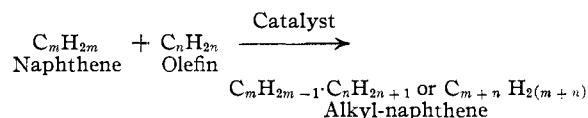


[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

**Reaction of Naphthenic Hydrocarbons with Olefins**

BY V. N. IPATIEFF, V. I. KOMAREWSKY AND ARISTID V. GROSSE

In a previous paper<sup>1</sup> the catalytic reaction of alkylation between paraffins and olefins, consisting in the addition of an olefin to a paraffin with the formation of higher molecular weight paraffins, was shown. In the present paper the reaction between naphthenes and olefins in the presence of aluminum chloride or boron fluoride will be described. Similarly to the reaction of paraffins the alkylation of naphthenes proceeds according to the general equation



The alkylation takes place at 50–75° under atmospheric or superatmospheric pressure (5–15 atmospheres).

Cyclohexane, methylcyclohexane and methylisopropylcyclohexane are easily alkylated by ethylene in the presence of aluminum chloride. Boron fluoride also catalyzes the alkylation of methylcyclopentane and methylcyclohexane with ethylene.

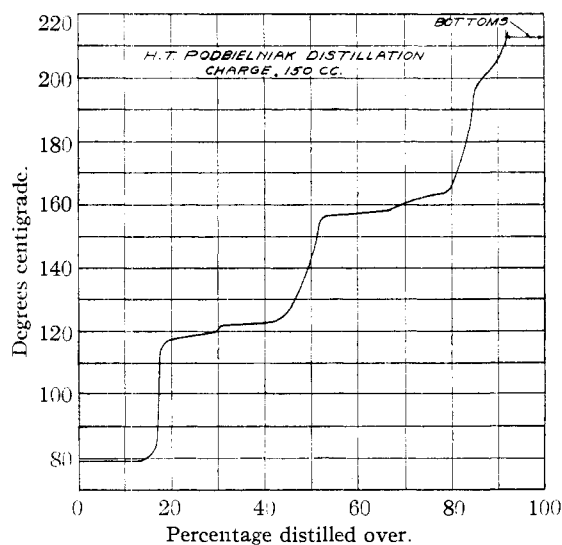


Fig. 1.

**Experimental Part****(A) Alkylation with Aluminum Chloride.**—

The alkylation product contains practically only

(1) V. N. Ipatieff and A. V. Grosse, *THIS JOURNAL*, **57**, 1616 (1935).

naphthenes in accordance with the equation given above.

(1) **Alkylation of Cyclohexane.**—A detailed description of a typical experiment at atmospheric pressure follows. A three-necked Pyrex flask (of 1-liter capacity), supplied with an electrically driven stirrer in the middle neck, contained 295 g. of cyclohexane. One neck served for introducing the catalyst, the other neck was supplied with a reflux condenser connected to a gas-holder, where all unreacted ethylene and the reaction gases were collected. Only glass ground joints were used. Ethylene and hydrogen chloride were introduced through a special tube leading to the bottom of the flask.

The whole apparatus was heated in a water-bath to 50–60°. The cyclohexane was then saturated under vigorous stirring with ethylene and hydrogen chloride. Thirty grams of aluminum chloride was added and the absorption of ethylene began. The experiment was run for thirteen hours, during which time the ethylene was passed through the reaction mixture at the rate of 4–5 liters per hour. Hydrogen chloride was introduced for a one half minute interval each hour. Additional aluminum chloride was introduced twice (7.5 g., 7.5 g.) during the experiment, making a total of 45.0 g.; 10.5 liters of the gas was collected in the gasholder during the whole run.

The reaction product consisted of (a) a clear liquid layer and (b) a pasty catalyst mass.

The balance of products before and after the reaction is given below.

BALANCE OF PRODUCTS			
Before reaction, g.		After reaction, g.	
Cyclohexane	295	Liquid layer	326
AlCl <sub>3</sub>	45	Pasty mass	67
Ethylene, absorbed	61	Ethane (in exit gas)	4.5
Hydrogen chloride	2–3	Total	398
	404	Losses	≈6

(a) The liquid layer was separated, washed with water and 10% sodium hydroxide, dried with calcium chloride and separated into two fractions by means of a Vigreux column.

	Boiling range, °C.	Weight, g.
Fraction 1	70–81–90	155
Fraction 2	90 and higher	162
		317

Fraction 1 represents unreacted cyclohexane, containing small quantities of methylcyclopentane, due to isomerization.

Fraction 2 contained the products of alkylation and was fractionated by means of a high temperature Podbielniak column. Data pertaining to the fractions obtained are given in Table I, whereas the distillation curve is given on Fig. 1.

All fractions (except bottoms, see page 1723) consist of practically pure naphthenes, as the organic combustion analyses prove.

TABLE I  
Charge 150 cc.

