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# Reaction of Methylcyclopentane with Olefins in the Presence of Sulfuric Acid and Hydrogen Fluoride Catalysts[1]

BY HERMAN PINES AND V. N. IPATIEFF

The study of the reaction of cycloparaffins with olefins was undertaken in order to gain a better understanding of the alkylation reaction[2] because the ring hydrocarbons readily can be detected and identified.

For this study methylcyclopentane[3] was chosen as the hydrocarbon to be alkylated in preference to the more accessible cyclohexane, for the reason that it undergoes alkylation more readily and at the same time permits the observation of whether or not the conversion of the cyclopentane to cyclohexane ring occurs. It is known that at room temperature the equilibrium is mostly toward the cyclohexane side.[4] Alkylation with the following olefins was investigated: *n*-butenes, isobutylene, 2-pentene, 3-methyl-1-butene, and a mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene. The alkylations were carried out in the presence of sulfuric acid and hydrogen fluoride, because these two catalysts, under the experimental conditions used, cause practically no isomerization of saturated hydrocarbons.

Reaction of methylcyclopentane with olefins apparently involves: (a) addition of methylcyclopentane to olefins accompanied by ring expansion and migration of alkyl groups within the ring; (b) hydrogen disproportionation, the naphthenes being usually the hydrogen donors, whereas the olefins are the hydrogen acceptors; (c) isomerization of straight-chain olefins to isoolefins followed by hydrogenation; (d) interreaction of partially dehydrogenated naphthenes to form polycyclic olefinic or polycyclic saturated hydrocarbons; (e) depolymerization and/or depolyalkylation.[5] The ease with which the abovementioned reactions occur depends to a great extent upon the olefins used. The unsaturated hydrocarbons formed during the reaction are usually found in the catalyst layer, from which they can be recovered by diluting it with water. In the hydrogen fluoride catalyzed reactions where the catalyst is removed by evaporation, the olefinic hydrocarbons as such or in the form of fluorides are separated from the saturated hydrocarbons by treating with sulfuric acid and diluting with water.

The structures of the various compounds obtained were determined by physical constants, elementary analysis, and conversion of the naphthenes to the corresponding aromatic hydrocarbons which can be readily converted to known derivatives.

## Discussion of Results

**Sulfuric Acid Catalyzed Alkylation.**—The reaction was carried out by contacting 3.0 moles of methylcyclopentane with 2.25 moles of olefins in the presence of 3 moles of 100% sulfuric acid. Most of the experiments were carried out at 10–17° with a contact time of two hours. The two layers which were formed were separated and investigated. The summary of the experimental data and results is given in Table I.

***n*-Butenes.**—The major part of the products formed resulted from the reaction of 1 mole of

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(1) Presented before the meeting of the Petroleum Division of the American Chemical Society in Cleveland, April, 1944.

(2) (a) V. N. Ipatieff and A. V. Grosse, THIS JOURNAL, **57**, 1616 (1935); (b) V. N. Ipatieff, A. V. Grosse, H. Pines and V. I. Komarewsky, *ibid.*, **58**, 913 (1936); (c) H. Pines, A. V. Grosse and V. N. Ipatieff, *ibid.*, **64**, 33 (1942); (d) S. H. McAllister, J. Anderson, S. A. Ballard and W. E. Ross, *J. Org. Chem.*, **6**, 647 (1941); (e) S. F. Birch, A. E. Dustan, F. A. Fidler, F. B. Pim and T. Tait, *Ind. Eng. Chem.*, **31**, 1079 (1939).

(3) H. Pines and V. N. Ipatieff (to Universal Oil Products Co.), U. S. Patents 2,291,254 (July 28, 1942) and 2,315,078 (March 30, 1943).

(4) H. Pines and V. N. Ipatieff, THIS JOURNAL, **61**, 1076 (1939).

(5) (a) V. N. Ipatieff and H. Pines, *Ind. Eng. Chem.*, **27**, 1364 (1935); (b) *J. Org. Chem.*, **1**, 464 (1936); (c) THIS JOURNAL, **58**, 1056 (1936).

TABLE I

| Experiment No. | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Reactants: Methylcyclopentane, g. | 252 | 252 | 252 | 252 | 252 | 252 |
| Reactants: Olefins (kind) | Butenes | Butenes | Isobutylene | 2-Pentene | 3-Methyl-1-butene | Diisobutylenes |
| Olefins, g. | 126 | 124 | 126 | 157 | 157 | 126 |
| Sulfuric acid, 100%, g. | 270 | 274 | 274 | 273 | 275 | 275 |
| Cond. of expt.: Temp., °C. | 10–17 | 40–47 | 10–15 | 10–14 | 10–16 | 10–17 |
| Cond. of expt.: Duration, hr. | 2.0 | 2.0 | 2.0 | 2.0 | 3.5 | 2 |
| Products recovered | | | | | | |
| Hydrocarbon layer, g. | 324[a] | 313[b] | 302[c] | 340[d] | 327[e] | 317[f] |
| Catalyst layer, g. | 306 | 331 | 333 | 338 | 352 | 335 |
| Mechanical losses | 15 | 8 | 7 | 5 | 5 | 1 |
| Distn. of methylcyclopentane in reaction product, mole % | | | | | | |
| Methylcyclopentane recovered | 59.0 | 58.3 | 49.2 | 33.3 | 33.3 | 55.0 |
| As alkyl monocyclic | 27.7 | 14.3 | 7.6 | 7.8 | 5.6 | 2.7 |
| As dicyclic ($C_{12}H_{22}$)[g] | 10.0 | 6.0 | 13.6 | 25.3 | 20.7 | 20.0 |
| As alkyl dicyclic[g] | 3.3 | 2.3 | 3.0 | 5.3 | 2.7 | [i] |
| As polycyclic[h] | .. | 7.3 | 7.0 | .. | 10.0 | 5.3 |
| In catalyst layer | .. | 11.7 | 19.6 | 28.3 | 26.7 | 17.0 |
| Distn. of olefins, mole % | | | | | | |
| As corres. paraffins | .. | 15.5[j] | 24.9 | 28.4[k] | 36.8[l] | 19.6[m] |
| As hydrogenated dimers[o] | 1.0 | 15.5 | 24.0 | 17.7 | 25.8 | 45.2[n] |
| As alkyl monocyclic | 36.8 | 19.0 | 10.2 | 10.2 | 8.9 | 3.8 |
| As alkyl dicyclic | 4.5 | 1.7 | .. | 7.9 | 1.3 | [i] |
| In catalyst layer | 57.7 | 47.0 | 36.5 | 36.8 | 13.3 | 20.2 |

