

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

## Studies in the Terpene Series. XVIII.<sup>1</sup> Isomerization Accompanying the Dehydrogenation of 1,1,3-Trimethylcyclohexane and of 1,1,3-Trimethyl-*x*-cyclohexene<sup>2</sup>

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The dehydrogenation of unsaturated hydrocarbons containing a geminal carbon atom such as 1,1,3-trimethyl-*x*-cyclohexene over platinum-alumina catalyst at 330° is accompanied by removal and migration of a methyl group. The product of the dehydrogenation consisted of *m*-xylene and trimethylbenzenes. The saturated hydrocarbon, 1,1,3-trimethylcyclohexane, under similar conditions, forms only *m*-xylene. When *s*-butyl chloride is added to the 1,1,3-trimethylcyclohexane the dehydrogenation is accompanied by a migration of a methyl group, which results in the formation of trimethylbenzenes. Similar results were obtained using platinum-charcoal as a catalyst. Chromia-alumina catalyzes the dehydrogenation of 1,1,3-trimethylcyclohexane and of 1,1,3-trimethyl-*x*-cyclohexene to *m*-xylene; if, however, small amounts of *s*-butyl chloride are added to the hydrocarbon a methyl group shift occurs only in the trimethylcyclohexene with the formation of 1,2,4- and 1,3,5-trimethylbenzene.

Catalytic dehydrogenation is one of the methods which has been used in our laboratories for the study of the structure of terpenes. This method was until now applied only to the investigation of the structure of saturated mono- or bicyclic terpenes or terpene-like products using as a catalyst platinum deposited on alumina.<sup>4-6</sup> The procedure consisted of hydrogenating the unsaturated terpenic hydrocarbons before submitting them to dehydrogenation, to avoid any possible side reactions of the cycloolefins, which might occur prior to dehydrogenation to the corresponding aromatic hydrocarbons.

TABLE I

DEHYDROGENATION OF 1,1,3-TRIMETHYLCYCLOHEXANE AND OF 1,1,3-TRIMETHYL-*x*-CYCLOHEXENE IN THE PRESENCE OF PLATINUM-ALUMINA CATALYST

| Experiment <sup>a</sup>                              | 1              | 2              | 3              | 4              | 5              | 6              | 7              |
|--|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Catalyst   | N <sup>b</sup> | N <sup>c</sup> | N <sup>c</sup> | N <sup>c</sup> | N <sup>c</sup> | N <sup>c</sup> | N <sup>d</sup> |
| Charge   | A <sup>f</sup> | A <sup>f</sup> | B <sup>g</sup> | A <sup>f</sup> | A <sup>e</sup> | A <sup>f</sup> | A <sup>f</sup> |
| Gas formed, mole                                     | 0.15           | 0.39           | 0.40           | 0.41           | 0.27           | 0.15           | 0.24           |
| Composition of gas, vol. %                           |                |                |                |                |                |                |                |
| Methane  | ...            | 32             | 31             | 32             | 18             | 13             | 26             |
| Hydrogen   | ...            | 68             | 69             | 68             | 80             | 87             | 74             |
| Product obtained                                     |                |                |                |                |                |                |                |
| 1,1,3-Trimethylcyclohexane in the liq. prod., vol. % | 68             | 40             | 28             | 23             | 50             | 77             | 59             |
| Composition of aromatic hydrocarbons formed, vol. %  |                |                |                |                |                |                |                |
| <i>m</i> -Xylene                                     | 100            | 100            | 62             | 100            | 32             | 64             | 85             |
| 1,2,4-Trimethylbenzene                               | ...            | ...            | 38             | ...            | 32             | 36             | 13             |
| 1,2,3-Trimethylbenzene                               | ...            | ...            | ...            | ...            | 21             | ...            | 2              |

