(4.6 g.), respectively. It melted at 286–289° (recorded[14] 285°) and had a neutralization equivalent of 87 (calcd. 86). Oxidation with permanganate yielded trimesic acid, the methyl ester of which melted at 139–142° (recorded[15] 145–146°). The corresponding yields of dicarboxylic acid from *t*-butylbenzene under identical conditions were 2.4 and 11.8%.

5-*sec*-Butylisophthalic Acid.—*sec*-Butylbenzene (0.15 mole) was metalated at 60° in the presence of 0.20 mole of sodium L-menthoxide. Yields of 7.0% and 4.3% of the dicarboxylic acid were obtained, with a neutralization equivalent of 112.1 (calcd. 111.1) after crystallization from aqueous ethanol and ligroin–isopropyl alcohol. It melted at 251.5–256°. *Anal.* Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.31. Found: C, 65.55; H, 6.59.

Oxidation of a portion of the dicarboxylic acid with permanganate yielded crystals of trimesic acid, with a neutralization equivalent of 74.7 (calcd. 70.0). The trimethyl ester melted at 140–143.5° (recorded[15] 145–146°), and showed no depression of the melting point when mixed with trimethyl trimesate obtained from the metalation of isopropylbenzene. Mixed melting points with dimethyl terephthalate, which has a similar melting point, showed strong depression.

CAMBRIDGE, MASS.

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[14] O. Doebner, *ibid.*, **23**, 2377 (1890); **24**, 1746 (1891).

[15] W. Emerson, T. Shafer and R. Heimsch, *J. Org. Chem.*, **16**, 1839 (1951).

[CONTRIBUTION FROM THE BASIC RESEARCH DIVISION, SUN OIL COMPANY]

The Reactions and Relative Reactivities of Naphthenes and Isoparaffins in Low-temperature Reactions with Carbonium Ions[1]

BY A. SCHNEIDER

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A series of hydrogen fluoride-catalyzed alkylations of methylcyclopentane dissolved in isobutane, isopentane, 2-methylpentane and in methylcyclohexane has been performed employing propylene and isobutylene. Methylcyclopentane was largely consumed in these alkylations. The major reactions were hydrogen transfer, alkylation of the methylcyclopentane by the olefin and isoparaffins and "self-alkylation" of the methylcyclopentane forming dimethyldecahydronaphthalenes. Tetramethylcyclohexanes were established to be the major product of alkylation of methylcyclopentane dissolved in isobutane with isobutylene.

In a series of alkylations of methylcyclohexane dissolved in isobutane, isopentane and in 2-methylpentane with isobutylene and butene-2, the naphthene was relatively unreactive. An order of reactivity was found: methylcyclopentane > 2-methylpentane > isopentane > isobutane > methylcyclohexane. Mechanisms for the alkylations and a possible explanation of naphthene-inhibition of disproportionation in aluminum chloride-catalyzed isomerizations are presented.

Introduction

The presence of small concentrations of cyclohexane or methylcyclopentane[2] or benzene[3] in the hydrocarbon feed of an aluminum chloride-catalyzed isomerization of *n*-pentane to isopentane suppresses disproportionation of the paraffin. It has been shown that cyclohexane is an ineffective inhibitor under the mild conditions used in aluminum bromide-catalyzed isomerization of 2,2,4-trimethylpentane.[4] This is evidence that the product of isomerization of cyclohexane, methylcyclopentane, is in fact the inhibitor when cyclohexane is used to inhibit disproportionation under the relatively severe conditions of pentane isomerization. Although the mechanism of such disproportions is as yet not completely understood, it seems reasonable to assume that the activity of benzene is in some way associated with its ability to accept carbonium ions. The work described here was undertaken to study the unusual carbonium ion-type of reactivity of methylcyclopentane.

The approach adopted was to subject solutions of various concentrations of the naphthene in isoparaffins such as isobutane or isopentane to hydrogen fluoride-catalyzed alkylation with olefins at ambient temperatures. By determining the extent of conversion of the naphthene and isoparaffin, it was hoped to establish a relative order of reactivity for these compounds. In addition to this, the nature of the products formed in these reactions was of considerable interest.

The work of Pines and Ipatieff[5] on acid-catalyzed alkylations of methylcyclopentane with olefins serves as a basis for understanding the nature of the products in the work at hand. These authors established that alkylate of the expected molecular weight was formed in only small yield. Accompanying this direct alkylation, self-alkylation of the naphthene resulted in considerable dimer, trimer and alkylated dimer. One of the main points of interest was the observation that alkylation of methylcyclopentane is accompanied by ring expansion of the product forming polyalkylcyclohexanes; a mechanism of formation of this type of compound was proposed.

Experimental

Materials.—Isobutane (C.P.), isobutylene (C.P.) propylene (C.P.) and butene-2 (C.P.) were used directly from cylinders supplied by the Matheson Co., Phillips Petroleum Co. "Pure" grade isopentane and 95 mole %; technical grade methylcyclopentane and 2-methylpentane ($n^{20}D$ 1.3715) were used without further purification. Eastman Kodak Co. "White Label" grade methylcyclohexane showed no appreciable amount of impurity on infrared spectroscopic analysis and was used without further purification.

Anhydrous hydrofluoric acid was obtained by distilling and condensing the material from a cylinder of the anhydrous acid supplied by the Matheson Co.

Procedure for Alkylation.—The alkylations were performed in a one-liter, Universal Oil Products type contactor. The olefin was added over a period of 5 to 15 minutes to a stirred mixture of the saturated hydrocarbons and hydrofluoric acid sealed in the contactor while the temperature was maintained at around 20° by immersing the vessel in a pan of water. After the addition was complete, stirring was continued for an additional 5 to 20 minutes.

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[1] Paper presented before the Division of Petroleum Chemistry, American Chemical Society, Los Angeles, Calif., March 15, 1953.