[a] See Fig. 1 for distillation curve. [b] See Fig. 2. [c] See Fig. 3. [d] See Fig. 4. [e] See Fig. 5. [f] See Fig. 6. [g] Calculated on the basis of 2 moles of methylcyclopentane reacting to produce 1 mole of dicyclic hydrocarbons. [h] Polycyclic hydrocarbons containing more than two rings per molecule. [i] Not determined. [j] Contains 15% of isobutane. [k] Consists of isopentane. [l] In addition to the 36.8 mole % of isopentane found, there was also 10.7 mole % of isobutane. [m] Of the diisobutylene, 4.5 mole % was converted to isobutane. [n] Consists of dodecanes. [o] Calculated on the basis of 2 moles of olefins reacting to produce 1 mole of hydrogenated dimer.

butenes with 1 mole of methylcyclopentane; 1,3-dimethyl-5-ethyl- and 1,3-dimethyl-4-ethylcyclohexane accounted for 83% of the methylcyclopentane which reacted. The structure of the dimethylethylcyclohexanes formed was determined by converting the products, by means of dehydrogenation, to the corresponding aromatics[4] and converting the latter by means of oxidation with dilute nitric acid at atmospheric or superatmospheric[6] pressure or by means of bromination to known solid derivatives. Alkylcyclopentanes under similar conditions did not undergo dehydrogenation.

The hydrocarbon layer also contained minor

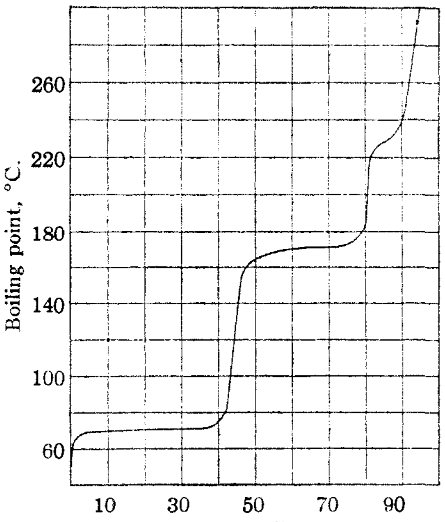

Fig. 1.—Methylcyclopentane + *n*-butenes at 10–17°.

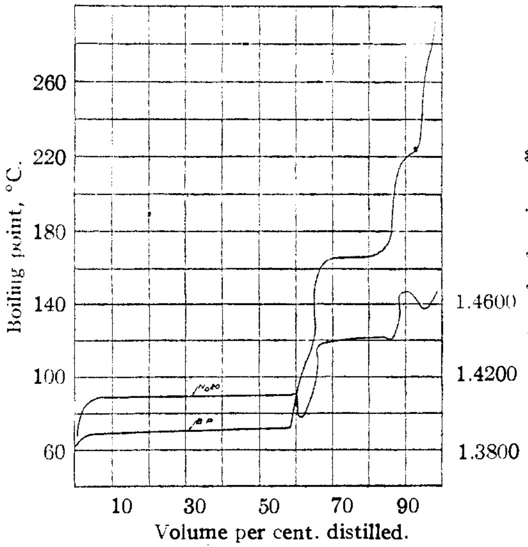

Fig. 2.—Methylcyclopentane + *n*-butenes at 40–47°.

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(6) H. Pines, A. V. Grosse and V. N. Ipatieff, THIS JOURNAL, **61**, 640 (1939).

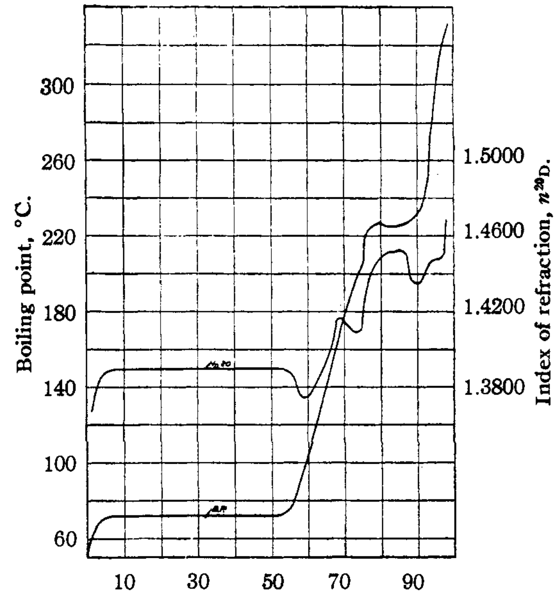


Fig. 3.—Methylcyclopentane + isobutylene.

