[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORIES, NORTHWESTERN UNIVERSITY, AND UNIVERSAL OIL PRODUCTS COMPANY]

Studies in the Terpene Series. V.[1] The Action of Dilute Aqueous Salt Solutions on 3,3,5-Trimethylcyclohexanol and 1,1,3-Trimethyl-X-cyclohexene

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During the study of the dehydration of dicyclic terpenic alcohols by means of dilute aqueous acid acting salt solutions, it was found that in some instances the formation of the hydrocarbons produced could not be explained unless the migration of alkyl groups within the ring is assumed. In order to throw more light on the mechanism of the formation of the various hydrocarbons, the dehydration of monocyclic alcohols containing a geminal carbon atom was investigated. The readily available 3,3,5-trimethylcyclohexanol was selected for this study. It was found that by treatment of this alcohol with an equal volume of a 2% aqueous magnesium chloride solution at 350° dehydration is accompanied by a methyl group migration. The hydrocarbons formed consisted of a mixture composed of 1,2,4- and 1,1,3-trimethyl-*x*-cyclohexene. These hydrocarbons on hydrogenation yielded the corresponding trimethylcyclohexanes which according to an infrared absorption analysis and dehydrogenation consisted of 20% of 1,2,4- and 80% 1,1,3-trimethylcyclohexane. Although 1,2,4-trimethylcyclohexane may exist as stereoisomers, the absorption spectra corresponded only to the reference samples. Similar isomerization occurred when 1,1,3-trimethyl-*x*-cyclohexene was treated with aqueous magnesium chloride solution under conditions used for the carbinol. The 1,1,3-trimethylcyclohexane, on the other hand, was very stable toward the action of aqueous magnesium chloride solution even at a temperature of 400°.

The 1,1,3-trimethyl-*x*-cyclohexene was obtained in almost quantitative yield from 3,3,5-trimethylcyclohexanol by dehydration over activated alumina at 375°.

A migration of methyl group during the dehydration of 3,3,5-trimethylcyclohexanol was not noticed when potassium hydrogen sulfate was used as a dehydrating catalyst. Such a migration was expected since a hydrogen transfer within the carbonium ion formed by the loss of the hydroxy ion of this type of secondary alcohol usually occurs in the presence of acid-type catalysts. This hydrogen transfer would probably cause the formation of a neopentyl type of carbonium ion which would then undergo rearrangement similar to that of 2,2-dimethylcyclohexanol.[2]

The dehydrogenation of 1,2,4- and 1,1,3-trimethylcyclohexane over platinized alumina catalyst[3] was studied. It was found that whereas 1,2,4-trimethylcyclohexane underwent dehydrogenation at 240° to form 1,2,4-trimethylbenzene to the extent of 72%, 1,1,3-trimethylcyclohexane under similar experimental conditions yielded only 14% of aromatics. At 300° 1,1,3-trimethylcyclohexane formed 80% of xylenes and liberated hydrogen and methane in molal proportions of 2:1. The xylenes, according to ultraviolet absorption, were composed of 8% of *o*-, 83% of *m*- and 9% of *p*-xylene. The formation of *o*- and *p*-xylene is probably due to isomerization of *m*-xylene during its formation.

Experimental Part

3,3,5-Trimethylcyclohexanol–Aqueous Magnesium Chloride.—One hundred grams of the alcohol was heated in an 850-cc. capacity rotating autoclave with 100 cc. of a 2% aqueous solution of magnesium chloride at 350° for three hours. The cycloalkenes which were obtained and which distilled at 135–152° were submitted to hydrogenation at 100 atmospheres pressure and at 80° in the presence of a nickel–kieselguhr catalyst. The hydrogenated product distilled at 137–142°. The infrared absorption of this product showed that it consisted of 20% of 1,2,4-trimethylcyclohexane.

Part of the hydrogenated product was passed over platinized alumina at 240°. The gases formed from dehydrogenation contained only hydrogen. The dehydrogenated material on nitration yielded a solid derivative melting at 182°. Mixed melting point with 3,5,6-trinitro-1,2,4-trimethylbenzene showed no depression.

Infrared Spectral Analysis (by W. S. Gallaway).—The infrared spectra were recorded on a large Gaertner spectrometer of the Littrow type equipped for automatic recording. Using a cell which provided a liquid film of 0.1 mm., the spectra of Fig. 1 were obtained.

Direct comparison of the sample recordings with those of pure hydrocarbons showed that only 1,1,3- and 1,2,4-trimethylcyclohexane were present in appreciable quantities. There appeared to be approximately 1 or 2% of unidentified material present. Measurement of the intensities of the absorption at 8.6, 8.9, 9.7 and 10.0 microns followed by the application of Beer's law yielded values ranging from 18 to 22% for the concentration of 1,2,4-trimethylcyclohexane.

The question of the existence of various *cis* and *trans* isomers of the 1,2,4-form is not of importance here since such an excellent match is obtained between the three spectra of Fig. 1. One can conclude from these data that the various isomers appear in nearly the same proportion in the sample as they do in the pure hydrocarbon which was prepared by hydrogenating 1,2,4-trimethylbenzene. Some variation in isomer ratio between sample and reference material is expected, however, and is probably the basis for the spread in the calculated composition.

