bicyclo[3.2.2]octane(XII), bicyclo[3.3.1]nonane(XIII) and protoadamantane(XIV) catalyzed by Pd/silica in excess hydrogen have been studied. At temperatures below  $\sim 200^{\circ}\text{C}$  some of the compounds probably isomerize by repeated roll-over of intermediate olefins. However, at higher temperatures a mechanism involving 1,2-C-C bond shift (analogous to carbonium ion rearrangements) must be responsible for skeletal rearrangement of some of these compounds, and probably predominates for reactions of all of them.

### INTRODUCTION

The transition metals, especially palladium, catalyze initial exchange with deuterium of hydrogen atoms on both faces of rings in cycloalkanes (1), inversion of optically active paraffins (2), and *cis-trans*-isomerizations of substituted cycloalkanes (3) at moderate temperatures. Recent studies (4, 5) of exchange reactions of model compounds consisting of some polycyclic saturated hydrocarbons on palladium catalysts have shown unambiguously that the mechanism responsible for all these reactions is repeated roll-over of intermediate olefins at the surface (6). When our studies were extended to higher temperatures some of these compounds isomerized to new products which could only be formed by breaking and making C-C bonds. This paper describes details of the latter reactions and discusses them in terms of the special structural features of these compounds.

### EXPERIMENTAL METHODS

**Compounds.** Preparations of I, II, VI, VII, VIII, XII, and XIII have been described previously (4, 5). Compounds III

and IV were prepared by the method of Alder, Monch and Wirtz (7). A mixture of 74% IX and 26% X, obtained by hydrogenating 2,2-dimethyl-3-methylenebicyclo[2.2.1]heptane (Adams Pt; 1 atm), was purified but not separated by glc. XI was obtained by the Wolff-Kishner reduction of camphor semicarbazone. XIV was obtained from Dr. A. Karim of this department. All the compounds were purified to  $>99\%$  before use.

**Reactions.** Reactions were carried out in a flow system using 5 g samples of a 2% wt Pd/silica catalyst (4) at a total pressure of 1 atm in hydrogen as previously described (4). Products were analyzed quantitatively by glc and identified by ms and nmr analyses. Control experiments showed that the silica support was catalytically inert.

### RESULTS

Some results for conversion of I to II at a flow rate of 10 ml (STP)  $\text{H}_2$ /min are shown in Table 1. The data reported at 188 and  $200^{\circ}\text{C}$  were obtained for comparison using a 0.5% wt Pd/Y-zeolite and 13% wt alumina-silica catalysts, respectively.