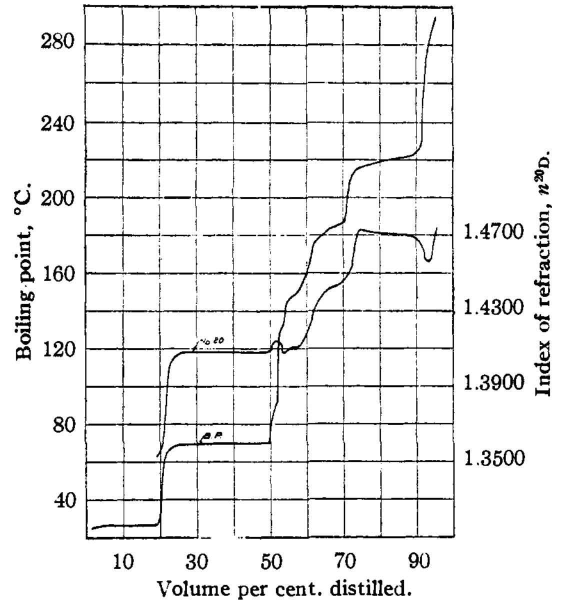
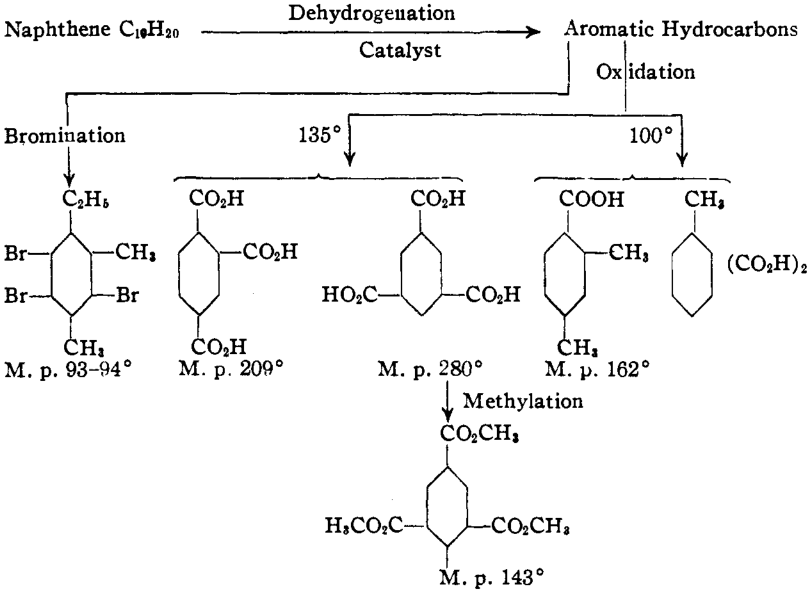


Fig. 4.—Methylcyclopentane + 2-pentene.

amounts of dicyclic hydrocarbons of the formula $C_{16}H_{30}$.

If the temperature of reaction was raised to 40° instead of 10–17°, the yield of dicyclic saturated hydrocarbons increased, and about 30% of the methylcyclopentane which entered reaction was found in the acid layer. The hydrocarbons boiling at 171° were analyzed according to the scheme shown.



**Isobutylene.**—The reaction of methylcyclopentane with isobutylene was much more complicated than that with *n*-butenes, inasmuch as it was accompanied by hydrogen transfer. At a reaction temperature of 10 to 17°, about 10% of the isobutylene charged reacted with methylcyclopentane to form alkylated cyclohexane; 25% was converted to isobutane and a similar amount to hydropolymers consisting primarily of octanes; the remainder of the isobutylene reacted with sulfuric acid. Of the methylcyclopentane reacted, about 50% yielded di- and polycyclic saturated hydrocarbons, whereas 40% underwent partial dehydrogenation and formed reaction products with sulfuric acid.

**Pentene-2.**—Pentene-2 did not combine as readily with methylcyclopentane as did *n*-butenes, and the yield of alkylated naphthenes was smaller. Isomerization of pentene-2 followed by hydrogenation formed isopentane The hydrogen required for that reaction was available from condensation of methylcyclopentane to yield polycyclic hydrocarbons. About 18% of the pentene polymerized to decenes, and the latter gave decanes because of hydrogen transfer reaction. About 42% of methylcyclopentane which reacted underwent dehydrogenation to unsaturated cyclic hydrocarbons found in the sulfuric acid layer.

**3-Methyl-1-butene.**—The results obtained were similar to those obtained when methylcyclopentane reacted with pentene-2. In addition to alkylated naphthenes, isopentane, dec-

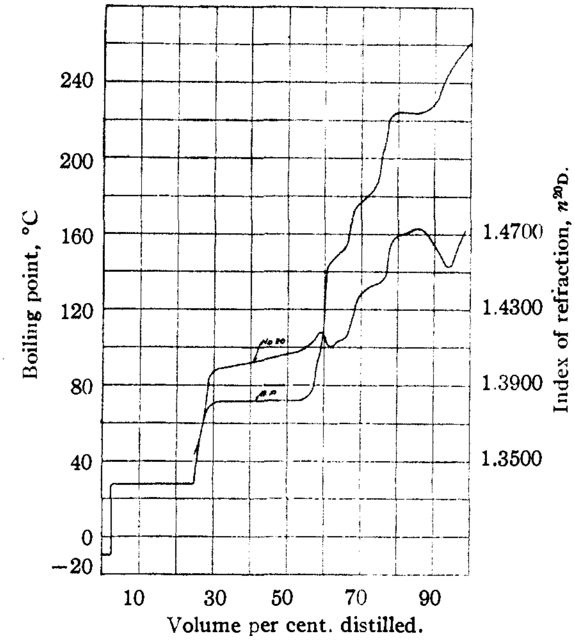


Fig. 5.—Methylcyclopentane + 3-methyl-1-butene.

anes, and polycyclic hydrocarbons were produced.

**2,4,4-Trimethyl-1- and -2-pentene (Diisobutylene).**—These olefins, obtained from the polymerization of isobutylene, on reaction with methylcyclopentane yielded alkylnaphthenes. Part of the olefins used was converted to dodecanes, octanes, and isobutane. The formation of dodecane and isobutane indicated that part of the original olefins underwent depolymerization to isobutylene which, through hydrogen transfer, was converted to isobutane. Part of the isobutylene probably reacted with diisobutylene to form triisobutylene which underwent hydrogenation to dodecane.

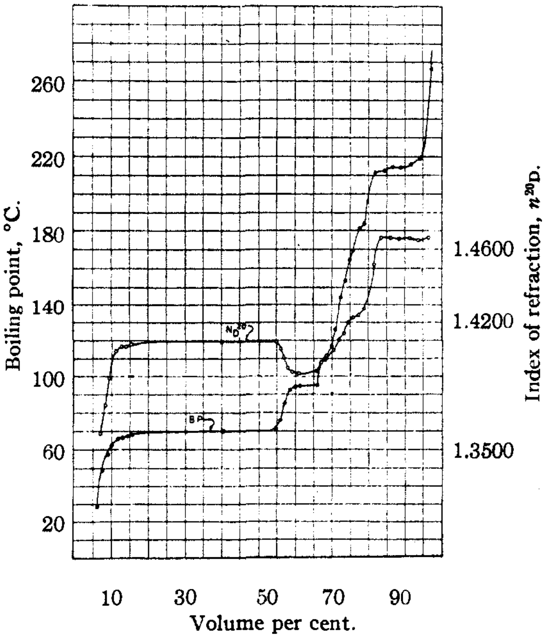
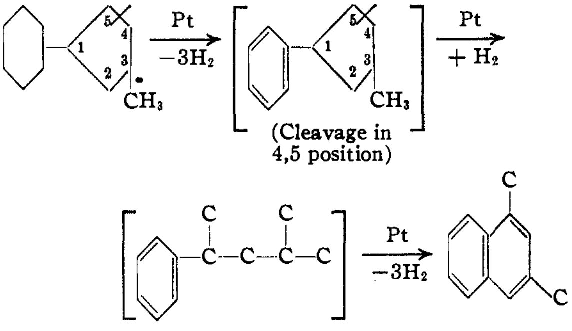


Fig. 6.—2,2,4-Trimethyl-1- and 2-pentene.