[2] B. L. Evering and E. L. d'Ouville, THIS JOURNAL, **71**, 440 (1949).

[3] J. M. Mavity, H. Pines, R. C. Wackher and J. A. Brooks, *Ind. Eng. Chem.*, **40**, 2374 (1948).

[4] F. E. Condon, THIS JOURNAL, **73**, 3938 (1951).

[5] H. Pines and V. N. Ipatieff, *ibid.*, **67**, 1631 (1945).

TABLE I

HYDROGEN FLUORIDE-CATALYZED ALKYLATIONS OF METHYLCYCLOPENTANE DISSOLVED IN ISOBUTANE WITH ISOBUTYLENE AT 23–24°

Experiment	1	2	3	4
Charge, g. (moles)				
Methylcyclopentane	10 (0.12)	42.5(0.506)	86.5(1.03)	168 (2.00)
Isobutane	213 (3.67)	117 (2.01)	167.5(2.89)	86 (1.48)
Isobutylene	62 (1.11)	55 (0.98)	86.5(1.54)	119.5(2.14)
Hydrogen fluoride	113 (5.65)	136 (6.80)	158 (7.90)	141 (7.05)
Contact time, minutes	30	8	10	25
Prod. recvd. wt. % of chg.[a]	96	97	96	99
Product, g. (moles)[b,c]				
Acid layer	108	145	173	189
Isobutane	160 (2.76)	110 (1.90)	167 (2.88)	125 (2.16)
Isopentane	3 (0.04)[d]	0[d]	0[d]	0[e]
Methylcyclopentane	0	0	4.1(0.049)	22.0(0.262)
Hexanes	1.1(0.012)	0	1.6(.019)	20.0
Heptanes	3.0(.03)	6.1(0.06)	2.8(.03)	
Octanes	71.0(.62)	12.7(.11)	16.2(.142)	
Nonanes	0.7(.006)	1.4(.011)	2.3(.018)	
C_4-Alkylated methylcyclopentane	6.5(.05)	37.0(.26)	70.0(.500)	70.0(0.500)
Dimethyldecahydronaphthalenes	....	7.0(.042)	14.0(.084)	41.5(.249)
Higher boiling material	20.0	5.5	18.5	9.0
% recovery of org. reagents[f]	93	88	92	90
Yield of C_4-alkylated methylcyclopentane[g]	56	52	49	25
% conver. of methylcyclopentane[h]	100	100	95.2	87
% conver. of isobutane[h]	24.8	6	0	+145[i]

[a] Includes weights of recovered organic and acid layers. [b] Washed and dried product was debutanized in a total condensation, vacuum-jacketed silvered column (24″ long, 1/2″ internal diameter packed with 1/8″ glass helices), fitted with a Dry Ice and acetone-refrigerated head. [c] Weights of some of the products were calculated from the distillation curves. [d] Debutanized product fractionated in a Podbielniak Hypercal column. [e] Fractionated in column similar to (b) fitted with water-cooled condenser. [f] Based on the hydrocarbons charged. [g] Based on the moles of olefin charged. [h] Uncorrected for losses in handling. [i] A yield of 145% of the isobutane charged was recovered; the result of hydrogen transfer.

To work up the product, the contents of the contactor were cooled to zero and the hydrofluoric acid drawn off. The organic phase was admitted into a copper bomb, sealed in, washed thoroughly with water in the closed system and distilled in a low-temperature column to strip out butanes and pentanes. The higher boiling product was submitted to precise fractionation in a concentric tube column[6] and the distillate cuts analyzed by infrared.

Dehydrogenation.—The product of alkylation with isobutylene of methylcyclopentane in isobutane (expt. 2, Table I) was fractionated and a sample of distillate boiling from 160.4 to 161.5°, corresponding in physical properties to a C_{10}-naphthene (3.70 g., 0.0265 mole) was dehydrogenated by passage at the rate of one drop every 15 seconds over a platinum-on-charcoal catalyst at 316°. The method of catalyst preparation and the procedure of dehydrogenation were essentially those described by Rampton.[7] The refractive index of the material rose from an initial of $n^{20}D$ 1.4342 to 1.5036 on the second pass over the catalyst. The first pass produced 1.64 liters of hydrogen (at N.T.P.) and the second pass an additional 0.11 liter. Assuming 3 moles of hydrogen per mole of material, the theoretical volume of gas obtainable from this sample is 1.781. Thus, a 98.5% conversion to aromatics was achieved.

On cooling to zero, the catalysate deposited crystals, which, after two recrystallizations from ethanol, melted at 76–77°; a mixed-melting point with an authentic sample of 1,2,4,5-tetramethylbenzene showed no depression. Only 0.4 g. of the solid could be recovered by cooling the catalysate to zero.

Dehydrogenation under similar conditions of a 47-cc. sample of the product boiling from 160–170° (isolated from expt. 4 by fractionation) resulted in an increase in refractive index from 1.4371 to 1.4734 and the liberation of 11.6 of a theoretically available 17.2 liters of hydrogen, corresponding to a 69.3% conversion. The product from the dehydrogenation (33.2 g.) was fractionated in a micro column and the material boiling above 185°, 11 g., deposited 4.8 g. of crytals melting at 80.5–81°. A mixed melting point with 1,2,4,5-tetramethylbenzene showed no depression. The filtrate was examined qualitatively by Raman and infrared spectroscopy. The following constituents were found to be present in relatively large concentrations: 1,2,3,4-, 1,2,-3,5- and 1,2,4,5-tetramethylbenzenes. In relatively small concentrations were 1,2-dimethyl-4-ethylbenzene and 1,3-dimethyl-2-ethylbenzene. Traces of several other isomers also were detected.

