

7. The value  $350 \pm 35$  is obtained for the average degree of polymerization of the corresponding cellulose acetate by application of the

Kraemer equation (5) to the viscosity of the acetone solution of the cellulose acetate.

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## Isomerization of Alkylcyclopentanes

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Methylcyclopentane with aluminum chloride undergoes isomerization to cyclohexane.<sup>1</sup> An indirect proof of the isomerization of the cyclopentyl to the cyclohexyl ring was given by Tarazova,<sup>2</sup> who showed that by brominating 1,2-methylethylcyclopentane with bromine, using aluminum bromide as a catalyst, tetrabromo-*p*-xylene is obtained. It has not been shown, however, whether or not it is essential for a methyl group to be attached to the cyclopentyl ring in order to have isomerization.

It has now been found that alkylated cyclopentanes undergo isomerization in the presence of aluminum chloride to yield methylated cyclohexanes. Ethylcyclopentane yielded methylcyclohexane; propyl- and isopropylcyclopentane isomerized to 1,3-dimethylcyclohexane; while *n*-butyl-, *s*-butyl- and *t*-butylcyclopentane yielded 1,3,5-trimethylcyclohexane. The isomerization took place at a temperature of 50° and the yield of isomerized product obtained exceeded 80%. The structure of the isomerized product was determined by dehydrogenating it into the corresponding aromatic hydrocarbon using, as a catalyst, platinized aluminum oxide. The aromatic hydrocarbons were identified by their bromo or nitro derivatives, which were checked by analysis and mixed melting point. Alkylated cyclopentanes do not undergo dehydrogenation under similar conditions.

It is probable that, analogous to the isomerization of alkylated cyclohexane,<sup>3</sup> the reaction proceeds via the formation of polymethylated cyclopentane which isomerized to methylated cyclohexane.

Ethyl-, *n*-propyl-, and *n*-butylcyclopentane were prepared from cyclopentanone and the corresponding alkylmagnesium bromide according to the method of Chavanne and Becker.<sup>4</sup> Iso-

propyl- and *s*-butylcyclopentane were prepared by hydrogenating dimethyl- and methylethylfulvene. The fulvenes were obtained by condensing cyclopentadiene with acetone and methyl ethyl ketone in the presence of sodium ethoxide.<sup>5</sup> An attempt was also made to prepare isopropylcyclopentane from isopropylmagnesium bromide or chloride and cyclopentanone, but the main product of the reaction was cyclopentenylcyclopentanone. A similar observation was also made by Meerwein.<sup>6</sup> The method of preparation of *t*-butylcyclopentane will be described in a separate paper.<sup>7</sup>

### Experimental Part

**Preparation.** Ethyl-, *n*-propyl- and *n*-butylcyclopentane were prepared from cyclopentanone and ethyl-, *n*-propyl-, and *n*-butylmagnesium halide, respectively, using the procedure described by Chavanne and Becker.<sup>4</sup> The carbinols which were obtained as intermediate products were dehydrated to form the corresponding alkylcyclopentenes. The dehydration was carried out by passing the carbinols over 40 g. of activated alumina with a rate of 40 cc. per hour and a temperature of 345°. The alkylcyclopentenes were hydrogenated to alkylcyclopentanes at 100° in the presence of 10% by weight of nickel catalyst and 100 atmospheres of hydrogen. The yields on dehydration and hydrogenation were almost quantitative.

**Isopropyl- and *s*-Butylcyclopentane.**—Twenty-four grams (*ca.* 1 mole) of sodium was dissolved in 300 cc. of absolute ethanol. To the solution of sodium ethoxide was added a mixture of freshly distilled cyclopentadiene (1 mole) and acetone (1 mole). (For the preparation of *s*-butylbenzene methyl ethyl ketone was used.) The temperature of the flask was kept at 40° by controlling the rate of addition of the reagents, which required one hour. The dimethylfulvene formed was steam distilled; the distillate was of an orange color. It was separated from the water layer and diluted with three volumes of isopentane. During the reaction care was taken to prevent the fulvene from coming in contact with air.

The isopentane solution of the dimethylfulvene was hydrogenated with 18 g. of nickel catalyst (nickel on kieselguhr). The hydrogenation was carried out at the beginning at room temperature and 50 atmospheres pressure.

(1) Nenitzescu and Cantunari, *Ber.*, **66B**, 1097 (1933).

(2) Tarazova, *C. A.*, 8173 (1935); *B. C. A.*, **AII**, 283 (1937).

(3) Grignard and Stratford, *Compt. rend.*, **178**, 2149; *Bull. soc. chim.*, [4] **35**, 931 (1934).

(4) Chavanne and Becker, *Bull. soc. chim. Belg.*, **36**, 591 (1927).

(5) Thiele, *Ber.*, **33**, 671 (1900).

(6) Meerwein, *Ann.*, **405**, 155 (1914).

(7) Pines and Ipatieff, abstracts of the Division of Organic Chemistry of the American Chemical Society, Baltimore, April 3-7, 1939.


TABLE I  
 PROPERTIES OF ALKYL CYCLOPENTANES

Methods: A, cyclopentanone and alkylmagnesium halides; B, cyclopentadiene and ketone; C, reference 7.