Sixty-two per cent. of the methylcyclopentane which reacted was converted to di- and polycyclic saturated hydrocarbons transferring the hydrogen to saturate the olefins. The dicyclic hydrocarbons corresponding to $C_{12}H_{22}$ were probably composed of methylcyclohexylcyclopentanes, since dimethylnaphthalenes were produced on dehydrogenation. The formation of the latter could be explained by the fact that methylcyclohexylcyclopentane, on dehydrogenation, may form initially methylcyclopentylbenzene and hydrogen, and the cyclopentyl ring, being unstable, undergoes cleavage to form hexylbenzene.[7] In the presence, however, of a dehydrogenating catalyst, such as platinum deposited on carriers, hexylbenzene may undergo further dehydrocyclization to substituted naphthalene.[8] An example of such cleavage is indicated by the accompanying equations.



The formation of 1,4-dimethylnaphthalene could be explained by the 5,4 ring rupture of 2-methyl-1-cyclohexylcyclopentane.

The melting point of the dimethylnaphthalenes obtained is depressed by the addition of pure 2,3-, 2,6-, and 2,7-dimethylnaphthalenes. The 1,2-, 1,4-, 1,6-, and 1,8-dimethylnaphthalenes are liquid; 1,3-, 1,5-, and 1,7-dimethylnaphthalenes are the only other possibilities. It was assumed that 1,3-dimethylnaphthalene was formed, since in the case of the last two isomers the migration of a methyl group from a cyclopentyl to a cyclohexyl ring would have to take place.

**Hydrogen Fluoride Catalyzed Alkylation.**—The experimental conditions used in hydrogen fluoride catalyzed reactions (Table II) were similar to those employed in similar reactions in the presence of sulfuric acid. After the reaction was complete, the hydrocarbon layer was not separated from the catalyst layer as in the case of sulfuric acid, but the hydrogen fluoride was removed by distillation. The organic fluorides, or the unsaturated hydrocarbons originally present

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(7) J. Denissenko, *Ber.*, **69**, 1353 (1936).

(8) S. R. Sergienko, *Doklady* U.S.S.R., **27**, No. 9, 960 (1940).

in the catalyst layer, were thus mixed with the saturated hydrocarbons of the upper layer. The latter was therefore treated with sulfuric acid at 0° to remove the components of the catalyst layer, which were then liberated by diluting the sulfuric acid extract with water. Based on results obtained in our laboratories, treatment with sulfuric acid under given conditions does not change the composition of the saturated cyclic hydrocarbons and also does not materially affect the olefinic hydrocarbons which have been formed.

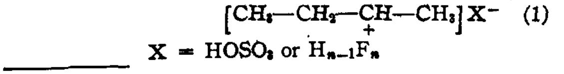
At 10° the reaction of butenes with methylcyclopentane was not very pronounced; at 55–65° the saturated hydrocarbons included, among others, paraffins corresponding to octanes, alkylated cyclohexanes of the formula $C_{10}H_{20}$, and dicyclic hydrocarbons corresponding to methylcyclopentylcyclohexane. The unsaturated hydrocarbons obtained by means of sulfuric acid extraction consisted of hydrocarbons containing, on the average, two double bonds per molecule; these hydrocarbons, after hydrogenation, were converted to dicyclic and alkylated dicyclic hydrocarbons.

TABLE II

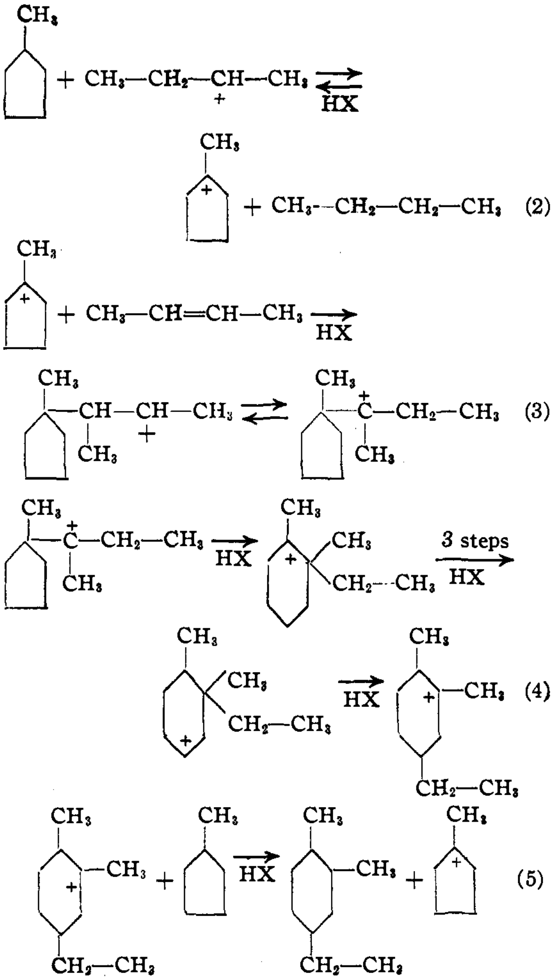
| Experiment no. | | 7 |
|---|---|---|
| Reactants used | Methylcyclopentane | 252 |
| | *n*-Butenes | 124 |
| | Hydrogen fluoride | 155 |
| Condns. of expt. | Temp., °C. | 55–65 |
| | Duration, hrs. | 2.8 |
| Prods. recovered after | wt. stabilization, g. | 284 |
| | wt. caustic wash, g. | 232 |
| | wt. sulfuric acid wash, g. | 214[b] |
| Condensable gases, g. | | 25.2 |
| Distribution of methylcyclopentane in the reaction product, mole % | Recovered methylcyclopentane | 33.7 |
| | As alkylmonocyclic | 9.5 |
| | As dicyclic | 7.3 |
| Distribution of olefins, mole % | As corresponding paraffins | 19.3[a] |
| | As hydropolymers | 29.0 |
| | As alkylated monocyclic | 12.5 |

[a] The gases consist of 68.8 mole % of *n*-butane, 19.2 mole % isobutane, 12 mole % isopentane. [b] See Fig. 7 for distillation curve.

