[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Reaction of Methylcyclopentane with Propene in the Presence of Aluminum Bromide–Hydrogen Bromide

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It has been reported previously[1] that methylcyclopentane reacts with olefinic hydrocarbons in the presence of either sulfuric acid or hydrogen fluoride to form alkylcyclohexanes and products resulting from a hydrogen transfer reaction. This study has now been extended in order to investigate the interaction of propene with methylcyclopentane in the presence of aluminum bromide–hydrogen bromide catalyst. The main purpose of this investigation was to determine whether the alkylation of methylcyclopentane can proceed without isomerization, which usually results in the expansion of the alkyl pentamethylene ring into an alkyl hexamethylene ring.

Since aluminum halide–hydrogen halide catalysts cause the isomerization of alkylcyclopentanes to alkylcyclohexanes[2] at room temperature, it was decided to carry out the alkylation reaction at −42°; at this low temperature the rate of isomerization of alkylcyclopentanes is relatively slow.

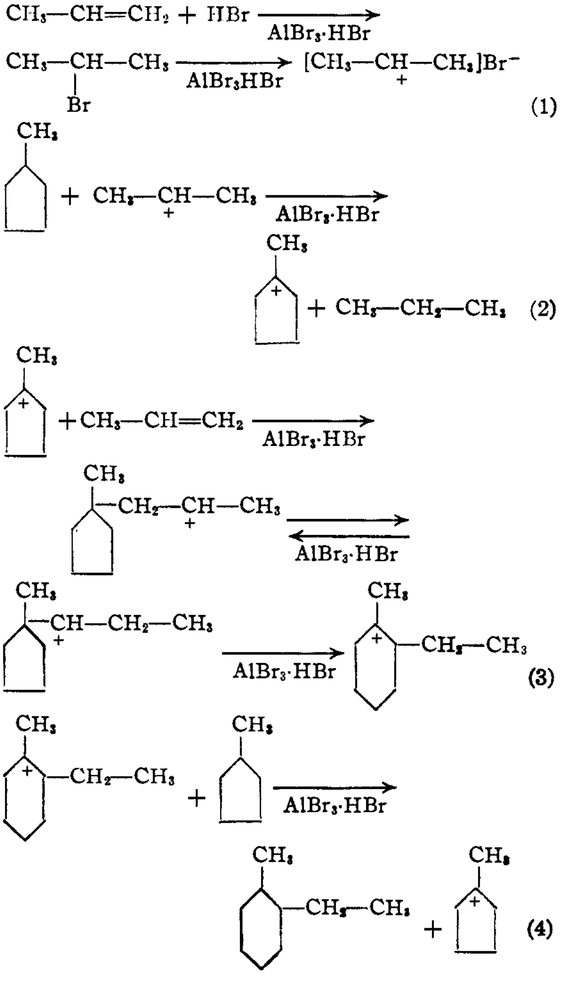
The alkylation of methylcyclopentane was carried out by passing propene and a small amount of hydrogen bromide into an agitated suspension of aluminum bromide in methylcyclopentane. The reaction product was then cooled to −76° and the liquid poured into water. The supercooling of the liquid before hydrolysis was necessary in order to avoid isomerization, which could occur if the decomposition were carried out at a higher temperature. The product obtained from this reaction, which consisted of saturated hydrocarbons, was distilled and analyzed. About 50% of the methylcyclopentane used for the reaction was recovered; the total hydrocarbons recovered from the reaction contained less than three per cent. of cyclohexane.

The higher boiling product consisted of a mixture of hydrocarbons, the major part of which distilled at 153–160°; and corresponded to a product of interaction of one mole of methylcyclopentane with propene. This hydrocarbon, which amounted to about 25 mole per cent. based on the propene used in the reaction, when passed over platinized alumina at 260°,[3] underwent almost quantitative dehydrogenation to aromatic hydrocarbons. The ease with which the dehydrogenation occurred indicates that the C_9H_{18} hydrocarbons consisted of alkylcyclohexanes. The gases obtained from the dehydrogenation reaction consisted of hydrogen only, which shows that geminal carbon atoms were not present in the cyclohexane ring.[4]

The aromatic hydrocarbons which were obtained from the dehydrogenation yielded, on oxidation with dilute nitric acid, about 70% of *o*-toluic acid. The presence of this acid indicates that the original product contained 1-methyl-2-ethylcyclohexane, which on dehydrogenation yielded *o*-ethyltoluene, and the latter oxidized to *o*-toluic acid.

The fractions boiling above 160° were also composed of alkylcyclohexanes since these compounds also underwent dehydrogenation to aromatic hydrocarbons: the structures of these compounds, however, were not identified because of their complexity.

The mechanism by which methylethylcyclohexane was formed from the interaction of methylcyclohexane and propene is the same as described previously.[1] The following are the probable steps that occur in this reaction



$$CH_3—CH=CH_2 + HBr \xrightarrow[AlBr_3\cdot HBr]{} \underset{\displaystyle Br}{CH_3—CH—CH_3} \xrightarrow[AlBr_3HBr]{} [CH_3—\overset{}{\underset{+}{C}}H—CH_3]Br^- \quad (1)$$

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[1] H. Pines and V. N. Ipatieff, THIS JOURNAL, **67**, 1631 (1945).

[2] H. Pines and V. N. Ipatieff, *ibid.*, **61**, 1076 (1939).

[3] V. N. Ipatieff and H. Pines, *ibid.*, **58**, 1056 (1936).

[4] V. N. Ipatieff, H. Pines and R. C. Olberg, *ibid.*, **68**, 1709 (1946).