	Method	Yield, %	B. p. <sup>a</sup> (760 mm.), °C.	dT/dP (770- 730 mm.)	d <sub>20</sub> <sup>4</sup>	d <sub>40</sub> <sup>4</sup>	-dD/dt (20-40°)	n <sub>D</sub> <sup>20</sup>
Ethylcyclopentane	A	75	103.6	0.047	0.7632	0.7478	0.00077	1.4196
<i>n</i> -Propylcyclopentane	A	55	130.7	.053	.7756	.7601	.00078	1.4269
Isopropylcyclopentane	B	75	126.8	.051	.7764	.7593	.00085	1.4261
<i>n</i> -Butylcyclopentane	A	45	156.8	.050	.7832	.7687	.00072	1.4317
<i>s</i> -Butylcyclopentane	B	45	154.6	.050	.7941	.7787	.00075	1.4361
<i>t</i> -Butylcyclopentane	C	..	145.2	.052	.7911	.7753	.00079	1.4342

<sup>a</sup> Boiling point was determined by Cottrell method: Cottrell, *THIS JOURNAL*, **41**, 721 (1919); Bruun and Hicks-Bruun, *Bur. Standards J. Research*, **6**, 871 (1931).

TABLE II

Reagents used		AlCl <sub>3</sub> , g.	Hydro- carbon recov., g.	n <sub>D</sub> <sup>20</sup>		% of prod. undergoing dehydrog.	Boiling range of dehydrogenated product, °C.	Identified as
 R =	G.			Before isomerization	After			
Ethyl-	16.0	3.38	14.4	1.4196	1.4229	80	101-108	Methylcyclohexane <sup>a</sup>
<i>n</i> -Propyl-	20.25	4.05	19.3	1.4270	1.4248	90	119-138	1,3-Dimethyl- cyclohexane <sup>b</sup>
Isopropyl-	20.46	3.90	19.7	1.4261	1.4245	80	125-136	
<i>n</i> -Butyl-	21.90	4.00	21.1	1.4317	1.4293	78	142-164	1,3,5-Trimethyl- cyclohexane <sup>c</sup>
<i>s</i> -Butyl-	23.70	4.04	23.2	1.4360	1.4291	75	142-165	
<i>t</i> -Butyl-	12.91	3.80	12.45	1.4342	1.4282	60	142-163	

Derivative prepared: <sup>a</sup> Dinitrotoluene. <sup>b</sup> Trinitro-*m*-xylene. <sup>c</sup> Tribromomesitylene and trinitromesitylene.

The pressure and temperature were then slowly raised to 100 atm. and 125°. The slow and progressive hydrogenation was necessary in order to avoid polymerization of the fulvenes. This method of hydrogenation is more effective than the one described by Kazansky and co-workers.<sup>8</sup>

*t*-Butylcyclopentane.—The method of preparation is described in a separate paper.<sup>7</sup>

**Isomerization of Alkylcyclopentane.**—The alkyl cyclopentane (about 0.2 mole) and aluminum chloride (about 0.03 mole) and 2 drops of water were sealed in a glass tube of 40-cc. capacity. The tube was kept at 50° with occasional shaking for eighteen hours. The product, which was then separated from the catalyst, was stable toward nitrating mixture, indicating the absence of olefinic or aromatic hydrocarbons. The aluminum chloride seemed to remain unchanged. The hydrocarbons were washed with water, dried, distilled, and converted to aromatic hydrocarbons by dehydrogenation.

The results obtained are given in Table II.

**Analytical Procedure. Dehydrogenation.**—The hydrocarbons after isomerization were passed at a rate of 7 cc. per hour over 35 g. of aluminum oxide containing 7% of platinum. This catalyst was obtained by impregnating alumina with the required amount of chloroplatinic acid solution, drying and reducing in a slow stream of hydrogen at 150 to 240°. The dehydrogenation was carried out at 240°; the gas evolved was collected in a gas holder, was measured, analyzed and shown to consist of hydrogen.

The liquid product obtained by this reaction was fractionally distilled.

**Bromination.**—To 1 cc. of the dehydrogenated product was added slowly at room temperature 5 cc. of bromine containing 1% of iodine. At the beginning a copious evolution of hydrogen bromide took place. The product was allowed to stand overnight, the excess of bromine was distilled off and the brominated product was crystallized from ethanol.

**Nitration.**—One cc. of the dehydrogenated product was treated with 10 cc. of nitrating mixture consisting of 1 part of 72% nitric acid and 3 parts of 96% sulfuric acid. The product was heated to boiling, cooled and poured over ice. The solid nitro compound was crystallized from ethanol.

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### Summary

Alkylcyclopentanes undergo isomerization with aluminum chloride at 50°. Ethylcyclopentane yielded methylcyclohexane; propyl- and isopropylcyclopentane gave 1,3-dimethylcyclohexane, while *n*-butyl-, *s*-butyl- and *t*-butylcyclopentane yielded 1,3,5-trimethylcyclohexane. The yield of isomerized product in most cases exceeded 80%.

(8) Kazansky, Plate and Gnatenko, *Ber.*, **69**, 954 (1936).