tonic acid was heated to solution in a boiling water-bath. After adding 25 drops of pyridine the heating was continued for eleven hours. The resulting solution was poured onto water, heated to solution, acidified with 5 ml. of dil. hydrochloric acid, treated with Norite, filtered, and cooled to precipitate the product. Recrystallization from water gave 4.2 g. (40.7% of the theoretical amount) of β-(1′-benzotriazolyl)-butyric acid, m.p. 150–152°.

Anal. Calcd. for $C_{10}H_{11}O_2N_3$: C, 58.53; H, 5.40; N, 20.48; neut. equiv., 205.2. Found: C, 58.20; H, 5.48; N, 20.58; neut. equiv., 205.4.

β-Phenyl-β-(1′-benzotriazolyl)-propiophenone.—A mixture of 1.19 g. (0.01 mole) of benzotriazole, 2.08 g. (0.01 mole) of benzalacetophenone and one drop of Triton B was melted together, heated 1.5 hours on a boiling water-bath, let stand 12 hours, and diluted with ether. Addition of petroleum ether precipitated 1.99 g. (61% of the theoretical amount) of β-phenyl-β-(1′-benzotriazolyl)-propiophenone, m.p. 106–107° after recrystallization from ethanol.

Anal. Calcd. for $C_{21}H_{17}ON_3$: C, 77.04; H, 5.23; N, 12.84. Found: C, 76.96, H, 5.41; N, 12.88.

1-(*p*-Methoxyphenyl)-1-(1′-benzotriazolyl)-butanone-3.—A mixture of 1.19 g. (0.01 mole) of benzotriazole, 1.76 g. (0.01 mole) of *p*-methoxybenzalacetone and one drop of Triton B was melted over a free flame and heated six hours on a boiling water-bath. The mixture was cooled, taken up in ether, and diluted with petroleum ether to precipitate 1.13 g. (38% of the theoretical amount) of 1-(*p*-methoxyphenyl)-1-(1′-benzotriazolyl)-butanone-3, m.p. 93–94° after recrystallization from ethanol.

Anal. Calcd. for $C_{17}H_{17}O_2N_3$: C, 69.13; H, 5.80; N, 14.23. Found: C, 69.13; H, 6.02; N, 14.32.

3-Phenyl-1,3-di-(1′-benzotriazolyl)-propanol-1.—A mixture of 1.19 g. (0.01 mole) of benzotriazole, 1.32 g. (0.01 mole) of cinnamaldehyde and one drop of Triton B was melted over a free flame and heated six hours in a boiling water-bath. Addition of 40 ml. of ether to the cooled reaction mixture precipitated 0.85 g. (46% of the theoretical amount) of 3-phenyl-1,3-di-(1′-benzotriazolyl)-propanol-1, m.p. 127° after recrystallization from benzene–carbon tetrachloride. The product is soluble in benzene and ethanol, and is insoluble in carbon tetrachloride and ether.

Anal. Calcd. for $C_{21}H_{18}ON_6$: C, 68.09; H, 4.90; N, 22.69. Found: C, 67.83; H, 5.13; N, 22.84.

β-(1′-Benzotriazolyl)-propionitrile.—A mixture of 1.19 g. (0.01 mole) of benzotriazole and 0.53 g. (0.01 mole) of acrylonitrile was heated to solution. Five drops of Triton B were added and the mixture heated on a water-bath for five hours. The oily reaction mixture was poured into 30 ml. of ether to precipitate the product as a white solid, soluble in acetone, hot water, ethanol, benzene, carbon tetrachloride and dioxane; insoluble in ether and petroleum ether. After three recrystallizations from carbon tetrachloride, there was obtained 0.40 g. (23–25% of the theoretical amount) of β-benzotriazolylpropionitrile, m.p. 79–80°.

Anal. Calcd. for $C_9H_8N_4$: C, 62.77; H, 4.68; N, 32.54. Found: C, 63.21; H, 4.55; N, 32.55.