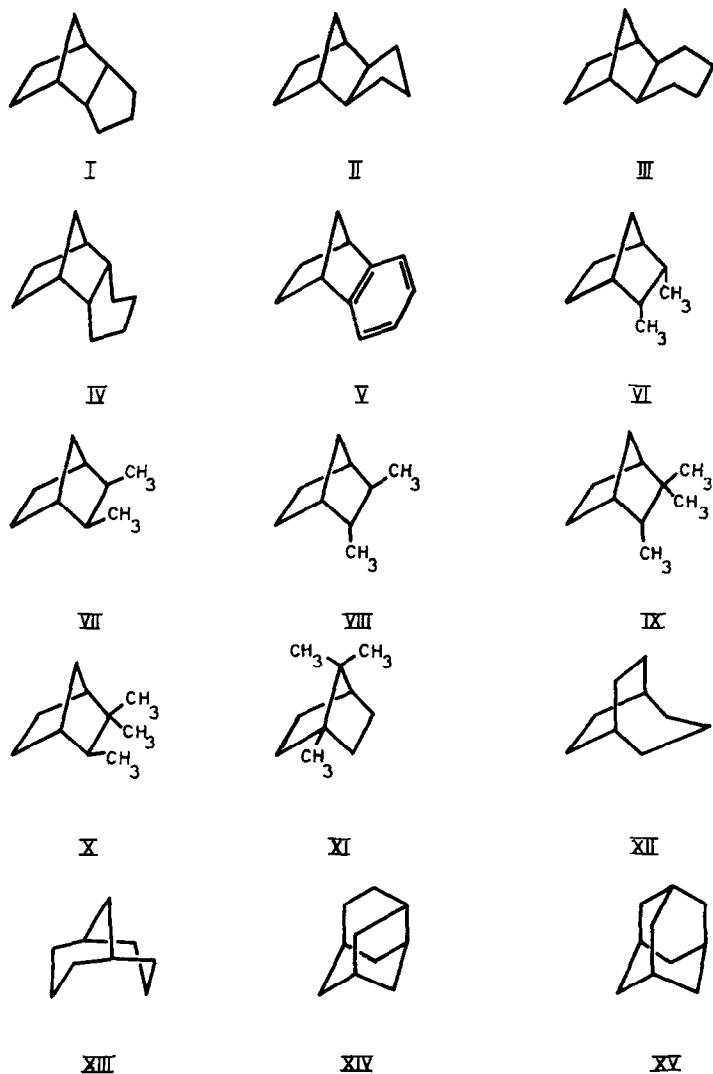


TABLE 1  
ISOMERIZATION OF I

| °C  | % Products |    | Cracked material |
|-----|------------|----|------------------|
|     | I          | II |                  |
| 150 | 99         | 1  | —                |
| 160 | 89         | 11 | —                |
| 180 | 15         | 85 | —                |
| 280 | 6          | 94 | —                |
| 458 | 79         | 18 | 3                |
| 188 | 4          | 90 | —                |
| 200 | 33         | 44 | 23               |

The Pd/Y-zeolite catalyzed the formation of 6% adamantane in this experiment.

Results for conversion of **III** are shown in Table 2. Reactions were very selective but at higher temperatures there was almost total conversion to the aromatic product **V**, identified by comparison of its ms and nmr data with those already published (8). Experiments of the following type (15 ml (STP) H<sub>2</sub>/min) revealed a distinction between isomerizing and dehydrogenating activities. When a 50:50 mixture of **I** and dicyclopentadiene was passed over a sample of catalyst at 340°C isomerizing activity declined rapidly. In a subsequent run using pure **I** and the same catalyst sample there was no isomerization even at 380°C. How-

TABLE 2  
REACTIONS OF III

| °C  | ml (STP)<br>H <sub>2</sub> /min | % Products |    |    |
|-----|---------------------------------|------------|----|----|
|     |                                 | III        | IV | V  |
| 144 | 27                              | 94         | 6  | —  |
| 170 | 24                              | 93         | 6  | 1  |
| 215 | 24                              | 87         | 8  | 5  |
| 250 | 15                              | 19         | 2  | 79 |
| 364 | 12                              | 2          | —  | 98 |

ever, the used catalyst was still active for dehydrogenating **III** giving 2% and 94% of **IV** and **V**, respectively, at 284°C. After heating in O<sub>2</sub> for 24 hr at 430°C followed by H<sub>2</sub> for 6 hr at 300°C pure **I** was now isomerized to 94% **II** at 318°C. When the catalyst sample was then heated at 530°C for 1 hr, isomerization of **I** at 318°C could not be detected, although **III** was now converted to 2% **IV**, and 75% **V** at 275°C.

Results for isomerizations of **VI**, **VII** and **VIII** are given in Table 3. At 290°C cracking was still insignificant but 43 and 11% of **VI** and **VIII**, respectively, were converted to a mixture of two other products which were not fully identified but which were isomeric with **VI** and **VIII** according to ms analysis.

Results for reactions of **IX**, **X** and **XI** are given in Table 4. The compounds listed as "others" consisted of unidentified isomers and mostly cracked material which became significant at higher temperatures.

Substantial conversion of **XII** to **XIII** was

TABLE 3  
ISOMERIZATIONS OF VI, VII AND VIII

| Reactant | °C  | ml (STP)<br>H <sub>2</sub> /min | % Products |     |      |
|----------|-----|---------------------------------|------------|-----|------|
|          |     |                                 | VI         | VII | VIII |
| VI       | 116 | 32                              | 82         | 9   | 9    |
|          | 126 | 22                              | 54         | 26  | 20   |
|          | 135 | 10                              | 19         | 41  | 40   |
|          | 155 | 200                             | 58         | 23  | 19   |
|          | 166 | 18                              | 3          | 9   | 88   |
|          | 146 | 13                              | 2          | 8   | 90   |
|          | 290 | 10                              | 1          | 4   | 47   |
| VII      | 133 | 12                              | 9          | 60  | 31   |
| VIII     | 290 | 10                              | 3          | 8   | 78   |