<sup>a</sup> The reaction tube was filled with 50 cc. of catalyst. The hourly liquid space velocity was 0.2-0.25. The temperature of dehydrogenation was 330°, with exception of experiment 1, where temperature of 300° was used. In each experiment 0.15-0.19 mole of hydrocarbons was used. <sup>b</sup> N = platinum-alumina catalyst; contains about 7% of platinum. <sup>c</sup> N<sup>c</sup> = from previous experiment without regeneration. <sup>d</sup> N<sup>d</sup> = regenerated by passing air followed by hydrogen. <sup>e</sup> A<sup>e</sup> = 1,1,3-trimethylcyclohexane contained 5% by volume of *s*-butyl chloride. <sup>f</sup> A<sup>f</sup> = 1,1,3-trimethylcyclohexane. <sup>g</sup> B = 1,1,3-trimethyl-*x*-cyclohexene.

(1) For previous paper in this series see V. N. Ipatieff, W. D. Huntsman and H. Pines, *THIS JOURNAL*, **75**, 6222 (1953).

(2) This work was made possible in part through the financial assistance of Universal Oil Products Company.

(3) Deceased, November 29, 1952.

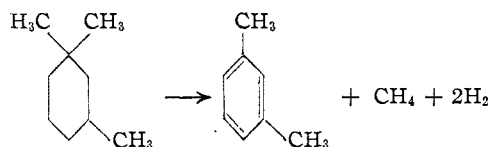
(4) V. N. Ipatieff, H. Pines and R. C. Olberg, *THIS JOURNAL*, **68**, 1709 (1946).

(5) V. N. Ipatieff, H. Pines and M. Savoy, *ibid.*, **69**, 1948 (1947).

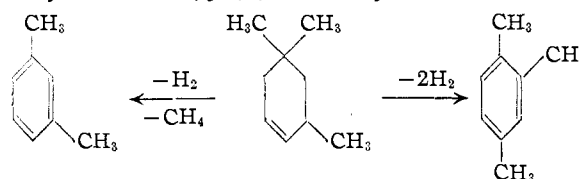
(6) H. Pines, R. C. Olberg and V. N. Ipatieff, *ibid.*, **70**, 533 (1948).

In order to determine the effect of an olefinic double bond upon dehydrogenation, 1,1,3-trimethyl-*x*-cyclohexene and 1,1,3-trimethylcyclohexane were passed over a platinized-alumina catalyst, containing 7% platinum and prepared according to a method described previously.<sup>6</sup> These hydrocarbons were chosen for this study since they have a structure similar to the terpenes and dihydroterpenes obtained from the catalytic conversion of pinane.<sup>5,6</sup>

In agreement with previous observations<sup>4</sup> it was found that platinized alumina causes the dehydrogenation of 1,1,3-trimethylcyclohexane to *m*-xylene and methane (Table I).



If, however, 1,1,3-trimethyl-*x*-cyclohexene is passed over the same catalyst, isomerization accompanies the dehydrogenation reaction and the aromatic hydrocarbons which formed were composed of 62% *m*-xylene and 38% 1,2,4-trimethylbenzene.



It was reported previously<sup>7</sup> that alumina-hydrogen chloride catalyst caused skeletal isomerization and hydrogen transfer of cycloolefins; alkylcyclohexanes were stable toward this catalyst. It was of interest to determine whether skeletal isomerization would accompany the dehydrogenation of 1,1,3-trimethylcyclohexane if passed over platinized alumina in the presence of hydrogen chloride or a compound which can liberate hydrogen chloride during the reaction. In order to have a better control of the amount of hydrogen chloride introduced, *s*-butyl chloride was used as a source of hydrogen chloride. A solution consisting of 4 mole per cent. of *s*-butyl chloride in 1,1,3-trimethylcyclohexane was passed over platinized alumina, which with pure 1,1,3-trimethylcyclohexane did not

(7) H. Pines, R. C. Olberg and V. N. Ipatieff, *ibid.*, **74**, 4872 (1952).

show any isomerizing properties (experiment 4). It was found that in the presence of added alkyl chloride, isomerization accompanied dehydrogenation and the aromatic hydrocarbons produced contained 32% of 1,2,4- and 21% of 1,2,3-trimethylbenzene (experiment 5); when the addition of *s*-butyl chloride was discontinued the degree of isomerization dropped from 68 to 36% (experiment 6), and to 15% when the catalyst was regenerated with air followed by hydrogen (experiment 7).