A sample of product from the 215 to 235° plateau corresponding in physical properties to a C_{12}-naphthene (26 cc., $n^{20}D$ 1.4711) in the distillation of the product from expt. 4 was dehydrogenated under the conditions mentioned above. The refractive index of the catalysate was 1.5578 and 13.5 l. of gas was evolved. Assuming 5 moles of hydrogen per mole of material, this corresponds to a 91% conversion in one pass. The catalysate (19 g.) was distilled in a micro column and material boiling above 250° (13.1 g.) crystallized by cooling to 5°. A sample of the crystals was filtered out and recrystallized from ethanol giving white plates m.p. 105–105.1°. A mixed-melting point with authentic 2,3-dimethylnaphthalene (obtained from the Edcan Laboratory, South Norwalk, Conn.) showed no depression. The picrate was prepared and melted at 125.5–126°, in agreement with the literature value for the picrate of 2,3-dimethylnaphthalene.[8]

Results and Discussion

Products of Alkylation with Isobutylene of Methylcyclopentane Dissolved in Various Saturated Hydrocarbons.—In the alkylation of methylcyclopentane with isobutylene or *n*-butylene catalyzed by either sulfuric acid or hydrogen fluoride, Pines and Ipatieff[5] observed the formation of considerable amounts of acid-soluble, highly olefinic oils. These investigators found no well-defined plateau in the distillation of the organic phase of a sulfuric acid-catalyzed alkylation of methylcyclo-

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[6] C. K. Donnell and R. M. Kennedy, *Ind. Eng. Chem.*, **42**, 2327 (1950).

[7] H. C. Rampton, *Anal. Chem.*, **21**, 1377 (1949).

[8] A. S. Bailey, K. C. Bryant, R. A. Hancock, S. H. Morrell and J. C. Smith, *J. Inst. Pet.*, **33**, 503 (1947).

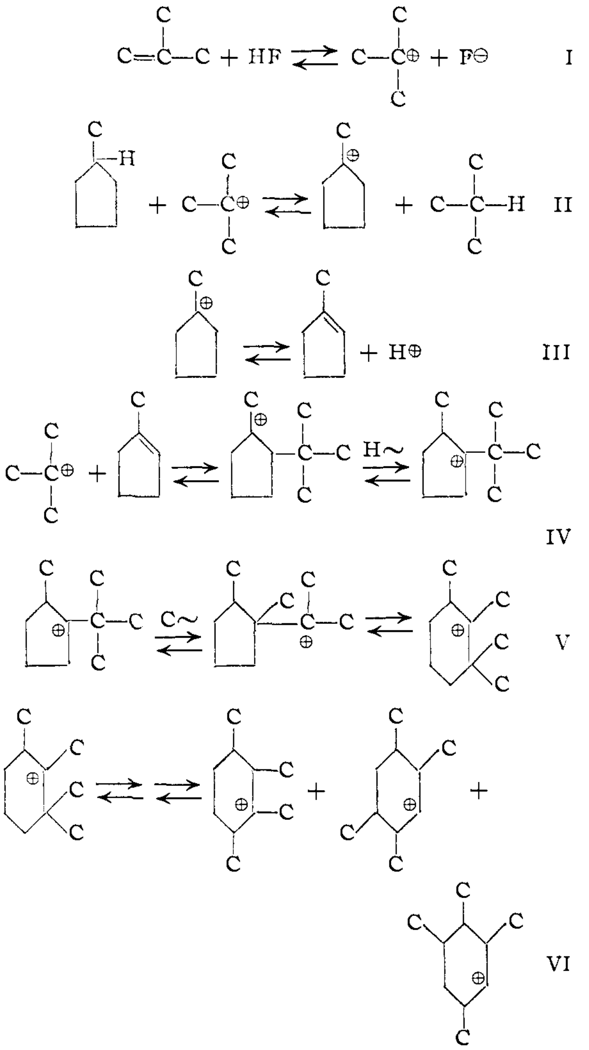
pentane with isobutylene corresponding to the product of direct alkylation of the naphthene by the olefin; the major isolated product was a mixture of dicyclic saturated hydrocarbons. In the work at hand, however, inclusion of an excess of isobutane in hydrogen fluoride-catalyzed alkylations of methylcyclopentane with isobutylene (Table I) resulted in the formation of little acid-soluble material except in an experiment in which the mole ratio of naphthene to isobutane exceeded 0.35 (*cf.* expt. 4). Furthermore, the debutanized products contained as much as 50% yields of C_4-alkylated naphthene based on the olefin charged and only minor amounts of dicyclic material (*cf.* expt. 2–4). Apparently the solvent isobutane acts as a saturating medium reducing the amount of acid-soluble oils formed and directing the reaction to yield largely the C_4-alkylated methylcyclopentane.

Infrared analysis of the debutanized product from expt. 1 distilling below 122° disclosed it to contain no methylcyclopentane or cyclohexane; it was a normal isobutane–isobutylene alkylate with respect to both the nature and the relative concentrations of the isoparaffins present. Cyclohexane was not found throughout this work. The larger the molar ratio of olefin to methylcyclopentane, the more complete was the conversion of the latter and the more normal alkylate was produced.

The physical properties of the large plateaus in the distillations of the products from expts. 2–4 boiling from 160 to 170° (Table V) correspond closely to those previously observed.[5] Physical property correlations indicate the content of naphthenes in this fraction to be in the range of 90–100%. Material from this fraction dehydrogenated to the extent of only 67% of theoretical indicating the presence of geminally substituted cyclohexanes and/or polyalkylated cyclopentanes. That the material which dehydrogenated consisted mainly of tetramethylcyclohexanes was demonstrated by the isolation and positive identification of durene from the dehydrogenated product and by the Raman and infrared qualitative analyses of the filtrate from the durene; in this, the major products were found to be the three tetramethylbenzenes and the minor constituents, dimethylethylbenzenes.

A cut of the 160–170° fraction of the alkylate, boiling from 161.6 to 161.8° had physical properties close to those of the product of hydrogenation of durene.[9] This material dehydrogenated quantitatively giving a product from which was isolated an 11% yield of durene.