TABLE 4  
REACTIONS OF IX, X AND XI

| Reactant | °C  | ml (STP)<br>H <sub>2</sub> /min | % Products |    |    |        |
|----------|-----|---------------------------------|------------|----|----|--------|
|          |     |                                 | IX         | X  | XI | Others |
| IX + X   | 160 | 20                              | 71         | 29 | —  | —      |
|          | 214 | 28                              | 47         | 49 | 1  | 3      |
|          | 274 | 28                              | 34         | 41 | 11 | 14     |
|          | 314 | 12                              | 17         | 22 | 21 | 40     |
|          | 376 | 28                              | 6          | 0  | 16 | 78     |
| XI       | 278 | 12                              | 1          | 2  | 97 | —      |
|          | 306 | 12                              | 2          | 2  | 96 | —      |
|          | 324 | 16                              | 4          | 5  | 71 | 20     |
|          | 365 | 12                              | 3          | 4  | 54 | 39     |

TABLE 5  
ISOMERIZATION OF XII AND XIII

| Reactant | °C  | % Products |      |        |
|----------|-----|------------|------|--------|
|          |     | XII        | XIII | Others |
| XII      | 204 | 80         | 18   | 2      |
|          | 261 | 18         | 71   | 11     |
| XIII     | 254 | 1          | 90   | 9      |
|          | 325 | 2          | 63   | 35     |

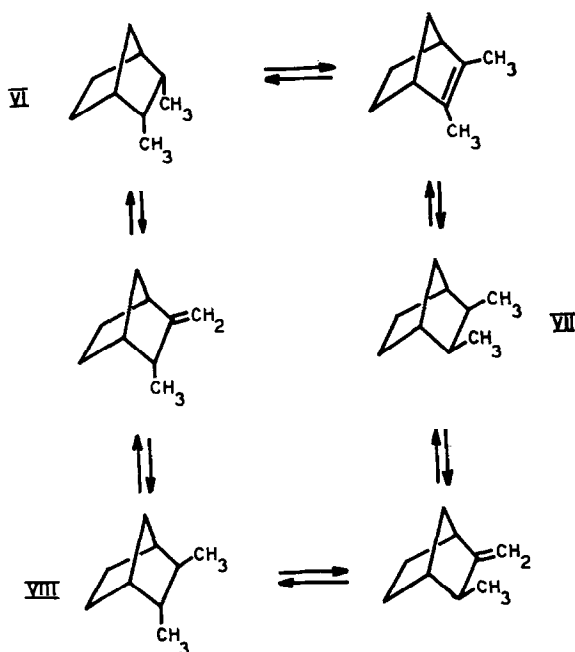
observed and results (10 ml (STP) H<sub>2</sub>/min) recorded in Table 5.

Isomerization of **XIV** was totally selective giving 3, 75 and 99% adamantane at 152, 240 and 300°C (10 ml H<sub>2</sub> (STP)/min), respectively.

## DISCUSSION

Since repeated roll-over of intermediate olefins on the surface has been shown to occur during reaction of paraffins at low temperatures on palladium (4, 5) schemes based on this mechanism can be constructed for interconverting **I** and **II**, **III** and **IV**, **VI**, **VII** and **VIII**, and **IX** and **X**. The following are the pathways for interconversion of **VI**, **VII** and **VIII**.

Palladium preferentially attacks tertiary C-H bonds (5) so the order of reactivity as expected from the steric environments of the tertiary H atom in the -CHCH<sub>3</sub>-CHCH<sub>3</sub>- units is **VI** > **VII** > **VIII** (Table 3). Although **VIII** largely predominates at equilibrium the ratios of **VII** to **VIII** from



**VI** are close to unity up to large conversions. If the above mechanism is correct, the different routes, **VI** to **VII**, **VI** to **VIII**, occur at approximately overall equal rates, which seems unlikely (9). However, Pecque and Maurel (10) have recently shown that hydrogenation of 2-methylene-3-methylbicyclo[2.2.2]octane and 2,3-dimethylbicyclo[2.2.2]oct-2-ene (very similar olefins to the above intermediates), either separately or as mixtures, on palladium results in the same ratio, near to unity, of the products *cis*-2,3-dimethyl and *trans*-2,3-dimethylbicyclo[2.2.2]octanes.