The above indicated chain mechanism is similar to the one proposed by Schmerling[5] for the alkylation of isoparaffins. The exchange reaction indicated in equation II is similar to the one described by Bartlett, Condon and Schneider.[6]

Experimental

The apparatus consisted of a reaction flask provided with a Dry Ice cooled reflux condenser, mercury-sealed stirrer and inlet tubes for aluminum bromide and for the gaseous reagents. The outlet tube was connected in series to ice and Dry Ice traps and the latter was connected to a gas holder. The reaction flask was surrounded with boiling propane in order to maintain the temperature constant at −42°. Propene, which was stored in an aluminum bomb, was dried over anhydrone; hydrogen bromide was dried by passing it over aluminum bromide.

The flask and all tubings were thoroughly dried by passing dry nitrogen through them for several hours. Methylcyclopentane was introduced into the flask while dry nitrogen was passing through. An ampoule containing aluminum bromide was inserted in the apparatus and was broken therein while nitrogen was passing through. The flow of nitrogen was then discontinued and propene was passed into the flask over a period of two hours. Simultaneously with the propene, hydrogen bromide was passed into the reaction flask. The liquid reaction product, while still at −42°, was transferred into a trap maintained at −76°. The contents of the trap were then poured into 500 ml. of water contained in a three-neck flask and agitated by means of a mercury-sealed stirrer. The flask was connected to a series of traps in order to collect any escaping gases, if such were present. No evolution of heat was noticed when the product was added into water.

The hydrocarbon layer was separated, washed with alkali, water, dried over calcium chloride and distilled on a column of about fifteen-plate efficiency and at a reflux ratio of 20:1. The various narrow boiling fractions were redistilled and analyzed.

EXPERIMENTAL CONDITIONS AND RESULTS

Reagents employed, *M:*

Methylcyclopentane	63 g.	0.75
Propene	23 g.	.55
Aluminum bromide	20 g.	.075
Hydrogen bromide per min.	10–20 cc.	

Experimental conditions:

Temperature	−42°
Duration of reaction	2 hours

Product recovered, g.:

Gases	None
Hydrocarbon layer, g.	78.9
Organic material obtained from the hydrolysis of the catalyst layer, g.	1.1

Cut 1.—According to the index of refraction, Cut 1 is composed of 95% of methylcyclopentane and 5% of cyclohexane.

It underwent only slight dehydrogenation when passed over platinized alumina at 270°. The yield of methylcyclopentane–cyclohexane fraction based on total material recovered was 62%.

INVESTIGATION OF THE PRODUCT

Sixty-three grams of the hydrocarbon layer, after being washed and dried, was distilled. The following fractions were separated:

	B. p.	G.	$n^{20}D$
(1)	70–72°	31	1.4109
(2)	72–153	1.8	1.4273
(3)	153–157	15.0	1.4391
(4)	157–170	2.4	1.4405
(5)	170–180	1.5	1.4419
(6)	180–200	1.9	1.4453
(7)	200–210	6.7	1.4484
(8)	>210	6.2	1.4662

Cut 3.—According to physical constants, Cut 3 corresponds to C_9H_{18}. The yield of this fraction based on methylcyclopentane reacted was 53 mole per cent. or 27.4 mole per cent. based on propene reacted.

Thirteen grams of the hydrocarbon was passed, at a rate of 7 cc. per hour and a temperature of 265°, over 25 g. of 10–14 mesh size activated alumina containing 7% of platinum. Seven liters of gas was formed containing 89.6% of hydrogen. Ninety-one per cent. of liquid hydrocarbons was recovered with $n^{20}D$ 1.4946. Based on the hydrogen produced, virtually all of the material submitted to dehydrogenation was converted to aromatic hydrocarbons.

The dehydrogenated product distilled as follows: (1) b. p. 149–158°, 14%, $n^{20}D$ 1.4810; (2) 158–161°, 38%, 1.4922; (3) 161°, 37%, 1.5008; (4) 161°, 11%, 1.4998.

One half gram of Cut 3, obtained from the dehydrogenation, was refluxed for twelve hours with an acid consisting of 15 ml. of concentrated nitric acid and 25 ml. of water. About 0.35 g. of a crystalline product was obtained which was filtered and crystallized from hexane.

The crystalline material in the form of needles melted at 103°. It did not show depression in melting point when mixed with a known sample of *o*-toluic acid. Sharp depression in melting point, over 25°, was noticed when the sample was mixed with *m*-toluic acid, melting at 111°.

Anal. Calcd. for $C_8H_8O_2$: C, 70.59; H, 5.88. Found: C, 69.67; H, 5.90.

Cut 7.—According to physical constants, Cut 7 corresponds to $C_{12}H_{24}$.

Anal. Calcd. for $C_{12}H_{24}$: C, 85.63; H, 14.37. Found: C, 85.59; H, 14.31.

Four grams of this product was dehydrogenated by passing it over platinized alumina at 200°. About 1.5 liters of gas was liberated, consisting of 98% hydrogen. The dehydrogenated product had an $n^{20}D$ 1.4921. The results obtained indicate that the product was composed of about 90% of aromatic hydrocarbons.

Summary

The reaction of methylcyclopentane with propene in the presence of aluminum bromide–hydrogen bromide catalyst has been investigated. The reaction was carried out at −42°.

The product obtained from the reaction consisted of alkylated cyclohexanes composed mainly of 1-methyl-2-ethylcyclohexane and of alkylcyclohexanes of the formula $C_{12}H_{24}$.

Under the condition of the reaction, methylcyclopentane underwent but slight isomerization. A mechanism of the alkylation is suggested.

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[5] L. Schmerling, THIS JOURNAL, 66, 1422 (1944).

[6] P. D. Bartlett, F. E. Condon and A. Schneider, *ibid.*, 66, 1531 (1944).