The mechanism presented by Pines and Ipatieff[5] for the formation of dimethylethylcyclohexane from the alkylation of methylcyclopentane with butene-2 involves addition of the methylcyclopentyl tertiary carbonium ion to the olefin followed by rearrangement, ring expansion and further rearrangement. This mechanism cannot be used to explain the formation of tetramethylcyclohexanes in the alkylation of methylcyclopentane with isobutylene without invoking such unusual Wagner–Meerwein rearrangements as the formation of seven-membered ring intermediates from six-membered rings. For this and other reasons to be discussed below, a preferred mechanism capable of explaining the formation of all the observed products of the alkylation is the addition to the olefin derived from methylcyclopentane of the carbonium ion produced from the olefin or, as in this work, from the isoparaffinic solvent by hydrogen exchange.



The carbonium ions on both sides of equation VI may be converted to hydrocarbons by hydrogen transfer with either methylcyclopentane or isobutane, initiating new sequences of reaction in the process. From this mechanism, the possibility seems good for the presence of geminal disubstituted cyclohexanes in the alkylate.

The next plateau appearing in the distillation of these products is that of a minor constituent boiling from 218 to 230°. This material was observed by Pines and Ipatieff[5] and found to form a mixture of dimethylnaphthalenes on dehydrogenation. In the work at hand, dehydrogenation produced a mixture of dimethylnaphthalenes from which 2,3-dimethylnaphthalene was isolated. The earlier workers postulated that methylcyclohexylcyclopentanes are formed in the alkylation reaction and that these

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(9) M. K. Dyakova, *et al.*, *J. Gen. Chem. U.S.S.R.*, **7**, 722 (1937); K. v. Auwers, *Ann.*, **420**, 108 (1920).

TABLE II

HYDROGEN FLUORIDE-CATALYZED ALKYLATIONS OF METHYLCYCLOPENTANE DISSOLVED IN VARIOUS ISOPARAFFINS WITH ISOBUTYLENE AT 25°

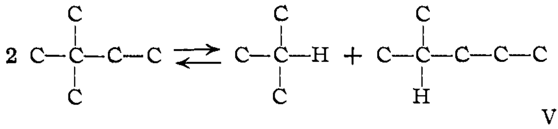
Experiment	5	6	7
Saturate other than methylcyclopentane charged	Isopentane	2-Methylpentane	Methylcyclohexane
Charge, g. moles			
Methylcyclopentane	85 (1.01)	43 (0.512)	42 (0.50)
Saturate	213 (2.96)	129 (1.50)	147 (1.50)
Isobutylene	61 (1.09)	76 (1.36)	63.5(1.13)
Hydrogen fluoride	143.5(7.18)	124 (6.20)	137 (6.85)
Contact time, minutes	10	40	40
Prod. recovd., wt. % of charge[a]	96	98	95
Product, g. (moles)[b,c]			
Acid layer	150	142	153
Isobutane	35.5(0.613)	28 (0.483)	25 (0.43)
Isopentane[d]	165.5(2.30)	1.5(0.02)	0
Methylcyclopentane	13.7(0.163)	15 (0.178)	0
Methylcyclohexane	....	....	114 (1.17)
Hexanes	6.9(0.081)	52.4(0.61)	3.8
Heptanes	2.8(.028)		
Octanes	5.9(.052)	8.0	0
Nonanes	5.5(.043)		0
C_4-Alkylated methylcyclopentane	17 (.121)	27.2(0.194)	12.6(0.090)
C_5-Alkylated methylcyclopentane	37 (.24)	....	....
C_6-Alkylated methylcyclopentane	....	13.3(.079)	......
Dimethyldecahydronaphthalenes	10 (0.06)	18.6(.112)	3.0(0.018)
C_4-alkylated methylcyclohexane	....	....	6.8(.044)
MCP–MCH alkylate	....	....	15.5(.086)?
Intermediate boiling material	9	13.8	0.0
Higher boiling material	14.5	7.0	21.5
% recovery of organic material[e]	92	82	87
% conversion of methylcyclopentane[f]	84	65	100
% conversion of isoparaffin[f]	22.3	59.3	22.4[h]
Rel. react. of methylcyclopentane[f,g]	3.8	1.11	4.7

[a] Includes weights of recovered organic and acid layers. [b] Washed and dried product was debutanized in a column similar to that in Table I, footnote *b*. [c] Weights of some of the products were calculated from the distillation curves. [d] Debutanized product fractionated in a Podbielniak Hypercal column. [e] Based on the hydrocarbons charged. [f] Uncorrected for losses in handling. [g] Calculated: $\frac{\text{moles methylcyclopentane converted}}{\text{moles methylcyclopentane charged}} \times \frac{\text{moles other hydrocarbon charged}}{\text{moles other hydrocarbon converted.}}$ [h] Methylcyclohexane.

are converted by a complicated series of reactions over the dehydrogenation catalyst to a mixture of dimethylnaphthalenes.