Fraction	Boiling range, °C. at 760 mm.	Vol., cc.	Weight, g.	Color	$n_D^{20}$	$d_4^{15}$	Chemical analysis			Molec. wt. in benzene	Nitrating test	Remarks
							C, %	H, %	Total			
1	79-80 → 100	26.2	20.0	W. w. <sup>a</sup>	1.4250						Abs. stable	Cyclohexane, solidifies at 0°C.
2	100 → 117-125	39.8	30.5	W. w.	1.4241	0.7725	85.59	14.33	99.92	113	Abs. stable	Dimethylcyclohexane
3	125-135	6.7	5.0	W. w.	1.4265						Abs. stable	
4	135-155	5.0	4.0	W. w.	1.4310		85.51	14.36	99.87	139	Abs. stable	
5	155-165	41.2	32.0	W. w.	1.4355	0.7905	85.51	14.38	99.89	143	Abs. stable	Tetramethylcyclohexane
6	165-185	6.7	5.5	W. w.	1.4385						Abs. stable	
7	185-205	8.9	7.2	W. w.	1.4442	0.8116				163	Abs. stable	
8	205-215	4.2	3.5	W. w.	1.4500		85.6	14.3	99.9	165	Abs. stable	
Botts	> 215	8.0	7.3	Yel.	1.4641					188	Stable	
Total		147	116									
Loss		3										

<sup>a</sup> W. w. = Water white.

Fractions 2 and 5, corresponding to the plateaus of the diagram, contain the main products of alkylation. They do not contain monoethyl- and diethylcyclohexanes, but their products of isomerization, namely, dimethyl- and tetramethylcyclohexenes. This is to be expected since V. Grignard and Stratford<sup>2</sup> have shown that the ethyl derivatives are isomerized into the methyl compounds by aluminum chloride.

The identification of these hydrocarbons was accomplished as follows.

Both fractions were dehydrogenated at 310-320° over Ni-Al<sub>2</sub>O<sub>3</sub> catalyst<sup>3</sup> to aromatic hydrocarbons. The aromatic content was determined with fuming 15% SO<sub>3</sub>-sulfuric acid. The aromatic hydrocarbon was identified by converting into a bromine derivative by the method of Klages and Allendorff.<sup>4</sup>

Fraction 2 was passed twice over the catalyst. The catalysate had  $n_D^{20}$  1.4811 and contained 90% aromatics. The tetrabromide melted at 243° and contained 75.0% Br (Parr bomb), whereas C<sub>6</sub>(CH<sub>3</sub>)<sub>2</sub>Br<sub>4</sub> contains 75.8% Br. The aromatic hydrocarbon was also oxidized by permanganate solution to isophthalic acid, m. p. 347°. These data prove that *m*-dimethylcyclohexane is present.

Fraction 5 passed twice, gave a catalysate with  $n_D^{20}$  1.4565 and contained 50% aromatics. The dibromide obtained melted at 200° (not sharp) and contained 55.4% Br (Parr bomb); calcd. for C<sub>6</sub>(CH<sub>3</sub>)<sub>4</sub>Br<sub>2</sub>, 54.7% Br. These data show that tetramethylcyclohexanes are present.

The quantity of these products in our experiment equaled 14 and 15% of the initial cyclohexane. These

figures are of course only relative and depend on such factors as (1) ratio of ethylene absorbed to initial cyclohexane, (2) quantity of catalyst, (3) time, and (4) temperature of the reaction.

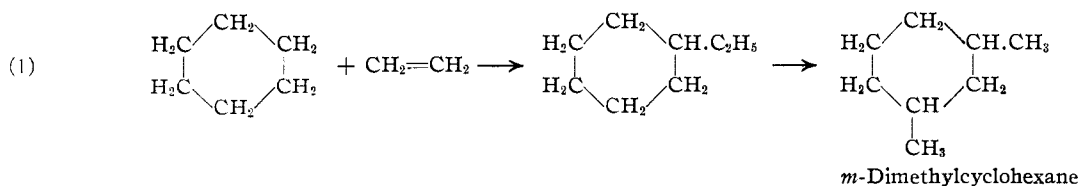
**Bottoms.** The pasty catalyst mass was decomposed with ice water and yielded 21.0 g. of a hydrocarbon oil. This was washed, dried, and distilled as follows.

	°C.	Grams
Fraction 1	80-90	1
Fraction 2	90-200	3
Residue	Above 200	17

The residue solidified on cooling and from it 12.7 g. of pure white crystals of a hydrocarbon (C, 87.60; H, 12.31; mol. wt., 245) melting at 127°, was isolated and identified as *hexaethylbenzene*.

The presence of hexaethylbenzene is very interesting and indicates the intermediate formation of hexaethylcyclohexane. Intermolecular dehydrogenation readily takes place in the presence of aluminum chloride;<sup>5,6</sup> the hydrogen of the cyclohexane was evidently taken up by ethylene, since about 4.5 g. of ethane was found in the exit gases (besides ethylene). Aromatic compounds are known to form addition compounds with aluminum halides<sup>7</sup> and a colorless crystalline Gustavson compound of the formula C<sub>6</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>6</sub>.2AlBr<sub>3</sub> was prepared by us synthetically from its components; this accounts for the absence of aromatics in the upper layer.