According to the above scheme conversion of **I** to **II**, and **IX** to **X** would require formation and roll-over of 2,3-trimethylene bicyclo[2.2.1]hept-2-ene and 2-methylene-3,3-dimethylbicyclo[2.2.1]heptane, respectively. Models show that there is considerable steric hindrance to the formation of the latter and roll-over of the former and this may explain why higher temperatures are necessary for reaction (Tables 1 and 4).

The results also show that carbonaceous residues poison the surface sites responsible for isomerizing **I** but not significantly the sites for aromatizing **III**. Since intermediate dehydrogenation to adsorbed alkene is in-

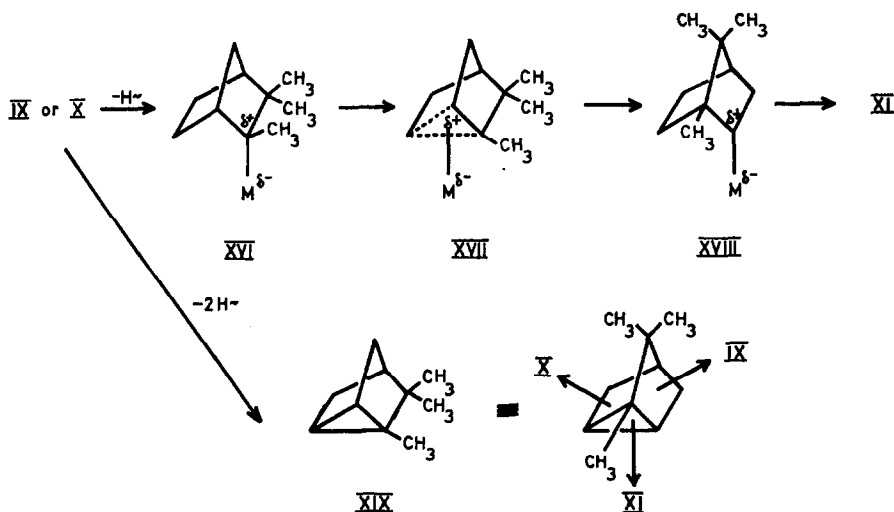
volved in both cases, if the above scheme for isomerization is correct, the mechanistic feature which distinguishes the sites is that roll-over of olefin is not required for aromatization.

In the higher temperature range a second mechanism involving C-C bond breaking and making is clearly necessary to account for the interconversion of **IX**, **X** and **XI**, **XII** and **XIII**, the protoadamantane(**XIV**) to adamantane(**XV**) rearrangement and the conversion of **VI**, **VII** and **VIII** into other isomers. Compounds of these structural types are well known to be particularly susceptible to carbonium ion rearrangements involving 1,2-C-C bond shifts (Wagner-Meerwein rearrangements) and hydride shifts (11). The preferential attack by palladium at tertiary C-H bonds indicates that the initially formed metal-alkyl species may be polarized in the C-M bond towards the metal as shown in **XVI**. The development of positive charge on carbon could result in a 1,2-bond shift either directly or *via* a species in which neighbouring C-C bond participation causes the electron deficiency to be shared by three carbon atoms as in **XVII**. This surface species resembles the bridged ion invoked to explain

the stereochemistry and kinetics of bicyclo(2,2,1)heptyl solvolysis reactions (11). Addition of hydrogen to the rearranged surface species **XVIII** then gives isomer **XI**. An

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alternative mechanism which can explain the rearrangement product involves the initial loss of *two* hydrogens from the hydrocarbon giving a nortricyclene intermediate (9) such as **XIX**. Cleavage of each of the three cyclopropane bonds gives the products as indicated by the arrows. The exact mode of formation of intermediates such as **XIX** and the nature of the bonding to the surface are unknown. The absence of cyclopropane-containing products does not rule out this mechanism because ring opening of the three-membered ring would occur with great ease under the reaction conditions employed.

The initial loss of three hydrogens forming an  $\alpha,\alpha,\gamma$ -trisorbed species which undergoes a bond shift giving an adsorbed cyclopropane is also a possible pathway for these rearrangements. But it is considered the least likely of the three. Although this species has been postulated as the intermediate in the platinum-catalyzed isomerization of neopentane to isopentane (12), palladium has negligible activity for isomerizing neopentane and, secondly, models show that  $\alpha,\alpha,\gamma$ -trisorbed species analogous to those proposed for acyclic systems are stereochemically frustrated in these bridged ring systems.

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