It is believed, however, that a much simpler explanation of the formation of the dimethylnaphthalenes exists, namely, that the dicyclic hydrocarbons formed in alkylation reactions with methylcyclopentane consist of dimethyldecahydronaphthalenes, the "self-alkylate" of this naphthene.[10]

Hydrogen transfer was clearly evident in the alkylation with isobutylene of a solution of methylcyclopentane in isopentane (Table II, expt. 5). Approximately 56% of the isobutylene charged was converted to isobutane by hydrogen exchange. That only a small part of the isobutane arose as a consequence of disproportionation of isopentane according to equation VII is inferred by the small amount of isohexanes in the product[11]



$$2\ \mathrm{C{-}\underset{C}{\overset{C}{C}}{-}C{-}C} \rightleftarrows \mathrm{C{-}\underset{C}{\overset{C}{C}}{-}H} + \mathrm{C{-}\underset{H}{\overset{C}{C}}{-}C{-}C{-}C}$$

VII

In the absence of the naphthene a considerable yield of both isobutane and isohexanes results from this sort of reaction.[12]

Approximately 16% of the naphthene and 78% of the isopentane originally introduced remained unconverted. Defining the molar reactivity ratio of methylcyclopentane to isopentane as

$$\frac{\text{moles methylcyclopentane converted}}{\text{moles methylcyclopentane charged}} \times \frac{\text{moles isopentane charged}}{\text{moles isopentane converted}}$$

a value of 3.8 is calculated for this experiment. As used in this work, the molar reactivity ratio is merely a convenient notation for comparing the reactivities of hydrocarbons under the experimental conditions cited. It is not intended to imply that this ratio is constant over widely varying initial concentrations of the hydrocarbons. However, it is believed that the naphthenes and isoparaffins studied here may be arranged in a series according to their reactivities in this type of reaction providing that comparable initial ratios of reagents are used in all experiments.

Precise fractionation of the product showed C_4- and C_5-alkylated methylcyclopentane to be present in a molar ratio of 1 to 2. Approximately 11% of

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[10] W. K. Conn and A. Schneider, THIS JOURNAL, **76**, 4578 (1954).

[11] A. Schneider and R. M. Kennedy, *ibid.*, **73**, 5017 (1951).

[12] Unpublished results from this Laboratory.

the isobutylene employed entered into direct alkylation with the naphthene and 22% underwent hydrogen exchange with isopentane producing the dimethylethylcarbonium ions which alkylated methylcyclopentane. Presumably, mainly trimethylethylcyclohexanes were produced in this fashion. The usual minor amount of dimethyldecahydronaphthalenes was observed.

A considerable portion (35%) of the isobutylene charged was converted to isobutane by hydrogen transfer in the alkylation of a solution of methylcyclopentane in 2-methylpentane with isobutylene (Table II, expt. 6). Little disproportionation of the isohexane occurred as evidenced by only small amounts of isopentane and isoheptanes in the product.[11] The molar reactivity ratio of methylcyclopentane to 2-methylpentane in this case was 1.1.

The amount of C_4-alkylated methylcyclopentane exceeded by 2.5 times that of the C_6-alkylated material; the latter material appeared as a rather diffuse plateau boiling from 208 to 218° in the distillation of the product. It appears that as the molecular weight of the isoparaffin increases the clean-cut nature of the reaction, characterized by the reaction with isobutane, disappears. A relatively large amount of dimethyldecalins was obtained.

As in expt. 5 and 6, the olefin underwent considerable conversion to isobutane (38%) by hydrogen transfer in the alkylation of methylcyclopentane dissolved in methylcyclohexane (Table II, expt. 7). No methylcyclopentane was recovered, whereas 78% of the hexahydroaromatic remained unreacted. The material boiling above methylcyclohexane was a complicated mixture in that no distinct distillation plateaus were obtained. A considerable portion of the product boiled above 230°. The methylcyclohexane appears to have exerted little of the saturating action shown by the isoparaffins discussed above.

The Alkylation with Propylene of Methylcyclopentane Dissolved in Excess Isobutane (Table III).—This experiment was designed to distinguish between the amount of hydrogen transfer (forming propane) and the extent of disproportionation of the isopentane (forming isobutane and isohexanes). A clean-cut hydrogen transfer was found in which 31% of the olefin was converted to propane. No isobutane and a small amount of isohexanes were found indicating the complete suppression of disproportionation. In hydrogen fluoride-catalyzed alkylations of isopentane with propylene, considerable disproportionation had been reported.[13] The molar ratio of reactivities of the naphthene to isoparaffin in this case was 2.5.

There was isolated a considerable yield of octanes which was found by infrared spectroscopic analysis to consist entirely of dimethylhexanes. The complete absence of trimethylpentanes is of interest in that it clearly shows that under the conditions of these reactions propylene either undergoes hydrogen transfer or acts as an acceptor of carbonium ions (in this case the *t*-amyl ion), but does not add as a carbonium ion to olefins.[14]

TABLE III

HYDROGEN FLUORIDE-CATALYZED ALKYLATION OF METHYLCYCLOPENTANE DISSOLVED IN ISOPENTANE WITH PROPYLENE AT 25°

Experiment	8
Charge, g. (moles)	
Methylcyclopentane	52 (0.619)
Isopentane	133 (1.85)
Propylene	25.5(0.608)
Hydrogen fluoride	133 (6.65)
Contact time, minutes	70
Prod. recovd. wt. % of chg.[a]	97
Product, g. (moles)[b,c]	
Acid layer	132.5
Propane	8.1(0.19)
Isobutane[d]	0.0
Isopentane	100.9(1.41)
Hexanes	2.9(0.034)
Methylcyclopentane	21.1(.251)
Heptanes	1.9(.019)
Octanes (dimethylhexanes)	14.1(.124)
Nonanes and trimethylcyclohexane	4.0(.031)
Decanes	2.5(.018)
C_5-Alkylated methylcyclopentane	13.9(.091)
Dimethyldecahydronaphthalenes	10.0(.060)
Higher boiling material	7.0
% recovery of organic reagents[e]	89
% conversion of methylcyclopentane[f]	59.4
% conversion of isopentane[f]	24.1
Rel. react. of methylcyclopentane[f,g]	2.5

[a] Includes weights of recovered organic and acid layers. [b] Washed and dried product was depropanized in a column similar to that in Table I, footnote *b*. [c] Weights of some of the products were calculated from the distillation curves. [d] Depropanized product fractionated in a Podbielniak Hypercal column. [e] Based on the hydrocarbon charged. [f] Uncorrected for losses in handling. [g] See Table II, footnote *g*.