1,2,3-Triazole-4-carboxylic Acid.—To a solution of 9.30 g. (0.097 mole) of 1,2,3-triazole-4-carboxyaldehyde in 150 ml. of hot water was added with stirring a solution of 10.70 g. (0.0677 mole) of potassium permanganate in 125 ml. of water. The resulting solution was heated to boiling and filtered hot. The precipitate was washed with water. The filtrate was then made basic with solid potassium hydroxide and concentrated to a volume of 75 ml., acidified with excess hydrochloric acid and cooled to precipitate the product. After recrystallization from water there was obtained 6.30 g. (83.2% of the theoretical amount) of 1,2,3-triazole-4-carboxylic acid, m.p. 218–219°, neut. equiv., 111.3; reported[7] m.p. 219°.

Ultraviolet Absorption Data.—Ultraviolet absorption measurements were made with a Beckman DU photoelectric spectrophotometer using 1.00-cm. silica cells and hydrogen and tungsten discharge lamps as light sources. The measurements were made with methanol solutions.

LOUISVILLE, KENTUCKY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Condensations by Sodium. XXXVII. The Dimetalation of Benzene, Thiophene, *p*-*t*-Butylphenol, Isopropylbenzene and *sec*-Butylbenzene and the Effect of Alkoxides on the *meta:para* Ratio for Benzene[1,2]

BY AVERY A. MORTON AND CHESTER E. CLAFF, JR.

RECEIVED MARCH 8, 1954

Amylsodium dimetalates benzene chiefly in the *meta* position but the ratio of *meta* to *para* can be altered by the alkoxide which is associated with the reagent. Thiophene is easily dimetalated in the 2,5-positions. *t*-Butylphenoxide is attacked in the 2.6-position. Isopropylbenzene and *sec*-butylbenzene are dimetalated in the 3.5-positions.

Introduction

Previous work[3] has shown that alkoxides affect greatly the degree and kind of metalation of *t*-butylbenzene. The present paper describes the variations achieved in yield and in the excess of *meta* over *para* dimetalation of benzene and gives a simple explanation for these effects. In addition, it reports that thiophene is dimetalated in the 2,5-positions, *t*-butylphenol in the 2,6-positions and isopropylbenzene and *sec*-butylbenzene in the 3,5-positions. These metalations and the previous work[4] show that amylsodium is an excellent agent for the dimetalation of hydrocarbons and other compounds.

The general method was to prepare amylsodium from amyl chloride and sodium metal, then convert some of this sodium reagent to alkoxide by addition of an alcohol or add a lithium or potassium alkoxide prepared separately if the cation influence was under study. Finally the compound to be dimetalated was added. Usually the reaction was at 60°. After the product was carbonated the dicarboxylic acid was precipitated by addition of mineral acid to the aqueous solution of the salts. The ratio of *meta* to *para* phenylenedisodium was determined by the convenient method of Bryce-Smith and Turner[5] which consists of esterifying with methanol–sulfuric acid and crystallizing the pure *para* and *meta* compounds from methanol. With the sodium reagent, part of the more soluble

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[1] This work was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

[2] A portion of this work was presented at the Boston Meeting of the American Chemical Society, 1951.

[3] A. A. Morton, C. E. Claff, Jr., and F. W. Collins, unpublished.

[4] A. A. Morton, E. L. Little, Jr., and W. O. Strong, Jr., THIS JOURNAL, **65**, 1339 (1943).

[5] D. Bryce-Smith and E. E. Turner, *J. Chem. Soc.*, 861 (1953)

