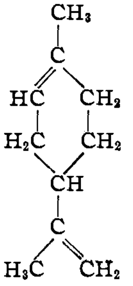
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF ILLINOIS INSTITUTE OF TECHNOLOGY]

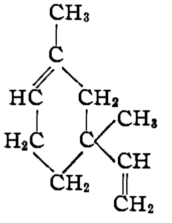
Polymerization of Isoprene

BY V. I. KOMAREWSKY AND C. C. SHIH

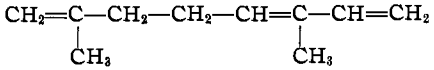
Since the discovery of isoprene in the oily distillate of caoutchouc and guttapercha,[1] a large amount of work was carried out on the macropolymerization of this hydrocarbon. Some investigators who studied this subject obtained and identified some low polymers. The production of dipentene[2] (I), diprene[3,4] (II) and beta-myrcene[5,6,7] (III) has been reported.



(I)



(II)



$$CH_2{=}\underset{CH_3}{C}{-}CH_2{-}CH_2{-}CH{=}\underset{CH_3}{C}{-}CH{=}CH_2$$

(III)

Due to the recent progress of acid polymerization of olefins[8] and the development of the refined analytical techniques for hydrocarbon studies, it was decided to carry out the polymerization of isoprene in the presence of sulfuric and phosphoric acids as catalysts; the products of the reactions were investigated by the combined methods of catalysis, refractometry, infrared spectrophotometry, and chromatographic adsorption.

Experimental Part

Apparatus and Procedure.—The reactions were carried out in a three-necked, 1/2 liter flask provided with a graduated dropping funnel, a mercury sealed stirrer and water and dry ice condensers. Experiments were conducted by using different acids, and varying the acid concentration, temperature, stirring period, and acid to isoprene ratio. After the products had been separated from the acid, the polymer layer from each experiment was washed with 10% solution of aqueous sodium hydroxide and then dried with sodium sulfate.

Isoprene.—The isoprene used was pure grade from Phillips Petroleum Products Co. It was distilled in a 100-plate Podbielniak column, b. p. 34°, $n^{20}\mathrm{D}$ 1.4216.

Identification of Products.—A preliminary distillation in a Vigreux column separated the unreacted isoprene from the polymers. The polymers were distilled in a 100-plate Podbielniak column and a dimer fractions with b. p. of 170–174° and $n^{20}\mathrm{D}$ of 1.4661 was obtained, which could not be further fractionated.

TABLE I

EXPERIMENTAL RESULTS

Expt.	Acid concn.	Temp., °C.	% by weight Unreac. isoprene	Dimer	Trimer	High poly.
			Sulfuric Acid[a]			
1	66	0	0	0	0	All
3	48	0	86.9	9.0	4.1	0
5	48	20	55.5	31.0	13.5	0
24	48	30	7.3	64.0	28.2	0.5
26	30	20	96.1	2.9	1.0	0
			Phosphoric Acid[b]			
12	85	20	0	0	0	All
13	52	20	97.0	2.1	0.9	0
15	70	20	69.0	13.4	17.6	0
28	70	30	62.2	14.4	15.8	7.6
29	70	0	98.0	0.7	1.3	0
33	70	20	51.0	22.7	26.3	0

[a] All experiments had stirring periods and acid to isoprene ratios of 40 minutes and 3 to 1, respectively. [b] All experiments had a stirring period of sixty minutes, except experiment 33 which had a stirring period of 180 minutes. The acid to isoprene ratios were all 3 to 1.

The dimer fraction was then catalytically hydrogenated with platinum–alumina catalyst at 180°. The hydrogenated product was distilled in the Podbielniak column and gave two definite fractions with boiling points of 158° and 172° and $n^{20}\mathrm{D}$ of 1.4149 and 1.4520, respectively. The dimers (50 g.) obtained using phosphoric acid as catalyst gave after hydrogenation 34.5 g. of 158° boiling fraction and 14.7 of 172° boiling fraction. The dimers (50 g.) obtained using sulfuric acid as catalyst gave after hydrogenation 16 g. of 158° boiling fraction and 33 g. of 172° boiling fraction.

The 158° boiling fraction corresponds to 2,6- or 2,7-dimethyloctane. The infrared adsorption spectrum (see Fig. 1) shows the preference for a 2,6-dimethyloctane configuration due to the presence of a doublet at 8.5 micron and the presence of bands at 13 and 13.6 microns.[9] Owing to the lack of the literature data for the derivatives of 2,6-dimethyloctatrienes no experimental attempts were made to determine the positions of the double bonds. By applying Whitmore's mechanism and the 1,4 addition scheme of polymerization, only 2,6-dimethyl-1,4,7-octatriene was found to be possible.

Twenty grams of the 172° boiling point fraction from the hydrogenated product was dehydrogenated at 300° over platinum–alumina catalyst and a product (19.5 g.) was obtained with a boiling point of 174° and $n^{20}d$ of 1.4857, which corresponds to that of *p*-cymene.

For confirmation, the dehydrogenated aromatic hydrocarbon was further oxidized by potassium permanganate solution to terephthalic acid, which was identified through its characteristic sublimation at 305°.

Due to the certainty of the presence of aliphatic hydrocarbons in the original dimer fraction, the latter was subjected to chromatographic adsorption (Silica gel, mesh size 200, by Davidson Chemical Co.). The aliphatic fraction separated first, as was shown by the refractive index. Bromination was carried out with the so enriched cyclic portion. The tetrabromide derivate thus obtained had the

---

(1) A. Bouchardat, *J. Pharm.*, **23** (1837).

(2) G. Bouchardat, *Bull. Soc. Chim.*, **24**, 111 (1875).