No well-defined distillation plateau was observed corresponding in physical properties to the alkylation product of methylcyclopentane with propylene. On the other hand, considerable amounts of the C_5-alkylation product of methylcyclopentane and of the self-alkylate of methylcyclopentane were produced. It is believed that the failure of an appreciable yield of the C_3-alkylation product of methylcyclopentane to be formed resides in the tendency of both propylene and methylcyclopentane to behave as olefins and carbonium ion acceptors under the conditions of these reactions. Thus, isopropyl positive ions are largely converted to propane by hydrogen transfer. The methylcyclopentyl tertiary positive ion appears almost quantitatively to lose a proton forming methylcyclopentene; in this form it is alkylated by the relatively more stable dimethylethylcarbonium ions. As shown above, this ion also alkylates propylene.

The facile loss of a proton from the methylcyclopentyl ion can serve as a basis for explaining most of its chemistry so far discussed. For example, the small yield of dimethyldecahydronaphthalenes always observed and the inability to make this the major product may well be a consequence of the great preponderance of methylcyclopentene over the corresponding carbonium ion in reaction III.

Alkylations of Solutions of Methylcyclohexane in Isoparaffins with Olefins (Table IV).—The sub-

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(13) C. B. Linn and A. V. Grosse, *Ind. Eng. Chem.*, **37**, 924 (1945).

(14) A. V. Grosse, E. J. Rosenbaum and H. F. Jacobson, *Ind. Eng. Chem., Anal. Ed.*, **12**, 191 (1940); (b) S. F. Birch, A. E. Dunstan, F. A. Fidler, F. B. Pim and T. Tait, *Ind. Eng. Chem.*, **31**, 1079 (1939).

TABLE IV

HYDROGEN FLUORIDE-CATALYZED ALKYLATIONS OF METHYLCYCLOHEXANE DISSOLVED IN VARIOUS ISOPARAFFINS WITH ISOBUTYLENE AND BUTENE-2 AT 25°

Experiment	9	10	11
Olefin charged	Isobutylene	Butene-2	Isobutylene
Saturate other than methylcyclohexane charged	Isobutane	Isobutane	2-Methylpentane
Charge, g. (moles)			
Methylcyclohexane	54 (0.55)	25 (0.26)	49 (0.50)
Saturate	120 (2.02)	213.5(3.68)	225 (2.52)
Olefin	61.5(1.10)	78 (1.39)	53.5(0.96)
Hydrogen fluoride	111 (5.55)	129 (6.45)	165.5(8.28)
Contact time, minutes	10	45	40
Prod. recovd., wt. % of chg.[a]	96	96	97
Product, g. (moles)[b,c]			
Acid layer	112.5	125.5	166.0
Isobutane	76 (1.31)	133 (2.29)	17.7(0.31)
Isopentane[d]	1.0(0.01)	7 (0.1)	28.2(.392)
Isohexane	1.4(.016)	12	80.5(.936)
Isoheptane	4.8(.048)		25.8(.258)
Methylcyclohexane	36.0(.37)[e]	18 (0.18)[f]	38.6(.39)[e]
Octane	49.3(.432)	95.9(0.84)	10.5(.092)
Nonane	2.9(.023)	9.9	12.8(.10)
Decane	5.2(.036)		20.6(.144)
C_4-Alkylated methylcyclohexane	10.6(.069)	12.5(0.081)	20.0(.130)
Higher boiling material	13.6	6.0	45.5
% recovery of organic reagents[g]	86	94	92
% conversion of methylcyclohexane[h]	33.3	28	21.2
% conversion of isoparaffin[h]	36.7	37.8	64.3
Rel. react. of methylcyclohexane[h,i]	....	....	0.35

[a] Includes weights of recovered organic and acid layers. [b] Washed and dried product was debutanized in a column similar to that described in Table I, footnote *b*. [c] Weights of some of the products were calculated from the distillation curves. [d] Debutanized product fractionated in a Podbielniak Hypercal column. [e] Determined by infrared spectroscopy. [f] Determined by refractive index measurements. [g] Based on the hydrocarbon charged. [h] Uncorrected for losses in handling. [i] Calculated:

$$\frac{\text{moles methylcyclohexane converted}}{\text{moles methylcyclopentane charged}} \times \frac{\text{moles other hydrocarbon charged}}{\text{moles other hydrocarbon converted.}}$$

stitution of methylcyclohexane for methylcyclopentane in the alkylations of isobutane with isobutylene or with butene-2 (expt. 9 and 10) changed completely the nature and distribution of products (*cf.* expt. 2). The hexahydroaromatic was converted only to the extent of around 30%, whereas methylcyclopentane under similar conditions was completely consumed. The molar reactivity ratio of methylcyclohexane to isobutane could not be accurately determined in expt. 9 and 10, since undoubtedly some of the isobutylene was converted to isobutane by hydrogen transfer; in any event, for both experiments the figure is well below 1.

The methylcyclohexane appears to have exerted little influence on the extent of conversion of isobutane to produce normal alkylate. Thus, in expt. 10, the molar consumption of isobutane was equal to the number of moles of butene-2 introduced. The alkylate from expt. 9 and 10 consisted predominantly of trimethylpentanes.

Diffuse plateaus at 180–190° in the distillations of these products indicated the presence of small amounts of alkylated methylcyclohexanes. From physical properties (Table V), this material in expt. 10 was found to consist of 30–35% naphthenes and 65–70% of paraffins. No attempt was made in this work to establish the structures of the alkylated methylcyclohexanes, but previous workers showed that in aluminum chloride-catalyzed alkylations of this naphthene with isobutylene, the olefin was incorporated without deep-seated rearrangements, forming *t*-butylmethylcyclohexane.[15]

The relative unreactivity of methylcyclohexane was further demonstrated in an alkylation with isobutylene of the naphthene dissolved in 2-methylpentane (expt. 11); here methylcyclohexane was converted to the extent of only 21% while the corresponding figure for the isoparaffin was 64%. This corresponds to a molar reactivity ratio of naphthene to isoparaffin of 0.35. The isoparaffin reacted mainly by disproportionation forming considerable amounts of C_5- to C_9-isoparaffins. It will be recalled that little disproportionation was observed in the comparable experiment with methylcyclopentane (expt. 6). It is noteworthy that the methylcyclopentane suppressed the disproportionation even though a much higher mole ratio of olefin to 2-methylpentane (0.91) was employed in that experiment than in the experiment with methylcyclohexane, where the ratio was 0.38.