Platinum deposited on activated coconut charcoal showed properties similar to that of platinumized alumina (Table II). The experiments show also that in order to prevent a skeletal isomerization it is desirable to hydrogenate the cycloolefins to the corresponding cycloparaffins prior to dehydrogenation.

TABLE II

DEHYDROGENATION OF 1,1,3-TRIMETHYLCYCLOHEXANE AND OF 1,1,3-TRIMETHYL-*x*-CYCLOHEXENE USING PLATINUM<sup>a</sup> CHARCOAL CATALYST

| Experiment <sup>a</sup>                                 | 8              | 9              | 10             | 11             | 12             |
|---|----------------|----------------|----------------|----------------|----------------|
| Charge, kind  | A <sup>b</sup> | A <sup>b</sup> | B <sup>d</sup> | A <sup>c</sup> | A <sup>c</sup> |
| moles   | 0.16           | 0.12           | 0.15           | 0.15           | 0.15           |
| Temperature, °C.  | 300            | 330            | 350            | 300            | 350            |
| Gas formed, moles                                       | 0.19           | 0.38           | 0.04           | 0.08           | ...            |
| Composition of gas, vol. %                              |                |                |                |                |                |
| Methane   | 29             | 30             | ...            | 18             | ...            |
| Hydrogen  | 71             | 70             | ...            | 82             | ...            |
| Product obtained  |                |                |                |                |                |
| 1,1,3-Trimethylcyclohexane in the liq. prod., vol. %    | 70             | 50             | 68             | 86             | 82             |
| Composition of the aromatic hydrocarbons formed, vol. % |                |                |                |                |                |
| <i>m</i> -Xylene  | 100            | 100            | 50             | 64             | 72             |
| 1,2,4-Trimethylbenzene                                  | ...            | ...            | 50             | 36             | 28             |

<sup>a</sup> The reaction tube was filled with 50 ml. of catalyst containing 20% of platinum. In experiment 8 a fresh catalyst was used, the same catalyst being in each of successive experiments. The reaction was carried out at an hourly liquid space velocity of 0.2. <sup>b</sup> A = 1,1,3-trimethylcyclohexane. <sup>c</sup> A' = 1,1,3-trimethylcyclohexane containing 5% by volume of *s*-butyl chloride. <sup>d</sup> B = 1,1,3-trimethyl-*x*-cyclohexene.

TABLE III

DEHYDROGENATION OF 1,3,5-TRIMETHYLCYCLOHEXANE AND OF 1,3,5-TRIMETHYL-*x*-CYCLOHEXENE IN THE PRESENCE OF CHROMIA-ALUMINA CATALYST

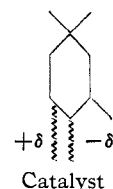
| Experiment <sup>a</sup>                              | 13             | 14             | 15              | 16             | 17             |
|--|----------------|----------------|-----------------|----------------|----------------|
| Charge   | B <sup>d</sup> | B <sup>d</sup> | B <sup>e</sup>  | A <sup>f</sup> | A <sup>g</sup> |
| Temperature, °C.                                     | 450            | 500            | 500             | 450            | 500            |
| Gas formed, moles                                    | 0.19           | 0.41           | 0.37            | 0.11           | 0.12           |
| Composition of gas, vol. %                           |                |                |                 |                |                |
| Methane  | 50             | ...            | ...             | 33             | 33             |
| Hydrogen   | 50             | ...            | ...             | 67             | 67             |
| Product obtained                                     |                |                |                 |                |                |
| 1,1,3-Trimethylcyclohexane in the liq. prod., vol. % | 75             | 0              | 66              | 70             | 82             |
| Composition of aromatic hydrocarbons formed, vol. %  |                |                |                 |                |                |
| <i>m</i> -Xylene                                     | 100            | 100            | 51 <sup>b</sup> | 100            | 100            |
| Trimethylbenzenes                                    | ...            | ...            | 44 <sup>c</sup> | ...            | ...            |