**Discussion of Cyclohexane Alkylation.**—The main reactions taking place in the alkylation may be represented by the equations



(2) V. Grignard, *Bull. soc. chim.*, [4] **35**, 931 (1924); Stratford, *Ann. Office Nat. Combustible Liquids*, **4**, 83, 315 (1929).

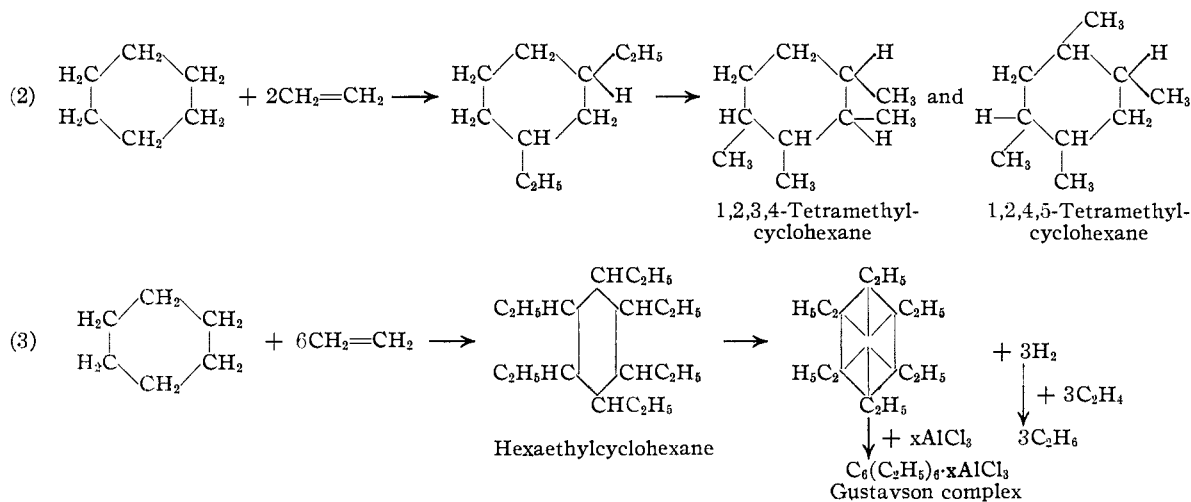
(3) Zelinsky and Komarevsky, *Ber.*, **57**, 667 (1924).

(4) Klages and Allendorff, *ibid.*, **31**, 1005 (1898).

(5) Friedel and Crafts, *Bull. soc. chim.*, [2] **39**, 306 (1883).

(6) Ipatieff and Komarevsky, *This Journal*, **56**, 1926 (1934).

(7) Gustavson, *J. prakt. Chem.*, **68**, 209 (1903); [2] **34**, 161 (1886).



Of course, intermediate compounds and mixed ethylmethyl derivatives can be present; it is also possible that some isomerization of cyclohexane to cyclopentane derivatives takes place.

Here again the analytical data and chemical tests prove that the alkylated product consists of naphthenes.

(B) Alkylation with Boron Fluoride.—Boron fluoride seems to be a more selective catalyst than aluminum chloride in the sense that it does not react with all naphthenes.

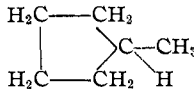
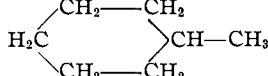
Cyclohexane does not react with ethylene in its presence, showing the same behavior as normal paraffins. Naphthenes containing a tertiary carbon atom, like methylcyclopentane and methylcyclohexane, are readily alkylated at 20–30° and ethylene pressures of 15 to 5 atmospheres. The results of two preliminary experiments are given in Table III.

The investigation of the alkylated product shows the presence of alkylnaphthenes. However, simultaneously with the alkylation some polymerization of ethylene and probably also some splitting of the naphthene ring, leading to paraffins, seems to take place.

TABLE II

Naphthene	$C_6H_{11}\cdot CH_3$	$CH_3\cdot C_6H_{10}\cdot C_3H_7-i$
Amount taken, g.	300.0	300.0
Reaction time, hours	10	2.5
Reaction temp., °C.	70	80
Ethylene absorbed, g.	51.0	18.0
Alkyl. prod., g., boiling above, °C.	254.0	50.0
Nitrating mixture test	110	175
	Completely stable	
Analyses, %	85.6	85.77
	14.3	14.35

TABLE III

Naphthene	Amount taken, g.	$BF_3$ , g.	$H_2O$ , g.	Ni powder, g.	Time of reaction, hrs.	Temp. nature of reaction, °C.	Ethylene absorbed, g.	Initial naphthene reacted, %
	60	15	2.0	5.0	20	20–30	50	33
	80	15	2.0	5.0	20	20–30	60	28

(2) Alkylation of Methylcyclohexane and Methyl-*i*-propylcyclohexane.—The alkylation of these naphthenes was accomplished similarly to cyclohexane. Up to the present only a preliminary study was made. The results are given in Table II.

### Summary

A new catalytic reaction consisting in the addition of olefins to naphthenes has been described.

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