The Relative Reactivities of Naphthenes and Isoparaffins.—The enhanced reactivity of methylcyclopentane over isobutane in these alkylations is demonstrated by the complete conversion of the naphthene in expt. 1 and 2 and its almost complete disappearance in expt. 3 and 4. As shown in the following tabulation, the methylcyclopentane was completely consumed in those experiments employing more than 1.9 moles of olefin per mole of naphthene, even though the naphthene was dissolved in

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(15) H. Pines and V. N. Ipatieff, *J. Org. Chem.*, **6**, 242 (1941).

TABLE V

PROPERTIES OF FRACTIONS OBTAINED IN DISTILLING THE PRODUCTS OF THE ALKYLATIONS

Expt.	Boiling range, °C.	n^{20}_D	d^{20}_4	Naphthenes, %[a]	Rings/molec.[b]	Probable structure
3	40–120	1.3955				Alkylate, isoparaffins
	120–150	1.4148				Alkylate, isoparaffins
	150–161.8	1.4338	0.7858	85		Tetramethylcyclohexane
	161.8–170[c]	1.4381	.7962	100		Tetramethylcyclohexane
	170–215	1.4415	.8009	95		Intermediate boiling
	215–235	1.4648	.8533		1.6	Dimethyldecahydronaphthalenes
	235–270	1.4557				Alkylated dimethylecalins
5	150–170	1.4354	.7891	89		Tetramethylcyclohexanes
	170–200	1.4425	.8029	98		Trimethylethylcyclohexanes
6	100–170	1.4318				Tetramethylcyclohexanes
	170–200	1.4403	.8002	100		Intermediate boiling
	200–220	1.4504	.8205		1.2	dimethylpropylcyclohexanes plus dimethyldecahydronaphthalenes
	220–235	1.4723	.8738		2.0	Dimethyldecalins
	235–260	1.4604				Alkylated dimethyldecalins
7	150–200	1.4365	.7904	84		Tetramethylcyclohexanes
	200–235.1	1.4643	.8535		1.8	Dimethyldecalins ??
	235.1–241.4	1.4704	.8650		1.8	Dimethyldecalins
8	130–175	1.4252	.7760	100		Trimethylcyclohexanes
	175–100	1.4374	.8004	100		Trimethylethylcyclohexanes
	200–250	1.4576	.8445		1.8	Dimethyldecalins plus alkylated dimethyldecalins
10	175.0–200	1.4291	.7699	30–35		*sec*-Butylmethylcyclohexane

[a] S. S. Kurtz, *et al.*, *Anal. Chem.*, 19, 175 (1947). [b] F. Eisenlohr, *Z. physik. Chem.*, **75**, 585 (1911). [c] The major portion of this cut boiled from 161.6 to 161.8°, n^{20}_D 1.4363; the properties of hydrogenated durene are b.p. 160–161.5°, n^{20}_D 1.4372, d^{20}_4 0.7934.[9]

large excesses of isobutane. When a mole ratio of 1.50 or less was used, small portions of the naphthene remained unreacted. In the two experiments in which methylcyclopentane was found in the products, the relative reactivities of the naphthene and isoparaffin, as measured by their conversions, cannot be determined since isobutylene reacts in part to form isobutane by hydrogen transfer. This is illustrated by the pronounced formation of isobutane from isobutylene in expt. 4 and probably accounts for the small apparent conversions of the isoparaffin in expts. 2 and 3.

Expt.	Mole ratios Isobutane:methylcyclopentane:isobutylene			Conversion of methylcyclopentane, %
1	30.9	1	9.33	100
2	3.96	1	1.92	100
3	3.81	1	1.50	95.2
4	0.75	1	1.05	87

From the results of the experiments with the various naphthenes and isoparaffins it is possible to assign an order of reactivity to the various compounds studied in accordance with their tendencies to be converted to other materials by reactions with carbonium ions: methylcyclopentane > 2-methylpentane > isopentane > isobutane > methylcyclohexane.

It is believed that the reactivity of a hydrocarbon in this group is a reflection not only of the relative ease of removal of its tertiary hydrogen atom by reaction with a carbonium ion, but also that an important factor is the ease and extent of conversion of the resulting carbonium ion to an olefin by loss of a proton.

The first-order rate constants, k_1, for the ionizations of a series of tertiary alkyl and naphthenyl chlorides corresponding to the hydrocarbons studied have been published; in addition, the ratios of the rate constants of elimination of a proton, k_e, to those of hydration, k_s, for the carbonium ions resulting from the ionizations of the halides have been reported.[16] The following tabulation gives these data:

R-Cl	k_1, hr.$^{-1}$	k_e/k_s
t-Methylcyclopentyl	1.38	0.96
t-2-Methylpentyl	0.053	.49
t-Amyl	.055	.52
t-Butyl	.033	.19
t-Methylcyclohexyl	.011	2.58

The order of reactivities of the hydrocarbons observed in the work at hand agrees quite well with that listed above for the k_1 values of the corresponding chlorides. There is a strong analogy between the solvolysis of a tertiary chloride and the hydrogen transfer reaction of an isoparaffin or a naphthene; in both types of reactions a carbonium carbon is formed by the loss of a negative ion. In one case, hydrogen bonding between polar solvent and the halogen atom is important and in the other, a strong interaction of tertiary hydrogen with a carbonium carbon is probably the major driving force. Thus, those factors in the alkyl or naphthenyl group which facilitate the ionization of the carbon–chlorine bond in solvolysis[17] probably aid in the hydrogen transfer reaction of the corresponding hydrocarbon.