<sup>a</sup> The reaction tube was filled with 50 cc. of catalyst consisting of chromia-alumina promoted with cerium and potassium. The hourly liquid space velocity was 0.35. <sup>b</sup> Contains 10% *o*-, 34% *m*- and 7% *p*-xylene based on aromatic hydrocarbons present. <sup>c</sup> Contains 34% 1,2,4- and 10% 1,3,5-trimethylbenzene based on aromatic hydrocarbons present. <sup>d</sup> B = 1,1,3-trimethyl-*x*-cyclohexene. <sup>e</sup> B' = 1,1,3-trimethyl-*x*-cyclohexene containing 5% by volume of butyl chloride. <sup>f</sup> A = 1,1,3-trimethylcyclohexane. <sup>g</sup> A' = 1,1,3-trimethylcyclohexane containing 5% by volume of *s*-butyl chloride.

Chromia-alumina also was investigated as a catalyst for the dehydrogenation of 1,1,3-trimethylcyclohexane and 1,1,3-trimethyl-*x*-cyclohexene; the only product formed was *m*-xylene. It was found, however, that in the presence of *s*-butyl chloride the dehydrogenation of 1,1,3-trimethyl-*x*-cyclohexene was accompanied by isomerization; the resulting product contained 1,2,4- and 1,3,5-trimethylbenzene (Table III).

### Discussion of Results

The results as summarized in Tables I, II and III indicate that in the presence of a platinum-containing catalyst the dehydrogenation of 1,1,3-trimethylcyclohexane does not seem to proceed *via* an olefin formation since on dehydrogenation the saturated hydrocarbon forms *m*-xylene only, while 1,1,3-trimethyl-*x*-cyclohexene under the same conditions yields 1,2,4-trimethylbenzene in addition to *m*-xylene. The skeletal isomerization, which accompanies the dehydrogenation of the trimethylcyclohexene seems to indicate that the reaction proceeds through an ionic mechanism. This may involve the addition of a proton to the cycloolefin to form a carbonium ion, or the formation of a polar bond between one carbon atom of the double bond pair and the catalyst as indicated by the formula



In the case of chromia-alumina catalyst either such an activated complex is not formed or a proton is not present.

The present study shows that the dehydrogenation of 1,1,3-trimethylcyclohexane proceeds without skeletal rearrangement which suggests that the reaction is non-ionic and that the intermediate product is not trimethylcyclohexene. In view of the present work which shows that 1,1,3-trimethylcyclohexane can undergo dehydrogenation to *m*-xylene, the multiplet theory of Balandin<sup>8</sup> will have to be reevaluated. This theory states that a cyclohexane containing a geminal carbon atom, such as 1,1-dimethylcyclohexane, which cannot be absorbed flat on the catalyst, does not undergo dehydrogenation. This statement was based in part on the work of Zelinski and Delzova<sup>9</sup> who reported that 1,1-dimethylcyclohexane does not undergo dehydrogenation when passed over platinum-charcoal catalyst.

The present study showed also that 1,1,3-trimethylcyclohexane containing small amounts of alkyl chloride undergoes isomerization during dehydrogenation when passed over a catalyst containing platinum. The alkyl chloride seems to become the source of carbonium ions or of protons which probably in the presence of the catalyst re-

(8) A. A. Balandin, *Z. physik. Chem.*, **B2**, 289 (1929). See also the chapter by B. M. Trapnell ("Balandin's Contribution to Heterogeneous Catalysis" published in "Advances in Catalysis," Vol. III, Academic Press, Inc., New York, N. Y., 1951, pp. 1-25).