TABLE I

DIMETALATION OF BENZENE BY AMYLSODIUM

Expt.	Reag.[a]	Alkoxide	Ratio m/p	Yields of Total acids, %	Yields of Di-acids, %	Yields of esters Diesters m, %	Yields of esters Diesters p, %	Yields of esters Benz., %	Yields of esters Cap., %	RNa loss, %
1	A	t-$C_5H_{11}OLi$	50	38	3	3	0.05	0.4	20	20
2	A	t-$C_5H_{11}OLi$	15	40	3	1	0.1	0.3	30	29
3	A	cy-$C_6H_{11}ONa$	5		34	24	5			
4	A	cy-$C_6H_{11}ONa^b$	3.9	56	35	16	4			13
5	A	cy-$C_6H_{11}ONa$	3.7	65	41	22	6	11	3	4
6	A	t-$C_6H_{11}ONa$	3.4		29	15	4			
7	A	cy-C_5H_9ONa	3.3	55	31	17	5	13	2	14
8	A	None	3.0	69	26	14	5	3	30	0
9	A	n-$C_5H_{11}ONa$	2.4	59	36	19	8	7	3	10
10	A	cy-$C_6H_{11}OK^c$	1.7	65	50	31	18	7	2	4
11	A	cy-$C_6H_{11}OK$	1.6	73	61	28	17	5	2	4
12	A	$((CH_3)_2CONa)_2$	1.5	61	39	14	9	6	5	8
13	A	cy-$C_6H_{11}OK$	1.4	72	58	26	18	7	2	3
14	A	t-$C_5H_{11}OK$	1.4	73	58	26	19	7	0.6	4
15	A	$((CH_3)_2COK)_2$	1.4	54	41	15	10	6	1	15
16	E^d	None		0.1	0	0	0			69
17	$E^{d,e}$	None	0	20	0.06	0	0.06	17	3^f	49

[a] A signifies amylsodium, E refers to ethylpotassium. [b] The reaction was at 90° instead of 60°. [c] The stirring was at 500 r.p.m. instead of 5000 r.p.m. [d] These reactions were at 20°. [e] The solvent was benzene. [f] Propionic acid instead of caproic.

meta isomer usually remained in the mother liquor and was recovered eventually as a low-melting residue. Accordingly, the yields of diester recorded in Table I are as a rule lower than the corresponding diacid and the ratios of *meta* to *para* are below the true value. That the loss was in the *meta* isomer was shown by various fractionations of a combined lot of residue to remove small amounts of impurity, probably ketone or carbinol.

Effect of Alkoxides on the Dimetalation of Benzene.—The diversity of effects by alkoxides on the dimetalation of benzene by amylsodium is shown by the first 15 experiments in Table I, arranged in order of decreasing proportion of *meta* to *para*, column 4. The range is from 50 to 1 in the presence of lithium *t*-pentoxide to 1.4 to 1 in the presence of potassium pinacoloxide. The proportion of *meta*, column 4, decreases as the cation changes from lithium to sodium to potassium. With less certainty also it seems to decrease as the anion changes from cyclohexoxide to *t*-pentoxide to cyclopentoxide to *n*-pentoxide to pinacoloxide, but the number of comparisons is limited. The total dimetalation (column 6) is higher in the presence of sodium or potassium alkoxides than it is in the control, no. 8, or in the presence of lithium alkoxides (no. 1 and 2) and this fact accords with the discussion previously given[3] of the manner by which alkoxides can affect a reaction.

In a previous paper,[4] dimetalation was reported to be exclusively *meta*, whereas, in a still earlier paper,[6] it had been only more *meta* than *para*. The difference at that time[4] was credited to high-speed stirring. In the light of the present results, some change might be attributed also to differences in the alkoxide or perhaps hydroxide content which had been introduced unknowingly as an impurity. For instance, some pentanol was once found[7] to be present in the amyl chloride added to sodium and traces of impurity[8] have had to be removed by filtration through a special drying column.

The reproducibility of these effects by various ions on metalations is certified by the previous work[3] on the metalation of *t*-butylbenzene, where a pair of alkoxides had the same relative influence over a wide range of conditions. It is shown again in the present work, where experiments 1 and 2 gave close to the same total acids and the same amount of diacids and differed only in the thoroughness with which the *meta* isomer was recovered. It is shown also by the fact that the results in this Laboratory (expt. no. 17) were substantially the same as obtained by the English workers,[4] although the apparati were not the same.