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(16) H. C. Brown and R. Silber, Paper presented before the Div. of Organic Chem. of the Am. Chem. Soc., New York Meeting, N. Y., Sept. 15–19, 1947.

(17) H. C. Brown, R. S. Fletcher and R. B. Johannesen, THIS JOURNAL, **73**, 212 (1951).

It is believed valid to compare the order of reactivity found for the hydrocarbons in this work with the order of k_e/k_s for the corresponding chlorides listed above. The variation in this ratio shows that, except for methylcyclohexyl chloride, the tendency for the carbonium ions to eject a proton is in the same sequence as the order of reactivity of the hydrocarbons observed in this work.

An explanation of the apparent discrepancy with regard to the relative unreactivity of methylcyclohexane in the alkylation reaction and the pronounced tendency of its carbonium ion to eliminate a proton as shown by the ratio k_e/k_s may be sought in the relatively small value of k_1 for the tertiary methylcyclohexyl halide. This indicates that methylcyclohexane forms a carbonium ion much more slowly than methylcyclopentane, for example; thus, for the hexahydroaromatic this step is probably rate-controlling and it behaves as a relatively inert solute in the experiments at hand.

The ratios k_e/k_s listed above are also evidence in support of the experimentally deduced conclusion that the methylcyclopentyl-*t*-carbonium ion loses a proton more readily than the carbonium ions of the isoparaffins studied.

Discussion of the Mechanism of Inhibition of Disproportionation in Aluminum Chloride-catalyzed Isomerizations of Pentane and Hexane.—The facts disclosed about the reactivity of methylcyclopentane in this work offer a new insight into the problem of the mechanism of disproportionation of the higher hydrocarbons. It has been shown previously that isopentane and isohexane containing minor amounts of alkyl fluoride undergo extensive disproportionation on treatment with boron trifluoride.[11] It is believed that the same conditions apply in disproportionations during aluminum chloride-catalyzed isomerizations as exist during disproportionations initiated by alkyl fluoride–boron trifluoride, namely, the simultaneous presence of appreciable concentrations of both carbonium ion and olefin derived from the isoparaffin. The inclusion of from 5 to 10% of methylcyclopentane provides a very active substance which reacts rapidly with carbonium ions derived from the isoparaffin. This, however, is not sufficient, since the naphthenylcarbonium ions might be expected to undergo hydrogen transfer with more isoparaffin. Here, the pronounced tendency of the *t*-methylcyclopentyl ion to lose a proton influences the course of the reaction. The conversion of the naphthenylcarbonium ion to its olefin corresponds essentially to the irreversible saturation of an isoparaffinic carbonium ion. Thus, the action of the methylcyclopentane in suppressing disproportionation is postulated to be one of reducing the concentration of "free," isoparaffinic carbonium ions.

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Cyclic Polyolefins. XXXIII. Compounds Derived from Cycloöctatetraenylmethyl Alcohol. Isomerization of Cycloöctatetraenylacetonitrile[1]

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N,N-Dimethylcycloöctatetraenylmethylamine (II) and cycloöctatetraenylacetonitrile (III) have been prepared by displacement reactions from cycloöctatetraenylmethyl bromide (I). The nitrile III was converted into an isomer (VIII or IX) by migration of one of the nuclear double bonds into conjugation with the nitrile group on heating with triethylamine, or on treatment with sodium hydroxide at room temperature. Both of the nitriles were converted to amides by treatment with alkaline hydrogen peroxide.

This paper reports an investigation of several cycloöctatetraene derivatives prepared from cyclooctatetraenylmethyl alcohol, an allylic-type alcohol obtained by copolymerization of acetylene with propargyl alcohol.[2]

Attempts to prepare the *p*-toluenesulfonate of cycloöctatetraenylmethyl alcohol under conditions used for other alcohols in the cycloöctatetraene series[2,3] and to use the ester as an intermediate in displacement reactions gave erratic results, probably because of side reactions between the reactive allylic-type tosylate and the base (usually pyridine) employed in its preparation. It was possible to prepare cycloöctatetraenylmethyl bromide from the alcohol and phosphorus tribromide in hexane in the presence of pyridine, however, and the pure bromide I was isolated by distillation in 65% yield. Reaction of the bromide with dimethylamine in benzene yielded N,N-dimethylcycloöctatetraenylmethylamine (II, 43%), which was characterized as the crystalline picrate and hydrochloride. Cycloöctatetraenylacetonitrile (III) also was prepared from the bromide by reaction with potassium cyanide in aqueous tetrahydrofuran in the presence of potassium iodide. The nitrile III was purified and isolated in 44% yield by conversion into a non-crystalline silver nitrate complex, followed by regeneration with ammonium hydroxide and chromatography on silica gel. Infrared spectra of the bromide, tertiary amine and nitrile contain the bands previously noted as characteristic of monosubstituted cycloöctatetraenes,[2] and accordingly provide evidence supporting the structures of these compounds. In addition, the spectrum of the nitrile III contains a sharp band at 4.4 μ characteristic of the (unconjugated) nitrile group.

Reaction of cycloöctatraenylacetonitrile with aqueous sodium hydroxide at room temperature did not yield the carboxylic acid, but resulted in partial isomerization forming a nitrile with an infrared ab-

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[1] Supported in part by the Office of Naval Research under contract N5ori-07822, Project Designation NR356-096.

[2] A. C. Cope and D. F. Rugen, THIS JOURNAL, **75**, 3215 (1953).

[3] A. C. Cope and R. M. Pike, *ibid.*, **75**, 3220 (1953).