(9) N. D. Zelinski and N. Delzova, *Ber.*, **56**, 1716 (1923).

move hydride ions from the hydrocarbon to form trimethylcyclohexylcarbonium ions, which then undergo skeletal isomerization. Chromia-alumina does not cause isomerization in this case or in the case of dehydrogenation of the cyclohexene.

### Experimental Part

**Materials.**—(a) Platinum-alumina catalyst was prepared according to the method described previously.<sup>6</sup> (b) Platinum-charcoal catalyst was prepared according to the method described by Linstead and co-workers<sup>10</sup> except that activated Burrell coconut charcoal (10–14 mesh) was used in place of Norit to facilitate its use in a vertical catalyst tube. (c) Chromia-alumina catalyst was prepared according to the method of Archibald and Greensfelder.<sup>11</sup> (d) 1,1,3-Trimethyl- $\alpha$ -cyclohexene and 1,1,3-trimethylcyclohexane were prepared by the method described previously.<sup>4</sup>

**Apparatus and Procedure.**—The apparatus consisted of a graduated buret connected to a Pyrex glass reaction tube containing the catalyst bed, a water-cooled receiver-condenser, and a calibrated gas collecting bottle containing saturated salt solution. The reaction tube was heated in a thermostatically controlled vertical furnace brought to the desired temperature in a slow stream of hydrogen.

The gaseous products formed were analyzed on a mass spectrograph at the laboratory of the Universal Oil Products Company.

The liquid products were distilled and analyzed. It was found that the bottoms of the distillation, amounting to

(10) R. P. Linstead, K. O. Michaelis and S. L. S. Thomas, *J. Chem. Soc.*, 1139 (1940).

(11) R. C. Archibald and B. S. Greensfelder, *Ind. Eng. Chem.*, **37**, 356 (1945).

about 1% of the total product had an index of over 1.510 probably indicating the presence of a diaryl hydrocarbon. The distillate was analyzed by infrared absorption. In some instances, the aromatic hydrocarbons were separated chromatographically from the naphthenes and submitted separately to analysis.

The structure of the aromatic hydrocarbons produced, such as *m*-xylene and 1,2,4-trimethylbenzene, was determined by means of solid nitro and bromo derivatives; they did not depress the melting point when mixed with the corresponding derivatives of known compounds.<sup>12</sup> The analyses were made according to the procedure described previously.<sup>6</sup> The wave lengths used for calculating the composition of the various samples are given in Table IV.

TABLE IV  
WAVE LENGTHS ( $\lambda$ ) OF CHARACTERISTIC INFRARED ABSORPTIONS, IN MICRONS

| Hydrocarbon                | Major $\lambda$ , $\mu$ | Minor $\lambda$<br>or<br>check $\lambda$ , $\mu$ |
|----------------------------|-------------------------|--|
| <i>o</i> -Xylene           | 13.49                   | 10.75  |
| <i>m</i> -Xylene           | 13.00                   | 11.42  |
| <i>p</i> -Xylene           | 12.55                   | 8.2  |
| 1,2,3-Trimethylbenzene     | 13.08                   | 9.2  |
| 1,2,4-Trimethylbenzene     | 12.40                   | 11.45  |
| 1,3,5-Trimethylbenzene     | 11.95                   | (None)   |
| 1,1,3-Trimethylcyclohexene | 7.7                     | 8.0, 8.5   |

(12) "Infrared Spectral Analysis" (by Ed. Baclawski), Research and Development Laboratories, Universal Oil Products Company, Riverside, Illinois.

EVANSTON, ILL.