(3) C. Harries, *Ber.*, **35**, 3256 (1902).

(4) S. V. Lebedev, *J. Russ. Phys.-Chem. Soc.*, **45**, 1249 (1913).

(5) I. Ostromislensky, *ibid.*, **47**, 1911 (1915).

(6) T. Wagner-Jauregg, *Ann.*, **488**, 176 (1932).

(7) T. Wagner-Jauregg and T. Lennartz, *Ber.*, **76**, 1161 (1943).

(8) Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," p. 571.

(9) Private communication of Dr. W. S. Gallaway.

melting point of 104°, which identified this product as dipentene.

The trimer fraction from the preliminary distillation with the Vigreux column had a b. p. of 235–245° and $n^{20}D$ of 1.4940 and was not further identified.

Discussion of Results

From the results presented in Table I, it can be seen that both sulfuric and phosphoric acids may be used as catalysts for the polymerization of isoprene to low polymers. Up to 92% of isoprene was polymerized by using sulfuric acid and up to 49% was polymerized by using phosphoric acid. By varying the concentration of the acid and the temperature of the reaction different ratios of the different polymers could be obtained. The increase of acid concentration and temperature promotes the formation of trimers and high polymers.

The best conditions for the formation of dimers with the acids investigated without simultaneous production of high polymers are as follows: for sulfuric acid, 48% acid, 20°, forty-minute stirring period, 3 to 1 acid to isoprene ratio; for phosphoric acid, 70% acid, 20°, sixty-minute stirring period, and 3 to 1 acid to isoprene ratio (experiments 5 and 15).

In the presence of lower acid concentrations, a decline in polymerization was noted (experiments 26 and 13). The dimers produced were composed of aliphatic and cyclic compounds. Phosphoric acid favored the formation of aliphatic dimer (experiment 15 gave a ratio of 7 to 3) as compared with the mixture obtained from sulfuric acid reactions (experiment 5 gave a ratio of 2 to 3).

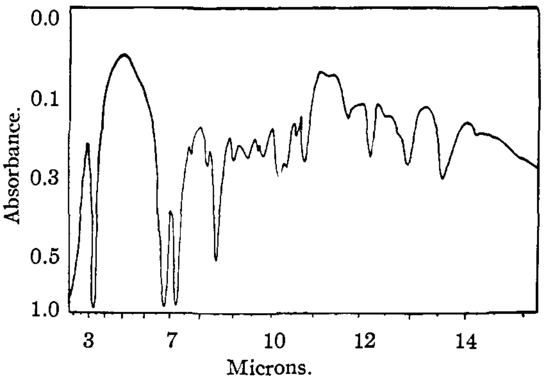


Fig. 1.—Infrared absorption spectra of 2,6-dimethyloctane.

Summary

1. Isoprene was polymerized to low polymers by using either sulfuric or phosphoric acid as catalyst without the formation of high polymers.

2. The low polymers consisted of dimers and trimers. The dimers were identified as the mixture of dipentene and an aliphatic dimer, which when hydrogenated gave 2,6-dimethyloctane.

RECEIVED MAY 31, 1949

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

Hydrogen Transfer. IV.[1] Reaction of *p*-Isobutyltoluene and of *p*-*s*-Butyltoluene with Methylcyclohexene

BY HERMAN PINES, D. R. STREHLAU[2] AND V. N. IPATIEFF

It has been shown previously[3] that a hydrogen transfer occurred when *p*-cymene was contacted with methylcyclohexene in the presence of either sulfuric acid or hydrogen fluoride. The main products of this reaction were methylcyclohexane and 1,3,3,6-tetramethyl-1-*p*-tolylindan; the methylcyclohexene acted as a hydrogen acceptor while *p*-cymene acted as a hydrogen donor. A hydrogen transfer reaction also occurred when *p*-ethyltoluene or *p*-propyltoluene was contacted with methylcyclohexene in the presence of the above-mentioned catalysts; the aromatic hydrocarbons were converted, respectively, to 1-*p*-tolyl-1-(2-methyl-5-ethylphenyl)-ethane and 1-*p*-tolyl-1-(2-methyl-5-propylphenyl)-propane.

Continuing this study, an investigation was made of the type of products which are formed when a branched chain alkyltoluene such as *p*-isobutyltoluene is treated with 4-methylcyclohexene in the presence of hydrogen fluoride or sulfuric acid. It was found that hydrogen transfer was the main reaction. The methylcyclohexene was converted to the extent of 33 mole per cent. to methylcyclohexane, 10 mole per cent. to dimethyldicyclohexyl and only 28 mole per cent. reacted with *p*-isobutyltoluene to form methylcyclohexylisobutyltoluene. Of the reacted *p*-isobutyltoluene, 28% was cycloalkylated by 4-methylcyclohexene and 60% underwent a hydrogen transfer reaction to form 1-*p*-tolyl-1-(2-methyl-5-isobutylphenyl)-2-methylpropane, compound I.

The cycloalkylated product corresponded to 4-isobutyl-2-(1-methylcyclohexyl)-toluene. This conclusion was based on the observations that during alkylation or cycloalkylation of *p*-cymene the carbon atom ortho to the methyl group was substituted[4] and that the reaction between benzene

---

(1) For paper III of this series see H. Pines, D. R. Strehlau and V. N. Ipatieff, THIS JOURNAL, **71**, 3534 (1949).

(2) Universal Oil Products Company Predoctorate Fellow (1945–1948).

(3) V. N. Ipatieff, H. Pines and R. C. Olberg, THIS JOURNAL, **70**, 2123 (1948).

(4) H. Pines, A. Weizmann and V. N. Ipatieff, *ibid.*, **70**, 3859 (1948).