**Mechanism of Reaction.**—The formation of dimethylethylcyclohexane from the interaction of *n*-butenes with methylcyclopentane can be explained by applying the mechanism for the alkylation of isoparaffins with olefins described by Schmerling[9] and subsequently discussed by Bartlett, Condon and Schneider.[10] The following are the probable steps occurring in this reaction



$$\begin{aligned} &CH_3—CH{=}CH—CH_3 + HX \rightleftarrows \\ &\quad CH_3—CH_2—CHX—CH_3 \rightleftarrows \\ &\quad [CH_3—CH_2—\underset{+}{C}H—CH_3]X^- \quad (1) \\ &\quad X = HOSO_3 \text{ or } H_{n-1}F_n \end{aligned}$$



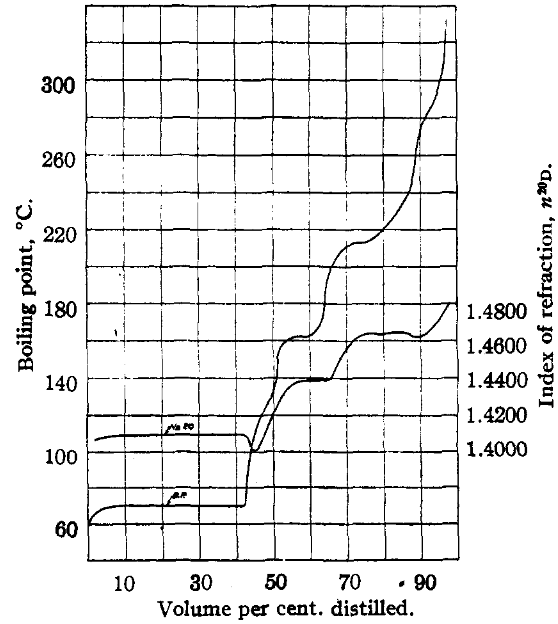


Fig. 7.—Methylcyclopentane + *n*-butenes + hydrogen fluoride.

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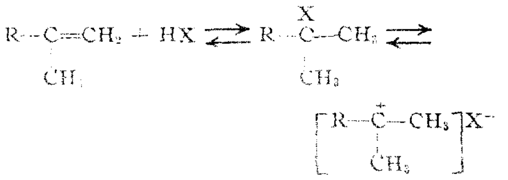
(9) L. Schmerling, THIS JOURNAL, 66, 1422 (1944).

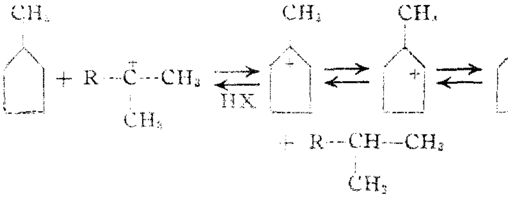
(10) P. D. Bartlett, F. E. Condon and A. Schneider, *ibid.*, 66, 1531 (1944).

The migration of a gem alkyl group (Step IV) in the presence of an acid-type catalyst was studied and will be described separately.[11]

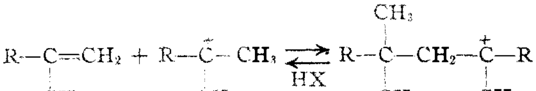
Isobutylene and 3-methyl-1-butene, when treated with methylcyclopentane in the presence of sulfuric acid, are converted in part to the corresponding isoparaffins and to the corresponding hydrogenated dimers. This can be ascribed to the fact that the rate of the transfer of hydrogen with its electron pair from methylcyclopentane to the aliphatic carbonium ion is faster than the addition of methylcyclopentyl carbonium ion to the aliphatic olefinic double bond. The reaction probably proceeds as shown.



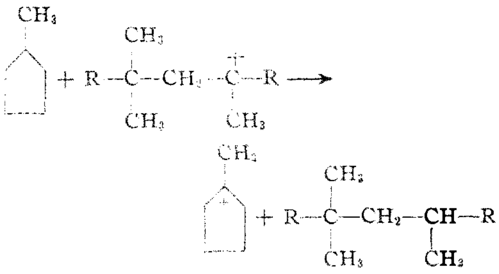
$$R-\underset{CH_3}{C}=CH_2 + HX \rightleftarrows R-\overset{X}{\underset{CH_3}{C}}-CH_3 \rightleftarrows \left[R-\overset{+}{\underset{CH_3}{C}}-CH_3\right]X^- \quad (6)$$



(7)

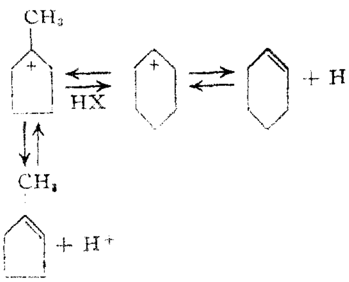


$$R-\underset{CH_3}{C}=CH_2 + R-\overset{+}{\underset{CH_3}{C}}-CH_3 \underset{HX}{\rightleftarrows} R-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{+}{\underset{CH_3}{C}}-R \quad (8)$$

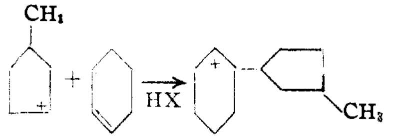


(9)

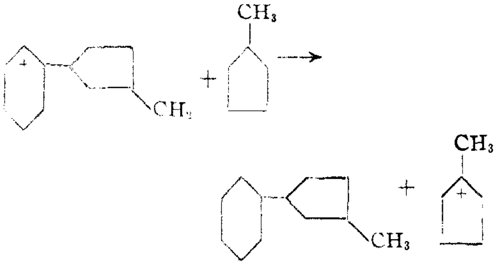
The formation of 1-methyl-3-cyclohexylcyclopentane can be explained as



(10)

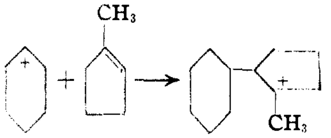


(11)

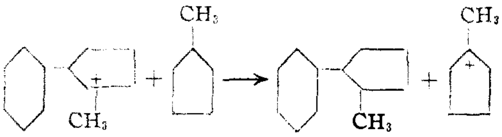


(12)

The formation of 1-methyl 2-cyclohexylcyclopentane can be explained by the addition of cyclohexyl carbonium ion to 1-methylcyclopentene.