Interpretation of the Effects in Dimetalation of Benzene.—The effects caused by alkoxides are explained in terms of the new concepts of cation influence[9,10] and dissociation[3,11,12] to radicals employed in these studies. In an aggregate of ions, steric as well as polar effects are present and the former often predominate because the reactive centers are packed closely together. Particularly is this condition true when one solid, phenylsodium, reacts with another solid, amylsodium. When amylsodium decomposes[3,11] to a metal and an alkyl, a reaction takes place with whatever corner of phenylsodium adjoins the metalating agent. When lithium *t*-pentoxide is present, the packing of the ions in the reactive aggregate is such as to bring the *meta* position of the ring into the sphere of reaction and *meta* substitution accordingly predominates almost to the exclusion of the *para*. As the cation becomes larger the reactive center moves farther along the benzene nucleus and *para* sub-

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(6) A. A. Morton and F. Fallwell, Jr., THIS JOURNAL, **60**, 1429 (1938).

(7) A. A. Morton, *et al.*, *ibid.*, **72**, 3785 (1950) (see particularly p. 3788).

(8) A. A. Morton and A. Brachman, *ibid.*, **73**, 4363 (1951).

(9) A. A. Morton, *Chem. Rev.*, **35**, 1 (1944).

(10) A. A. Morton, THIS JOURNAL, **69**, 969 (1947).

(11) A. A. Morton and E. F. Cluff, *ibid.*, **74**, 4056 (1952).

(12) A. A. Morton and A. E. Brachman, *ibid.*, **76**, 2973 (1954).

stitution becomes the rule. In a similar way, a change in the anion appears to affect the reaction. Less total metalation occurs in the presence of lithium alkoxide in accord with the principles discussed for associated salts in the previous paper.[3]

In complete agreement with the above results are the observations of Bryce-Smith and Turner,[5] that some alkylpotassium compounds cause more *para* than *meta* dimetalation. The reagents which caused the highest proportion (*ca.* 2.5) of *para* was ethylpotassium, and it was made from ethyllithium and sodium–potassium alloy in benzene, but the total yield of dicarboxylic acids was very small, only 0.3%. In this Laboratory, the low yield has been confirmed in experiment 17, Table I, and the product was *para* only. The cations in this case were exclusively potassium instead of a mixture of sodium and potassium and the high proportion of *para* substitution is accordingly understandable.

Another feature of considerable interest was the large amount of non-useful decomposition of ethylpotassium. The total carboxyl in experiment 17 was only 20% (column 5) of the amount theoretically possible. Dissociation of the potassium reagent to metal and alkyl was exceedingly rapid, too fast apparently for an initial adsorption of benzene so that metalation could occur. When the quantity of benzene was reduced, as in experiment 16, to the amount regularly used in the experiments with amylsodium, the decomposition of ethylpotassium was complete but no metalation took place. In both experiments the evolution of gas was rapid enough to cause foaming. Because of this large amount of non-useful dissociation of organoalkali metal reagent, the yield of *p*-phenylenedisodium prepared with any of the alkylpotassium reagents, reported in their paper,[5] was much lower than was obtained with the sodium reagents here described, in spite of the greater preference of the former for *para* substitution.

Dimetalation of Thiophene and Other Compounds.—Most of the dimetalation of thiophene (see Table II) was carried out in the presence of *t*-butylbenzene because one object was to see if the presence of thiophenylenedisodium would affect the metalation of *t*-butylbenzene in the same way as did the alkoxides. Thiophene was preferentially metalated but no special influence on the hydrocarbon was noted.

TABLE II

COMPARATIVE METALATION OF THIOPHENE AND *t*-BUTYLBENZENE

Temp., °C.	15	15	15	30–40
Time, hr.	5	5	5	3.5
Thiophene, mole	0.01	0.02	0.10	0.12
t-Butylbenzene. mole	0.24	0.24	0.24	0
t-Pentanol, mole	0.20	0.20	0	0.2
Thiophene diacid. g.		1.8	7.8	7.7
mole		0.01	0.045	0.045
%		50	45	37
t-Butylbenzoic acids,				
g.	2.2	0.3	0.58	
mole	0.012	0.0017	0.0032	
%	5.2	0.7	1.4	
Ratio *m/p*	55/45		47/53	

In a similar way, the dimetalation of *t*-butylphenoxide took place more readily than did that of *t*-butylbenzene. The yield was 17% and no influence on the hydrocarbon was observed.