[CONTRIBUTION NO. 1802 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

## Spiro [3.5]nonane<sup>1</sup>

By E. R. BUCHMAN, D. H. DEUTSCH AND G. I. FUJIMOTO

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Spiro(3.5)nonane (I) has been prepared by two methods. The more practical of these involved the application of the malonic ester synthesis to 1,1-di-(bromomethyl)-cyclohexane (IV) and conventional treatment of the product to give spiro(3.5)nonane-2-carboxylic acid (VI). The Hunsdiecker degradation of this acid yielded the corresponding bromide (VII) which was catalytically reduced to I. In the second method, spiro(3.5)nonan-2-one (IX) was obtained as a product of the reaction between pentamethyleneketene (VIII) and diazomethane. Reduction of IX *via* the semicarbazone gave I.

Only five of the parent spirane hydrocarbons have been reported in the literature<sup>2</sup>; none of these contains the cyclobutane ring. The present paper describes two independent syntheses of spiro(3.5)nonane (I), each of which proceeds from a suitable cyclohexane derivative with subsequent closure of the 4-carbon ring.<sup>3</sup>

(1) Presented before the Division of Organic Chemistry, American Chemical Society at the San Francisco Meeting, March, 1949. This research received support from the Office of Naval Research.

(2) There are sixteen theoretically possible parent monospirane hydrocarbons having eleven carbon atoms or less. Those reported are: (chronologically) (a) spiro(3.5)undecane, W. S. G. P. Norris, *J. Chem. Soc.*, 245 (1926); (b) spiro(4.5)decane, N. D. Zelinsky and N. I. Schuilkin, *Ber.*, **62**, 2180 (1929); *cf.* G. R. Clemo and J. Ormston, *J. Chem. Soc.*, 352 (1933); N. N. Chatterjee, *J. Indian Chem. Soc.*, **13**, 536 (1936); C. S. Marvel and L. A. Brooks, *THIS JOURNAL*, **63**, 2630 (1941); (c) spiro(4.4)nonane, N. D. Zelinsky and N. V. Elagina, *Compt. rend. acad. sci. (URSS)*, **49**, 568 (1945); *cf.* N. N. Chatterjee, *J. Indian Chem. Soc.*, **14**, 259 (1937); (d) spiro(2.2)pentane, M. J. Murray and E. H. Stevenson, *THIS JOURNAL*, **66**, 314, 812 (1944); see also V. A. Slabey, *ibid.*, **68**, 1335 (1946); (e) spiro(2.5)octane, R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **70**, 946 (1948).

(3) Regarding other syntheses of spiro(3.5)nonane derivatives, see

In the first route to I, use was made of the malonic ester synthesis, a standard means of obtaining cyclobutane acids. The appropriate dibromide, 1,1-di-(bromomethyl)-cyclohexane (IV), had been prepared by Boord and co-workers<sup>2e</sup> by the action of phosphorus tribromide on the glycol II. In the present work, this procedure was advantageously modified; II was converted to the ditosylate III and the latter, on treatment with sodium bromide, gave IV in over-all yield from the glycol of better than 50%. The ester V, resulting from the malonic ester synthesis carried out in isoamyl alcohol,<sup>4</sup> was saponified and decarboxylated in the usual manner. The acid VI when subjected to the Hunsdiecker reaction<sup>5</sup> gave rise to the bromide VII from which spirane I was prepared by catalytic

(a) G. A. R. Kon, *J. Chem. Soc.*, **121**, 513 (1922); (b) P. K. Paul, *J. Indian Chem. Soc.*, **8**, 717 (1931); (c) N. N. Chatterjee, *C. A.*, **30**, 5947 (1936); *J. Indian Chem. Soc.*, **14**, 127 (1937).

(4) *Cf.* H. Fecht, *Ber.*, **40**, 3883 (1907).

(5) *Cf.* J. Cason and R. L. Way, *J. Org. Chem.*, **14**, 31 (1949).