Preparation of 1,1,3-Trimethyl-*x*-cyclohexene and 1,1,3-Trimethylcyclohexane.—3,3,5-Trimethylcyclohexanol was passed over activated alumina at 375° at an hourly liquid space velocity of one. The hydrocarbons obtained distilled at 130° at 745 mm., $d^{20}{}_4$ 0.7885, $n^{20}{}_D$ 1.4397; yield 95%. It did not form a solid nitrosite with either amyl nitrite or ethyl nitrite. On hydrogenation at 60° in the

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(1) For Paper IV of this series, see V. N. Ipatieff and H. Pines, THIS JOURNAL, **67**, 1931 (1945).

(2) H. Meerwein *Ann.*, **405**, 129 (1914).

(3) H. Pines and V. N. Ipatieff, THIS JOURNAL, **61**, 1076 (1939).

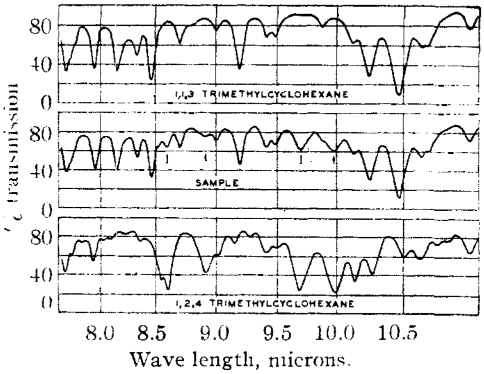

Fig. 1.

presence of nickel–kieselguhr catalyst and at 100 atmospheres hydrogen pressure, it yielded 1,1,3-trimethylcyclohexane boiling at 135° at 747 mm., d^{20}_4 0.7783, n^{20}_D 1.4290. According to infrared absorption analysis, this hydrocarbon was 99.5% pure, as compared with 1,1,3-trimethylcyclohexane prepared by the same method and which was purified by means of distillation on a column of seventy-five plate efficiency and at a reflux ratio of fifty to one. Center cuts of the distillate were used for reference infrared spectral analysis.

1,1,3-Trimethyl-x-cyclohexene–Aqueous Magnesium Chloride.—Seventy-three grams of the hydrocarbon was heated with 80 cc. of an aqueous 2% solution of magnesium chloride under the same experimental conditions as described for 3,3,5-trimethylcyclohexanol. The recovered product, which distilled between 133 and 152° after hydrogenation, consisted of 1,2,4- and 1,1,3-trimethylcyclohexane.

1,1,3-Trimethylcyclohexane–Aqueous Magnesium Chloride.—Fifty grams of this hydrocarbon was heated for three hours at 400° with 50 cc. of a 2% aqueous magnesium chloride solution. The recovered hydrocarbon consisted, according to physical constants and infrared absorption analysis, of unchanged 1,1,3-trimethylcyclohexane.

Dehydrogenation of 1,1,3-Trimethylcyclohexane.—1,1,3-Trimethylcyclohexane was passed at a rate of 10 cc. per hour over 30 cc. of 10–14 mesh activated alumina containing 7% of platinum, placed in a glass tube of 12 mm. diameter. At 240°, 14% and at 300°, 80% of the hydrocarbon underwent dehydrogenation with liberation of gases consisting of 67% of hydrogen and 33% of methane. The liquid product on nitration yielded trinitro-*m*-xylene melting at 181°, no depression in melting point was noticed when mixed with a known sample of trinitro-*m*-xylene.

Dehydration with Potassium Hydrogen Sulfate.—3,3,5-Trimethylcyclohexanol, 100 g., was mixed with 100 g. of potassium hydrogen sulfate and heated to reflux in a distilling flask. The dehydration product was distilled off as formed. The temperature in the distillation flask varied between 160–265°; mostly near 265°. The vapor temperature varied between 92–123°; mostly at 120–123°. Product consisted of 12-cc. water layer and 81.5-g. hydrocarbon layer; yield 94%. The hydrocarbon layer was distilled on modified Podbielniak column.

Fraction	B. p., °C.	Grams	n^{20}_D
1	128–131	18.9	1.4392
2	131–132	39.0	1.4397
3	132–139	15.65	1.4415
4	139–149	3.45	1.4492
Bottoms		4.05	1.4592

A twenty per cent. mixture of fractions 1–4, 15.5 g., was hydrogenated with nickel–kielselguhr catalyst in a 125-cc. autoclave at 60° and 73 atmospheres hydrogen pressure.

Infrared absorption analysis of the resulting hydrogenated product indicated that it consisted of 1,1,3-trimethylcyclohexane; 1,2,4-trimethylcyclohexane was absent.

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Summary

The dehydration of 3,3,5-trimethylcyclohexanol by means of 2% aqueous magnesium chloride solution at 350° was accompanied by isomerization; the hydrocarbons obtained consisted of 20% of 1,2,4-trimethyl-x-cyclohexene.

The treatment of 1,1,3-trimethyl-x-cyclohexene with the same catalyst under the same condition yielded 1,2,4-trimethyl-x-cyclohexene.

1,1,3-Trimethylcyclohexane does not undergo isomerization when heated with aqueous magnesium chloride solution at a temperature of 400°.

1,1,3-Trimethylcyclohexane was prepared by dehydration of 3,3,5-cyclohexanol by means of activated alumina at 375°.

1,1,3-Trimethylcyclohexane underwent dehydrogenation in the presence of platinized alumina at 300°; *m*-xylene was produced with the liberation of two moles equivalent of hydrogen and one mole equivalent of methane.

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