The dimetalations of *sec*-butylbenzene and isopropylbenzene follow closely the results for *t*-butylbenzene and benzene itself in the presence of sodium alkoxides in that the two sodium atoms entered *meta* to each other, and no 2,4-product was obtained. The reaction with *sec*-butylbenzene was carried out in the presence of sodium mentholoxide and the yield was 7%. The reaction with isopropylbenzene was compared with that of *t*-butylbenzene at two different temperatures. The former was attacked a little more easily than the latter in accord with the expectation based on the rule[9] that the fewer the methyl groups, the more easy the metalation, other factors being equal. Earlier[4] toluene was similarly attacked much more readily than the xylenes.

Experimental

General Procedure.—For the metalations by amylsodium, the conditions were identical with those described for the dimetalation of *t*-butylbenzene except that benzene, isopropylbenzene or *sec*-butylbenzene was used in place of *t*-butylbenzene, or that thiophene or *t*-butylphenol was used in place of or in conjunction with the alkoxide. Any small variations introduced are made clear in the tables. For the metalations with ethylpotassium, the quantities of reagents were made theoretically the same as for the sodium experiments but the methods of preparation were those described by Bryce-Smith and Turner. All reactions were at 60° in heptane as the medium except as specified in the tables.

Products from Benzene.—The separations of the two diesters were carried out according to the method described by Bryce-Smith and Turner.[5] However, some ester remained in the mother liquor even after cooling to a lower temperature than prescribed. This material was eventually recovered by addition of water. The total crude amount from eight experiments was 14.0 g. of brown solid which melted from 40 to 53°. Further crystallization from methanol, followed by vacuum sublimation of each fraction and recrystallization from methanol, yielded 9.5 g. of the *meta* diester, still a little impure and melting a little lower than the pure isomer. The remainder amounted to 0.8 g. which, by ultimate analysis, seemed to be a mixture of diester and ketone or tertiary carbinol. The loss in handling during these separations amounted to 3.7 g. much of which probably occurred during sublimation and may have been caused by the presence of small amounts of methyl benzoate.

Thiophene-2,5-dicarboxylic Acid.—The dicarboxylic acid derived from thiophene was identified by its neutralization equivalent and the melting point (142–144°) of its dimethyl ester (recorded[13] 145–145.5°).

2-Hydroxy-5-*t*-butylisophthalic Acid.—The hot solution of *p*-*t*-butylphenol (30 g. or 0.2 mole) in heptane was blown by nitrogen pressure into a standard preparation of amylsodium. *t*-Butylbenzene, 0.15 mole, was then added and the reaction mixture kept at 60° for three hours. When the aqueous solution of the carboxylic acids was acidified, the only product (8.2 g. or 17%) obtained was 2-hydroxy-5-*t*-butylisophthalic acid. It had a purple fluorescence in water and gave a deep red-brown color with ferric chloride in alcohol. The neutralization equivalent was 119.0. It began to decompose at 231°, and decarboxylation was rapid at 258° and crystals of *t*-butylphenol were obtained. The dimethyl ester, prepared with diazomethane, melted at 115–117.4° and also gave a red-brown color in the ferric chloride test.

Anal. Calcd. for $C_{14}H_{14}O_5$: C, 63.2; H, 6.77. Found: C, 63.6; H, 6.78.

5-Isopropylisophthalic Acid.—Isopropylbenzene (0.12 mole) was metalated at room temperature and at 75–80° in the presence of 0.20 mole of sodium isopropoxide. The dicarboxylic acid was obtained in yields of 3.2 and 14.8%

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(13) H. Jackel, *Ber.*, **19**, 192 (1886).

(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.

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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 ($n^{20}\text{D}$ 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).

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

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