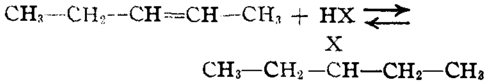


(13)

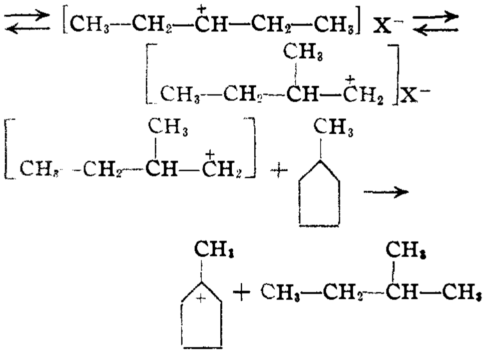


(14)

The formation of isopentane is explained from the reaction of 2-pentene with methylcyclopentane in the presence of sulfuric acid.



$$CH_3-CH_2-CH=CH-CH_3 + HX \rightleftarrows CH_3-CH_2-\overset{X}{CH}-CH_2-CH_3 \quad (15)$$



$$\rightleftarrows [CH_3-CH_2-\overset{+}{C}H-CH_2-CH_3]X^- \rightleftarrows \left[CH_3-CH_2-\overset{CH_3}{C}H-\overset{+}{C}H_2\right]X^-$$

(16)

It is known that acidic-type catalysts cause the isomerization of *n*-olefins to isoölefins[2c,12] as shown in equation (15).

The various carbonium ions can lose a proton to form olefinic hydrocarbons which can undergo polymerization; these hydrocarbons combine with the catalyst to form "catalyst layer."

### Apparatus and Procedure

The reactions of methylcyclopentane with butenes and higher olefins using sulfuric acid as a catalyst were made

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[11] During the study of dehydration of terpenic alcohols it was noticed that in some cases a non-gem alkyl group can also undergo migration within the ring.

[12] G. Egloff, G. Hulla and V. I. Komarewsky, "Isomerization of Pure Hydrocarbons," A. C. S. Monograph No. 88, Reinhold Publishing Corp., New York, N. Y., 1942.

in a three-necked flask of 2000-cc. capacity provided with a mercury-sealed stirrer, a thermometer, an inlet tube for the addition of olefins, and a cold finger reflux condenser cooled to −78° by means of Dry Ice–acetone mixture. Sulfuric acid of 100% concentration and methylcyclopentane were placed in the alkylating flask, which was cooled to the desired temperature (0–15°). The mixture was stirred and the olefins added at a rate of about 2 moles per hour. After the addition of olefins was completed, the mixture was stirred for an additional half hour and then allowed to stand for one hour. The catalyst layer was separated from the upper hydrocarbon layer, and the latter was treated with 96% sulfuric acid to remove any alkyl sulfates present. The hydrocarbons were first washed with water, then with dilute sodium hydroxide, and then again with water, and finally were dried over calcium chloride and fractionally distilled. The various fractions were analyzed.

The reaction of methylcyclopentane with butenes in the presence of hydrogen fluoride was made in an autoclave of 1100-cc. capacity provided with a stirring device and fitted with a nickel liner.

*n*-Butenes were added from a pressure charger into a well-stirred mixture of hydrogen fluoride and methylcyclopentane. After the reaction was considered complete, the gases were released through potassium hydroxide solution, dried over soda lime, and collected in a Dry Ice–acetone cooled container. The liquid products were washed with aqueous potassium hydroxide to remove dissolved hydrogen fluoride and then with 87% sulfuric acid to remove organic fluorides present. The hydrocarbons were washed with sodium hydroxide, and then with water; dried, and distilled. The sulfuric acid extract was diluted with water and the hydrocarbon layer thus obtained was investigated separately.

## Experimental

### Sulfuric Acid Catalyzed Reaction

**Exp. 1: *n*-Butenes.**—*Fraction b. p. 171°* at 729 mm., $n^{20}_{\mathrm{D}}$ 1.4406; $d^{20}_{4}$ 0.8011.

*Anal.*[13] Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37; mol. wt., 140. Found; C, 86.25; H, 13.93; mol. wt., 138.

**Dehydrogenation.**—Dehydrogenation took place by passing the material over platinum–alumina catalyst[8c] at 250°. According to the hydrogen liberated, 85% of the product underwent dehydrogenation.

**a. Bromination.**—One-half cc. of the dehydrogenated product was treated with 5 cc. of bromine containing 1% of iodine. The solid tribromo derivative with a m. p. 93–94° was crystallized twice from alcohol and found to correspond to that of dimethylethylbenzene.

*Anal.* Calcd. for $C_{10}H_{11}Br_3$: Br, 64.69. Found: Br, 64.48.

**b. Oxidation.**—(A) One-half gram of the dehydrogenated material and 40 cc. of nitric acid (1.5 vol. 72% $HNO_3$: 2.5 vol. $H_2O$) were heated in a sealed tube for two hours.[6]

Two acids were isolated: (a) 1,3,5-benzenetricarboxylic acid (trimesic acid) which is relatively insoluble in water; on methylation it yielded trimethyl trimesate; (b) 1,2,4-benzenetricarboxylic acid (trimellitic acid) melting at 209–210° with decomposition.

*Anal.* Calcd. for $C_9H_6O_6$: C, 51.43; H, 2.86. Found: C, 50.32; H, 3.59.

(B) Two cc. of the dehydrogenated hydrocarbons was refluxed with 92 cc. of nitric acid (1 vol. of 72% $HNO_3$:2.7 vol. of $H_2O$). A solid was formed and was separated by filtration, treated with 25% of aqueous sodium hydroxide, and extracted with ether. The aqueous layer was acidified with hydrochloric acid; the organic acids which precipitated were separated by filtration. The solid product was treated with hot water to remove any soluble di- or polycarboxylic acid formed. The water insoluble material was crystallized from dilute ethanol and melted at 162°; it corresponded to 2,4-dimethylbenzoic acid.

*Anal.* Calcd. for $C_9H_{10}O_2$: C, 72.00; H, 6.67. Found: C, 71.86; H, 6.80.

**Exp. 3: Isobutylene.**—*Fraction b. p. 90–99°;* $n^{20}_{\mathrm{D}}$ 1.3949, $d^{20}_{4}$ 0.6977.

*Anal.* Calcd. for $C_8H_{18}$: C, 84.11; H, 15.89. Found: C, 84.33; H, 15.45.

*Fraction b. p. 163–172°;* $n^{20}_{\mathrm{D}}$ 1.4365, $d^{20}_{4}$ 0.7868.

*Anal.* Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.71; H, 14.35.

Seven grams of the product was submitted to dehydrogenation by passing four times over platinum–alumina catalyst at 250–265°. Only 38% was converted to aromatics; the latter were removed with 15% fuming sulfuric acid. The aromatic-free hydrocarbons were analyzed.

*Anal.* Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.26; H, 14.60; $n^{20}_{\mathrm{D}}$ 1.4310.

On the basis of the dehydrogenation experiments, it can be concluded that the analyzed fraction consists of 62% of alkylated cyclopentanes and 38% of alkylated cyclohexanes.

*Fraction b. p. 225°;* $n^{20}_{\mathrm{D}}$ 1.4721; $d^{20}_{4}$ 0.8692.

*Anal.* Calcd. for $C_{12}H_{22}$: C, 86.67; H, 13.33. Found: C, 87.13; H, 13.21.

Nine grams of the product was submitted to dehydrogenation; 3.2 moles of hydrogen was liberated per 1 mole of hydrocarbon. The material resulting from dehydrogenation distilled as follows: Cut 1—b. p. 200–220°, 8%, $n^{20}_{\mathrm{D}}$ 1.4759; Cut 2—b. p. 220–230°, 36.5%, $n^{20}_{\mathrm{D}}$ 1.4860; Cut 3—b. p. 230–237°, 13.1%, $n^{20}_{\mathrm{D}}$ 1.5035; Cut 4—b. p. 237–250°, 8.4%, $n^{20}_{\mathrm{D}}$ 1.5392; Cut 5—b. p. 250–260°, 34.0%, $n^{20}_{\mathrm{D}}$ 1.5974.

Cut 5 solidified in ice. A solid compound (A) was separated into a solid with m. p. 72–73° and a liquid (B).

(A) *Anal.* Calcd. for $C_{12}H_{12}$ (dimethylnaphthalene): C, 92.28; H, 7.74. Found: C, 91.57; H, 7.68. Mixed melting point with 2,3-, 2,6-, and 2,7-dimethylnaphthalene showed depression.

(B) Formed a picrate, m. p. 140°, which corresponded to that of 1,4-dimethylnaphthalene.

*Fraction b. p. 266–276°;* $n^{20}_{\mathrm{D}}$ 1.4554. *Anal.* Calcd. for $C_{16}H_{30}$ (alkylated dicyclic hydrocarbon): C, 86.24; H, 13.58. Found: C, 86.24; H, 13.57.

**Exp. 5: 3-Methyl-1-butene.**—*Fraction b. p. 150°;* $n^{20}_{\mathrm{D}}$ 1.4137; $d^{20}_{4}$ 0.7356. *Anal.* Calcd. for $C_{10}H_{22}$ (decane): C, 84.41; H, 15.59. Found: C, 84.86; H, 15.23.

*Fraction b. p. 180–183°;* $n^{20}_{\mathrm{D}}$ 1.4426; $d^{20}_{4}$ 0.8014. *Anal.* Calcd. for $C_{10}H_{22}$: C, 85.67; H, 14.37. Found: C, 86.10; H, 14.14.

This product, on dehydrogenation, yielded 50% of aromatics which, on bromination, formed a solid tetrabromo derivative, which sublimed at 215°.

*Anal.* Calcd. for $C_{11}H_{12}Br_4$: Br, 68.93. Found: Br, 69.92. The original product contained dialkylcyclohexane.

*Fraction b. p. 225°;* $n^{20}_{\mathrm{D}}$ 1.4714; $d^{20}_{4}$ 0.8685. *Anal.* Calcd. for $C_{12}H_{22}$ (dicyclic naphthene): C, 86.66; H, 13.34. Found: C, 86.72; H, 13.46.

On dehydrogenation, 4.8 moles of hydrogen per 1 mole of hydrocarbon was evolved. The material distilled as follows: (a) b. p. 211–236°, 17.0%, $n^{20}_{\mathrm{D}}$ 1.4893; (b) 236–245°, 25.8%, $n^{20}_{\mathrm{D}}$ 1.5107; (c) 245–258°, 25.0%, $n^{20}_{\mathrm{D}}$ 1.5572; (d) 258–259°, 27.9%, $n^{20}_{\mathrm{D}}$ 1.6018.

From Cut (d) a solid was separated which after two crystallizations from hot alcohol melted at 92–93°. *Anal.* Calcd. for $C_{10}H_{12}$ (dimethylnaphthalene): C, 92.26; H, 7.74. Found: C, 92.24; H, 7.96.

*Fraction b. p. 266°;* $n^{20}_{\mathrm{D}}$ 1.4530; $d^{20}_{4}$ 0.8195. *Anal.* Calcd. for $C_{16}H_{32}$: C, 85.63; H, 14.37. Calcd. for $C_{17}H_{30}$: C, 86.36; H, 13.64. Found: C, 86.05; H, 14.17.

This fraction probably consisted of a mixture of products resulting from the reaction of 1 mole of methylcyclopentane

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[13] Microanalyses were made by Dr. T. S. Ma, University of Chicago.

with 2 moles of 3-methyl-1-butene and of 2 moles of methylcyclopentane with 1 mole of olefin.

*Fraction b. p. 335°;* $n^{20}D$ 1.4863; $d^{20}{}_4$ 0.8922. *Anal.* Calcd. for $C_{18}H_{32}$ (tricyclic): C, 87.01; H, 12.99. Found: C, 87.07; H, 13.09.

**Exp. 6: 2,4,4-Trimethyl-1- and -2-pentene.**—*Fraction b. p. 95°;* $n^{20}D$ 1.3920; $d^{20}{}_4$ 0.6921. *Anal.* Calcd. for $C_8H_{18}$: C, 84.11; H, 15.89. Found: C, 84.37; H, 15.55.

*Fraction b. p. 182°;* $n^{20}D$ 1.4241; $d^{20}{}_4$ 0.7576. *Anal.* Calcd. for $C_{12}H_{26}$ (dodecane): C, 84.61; H, 15.39. Calcd. for $C_{10}H_{20}$ (naphthenes): C, 85.63; H, 14.37. Found: C, 85.17; H, 14.95.

This product underwent dehydrogenation to aromatics to the extent of only 16%.

According to the analysis and physical constant the products consisted predominantly of dodecane.

*Fraction b. p. 215°;* $n^{20}D$ 1.4673; $d^{20}{}_4$ 0.8593. *Anal.* Calcd. for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.77; H, 13.10.

On dehydrogenation at 260°, it evolved 3.7 mols of hydrogen per 1 mol of hydrocarbons.

*Fraction b. p. 268°;* $n^{20}D$ 1.4671; $d^{20}{}_4$ 0.8452. *Anal.* Calcd. for $C_{16}H_{30}$: C, 86.40; H, 13.60 (alkylated dicyclic naphthenes). Found: C, 86.25; H, 13.61.

It underwent dehydrogenation at 260° with the evolution of 3.8 moles of hydrogen per 1 mole of hydrocarbons.

### Hydrogen Fluoride Catalyzed Reaction

**Exp. 7: *n*-Butenes.**—*Fraction b. p. 161-162°;* $n^{20}D$ 1.4380; $d^{20}{}_4$ 0.7927. *Anal.* Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.99; H, 14.25.

On dehydrogenation, the product yielded 82% of aromatics which, on oxidation with dilute nitric acid at 135°, yielded polycarboxylic acids, indicating that the original product consisted of polyalkylated cyclohexane.

*Fraction b. p. 214-219°;* $n^{20}D$ 1.4638; $d^{20}{}_4$ 0.8506. *Anal.* Calcd. for $C_{12}H_{22}$ (dicyclic naphthenes): C, 86.66; H, 13.34. Found: C, 86.40; H, 13.96.

*Fraction b. p. 238-258°;* $n^{20}D$ 1.4622; $d^{20}{}_4$ 0.8443. *Anal.* Calcd. for $C_{16}H_{30}$: C, 86.40; H, 13.60. Found: C, 86.24; H, 13.78.

### Sulfuric-Acid Extracted Product

The sulfuric acid extract obtained from the treatment of the product was diluted with water; a dark brown upper layer was separated; this was washed with water, aqueous sodium hydroxide, again with water and dried over sodium sulfate. Thirty grams of product which was thus obtained was fractionally distilled: Cut 1, 66-99° at 740 mm., 4.0%, $n^{20}D$ 1.4108; Cut 2, 99-200° at 740 mm., 6.0%, $n^{20}D$ 1.4580; Cut 3, 200-220°; 12.3%, $n^{20}D$ 1.4827, bromine no. 188; Cut 4, 85-135° at 7 mm., 17.0%, $n^{20}D$ 1.4955; Cut 5, 135-158° at 7 mm., 12.3%, $n^{20}D$ 1.5010, bromine no. 164; Cut 6, 158-190° at 7.5 mm., 15.0%, $n^{20}D$ 1.5083; Cut 7, 190-218° at 8 mm., 14.3%, $n^{20}D$ 1.5026.

**Cut 3.**—According to the bromine number, the product contains 2 double bonds per molecule. It was dissolved in 10 cc. of *n*-pentane and hydrogenated in an autoclave of 125-cc. capacity in the presence of 1 g. of a nickel-kieselguhr catalyst and of 100 atmospheres of hydrogen. The hydrogenation was made at 75°. From the drop in pressure it was calculated that 1.8 moles of hydrogen was absorbed per 1 mole of hydrocarbons; the product after hydrogenation was stable toward nitrating mixture (1 vol. 72% $HNO_3$:2 vol. 96% $H_2SO_4$) which indicated the absence of olefins or aromatics.

*Anal.* of hydrogenated product. Calcd. for $C_{12}H_{22}$ (dicyclic naphthenes): C, 86.66; H, 13.34. Found: C, 86.22; H, 13.72; $n^{20}D$ 1.4638.

**Cut 5.**—The product which by means of the bromine number determination contains 1.7 double bonds per molecule was hydrogenated according to the procedure described above. The product which absorbed 1.8 moles of hydrogen per mole of hydrocarbons charged and which was completely saturated was analyzed.

*Anal.* Calcd. for $C_{16}H_{30}$ (alkylated dicyclic naphthene): C, 86.40; H, 13.60. Found: C, 86.39; H, 13.45; $n^{20}D$ 1.4703.

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## Summary

The reaction of methylcyclopentane with olefins in the presence of sulfuric acid and of hydrogen fluoride has been investigated. *n*-Butenes, isobutylene, 2-pentene, 3-methyl-1-butene, and a mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene · were used for this study. The reaction involves the apparent: (a) addition of methylcyclopentane to olefins accompanied by ring expansion and migration of alkyl groups within the ring, (b) hydrogen disproportionation, (c) isomerization of straight chain olefins to isoolefins followed by hydrogenation, (d) reaction of partially dehydrogenated naphthene with cycloölefins or with saturated cyclic hydrocarbons to form polycyclic olefins or polycyclic saturated hydrocarbons, (e) depolymerization and/or depolyalkylation.

The reaction of methylcyclopentane with *n*-butenes in the presence of sulfuric acid forms high yields of 1,3,5-dimethylethyl- and 1,3-dimethyl-4-ethylcyclohexane.

The mechanism of alkylation is discussed.

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