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REACTIONS OF PARAFFINS WITH AROMATIC HYDROCARBONS. II. VARIOUS AROMATIC HYDROCARBONS AND 2,2,4-TRIMETHYLPENTANE

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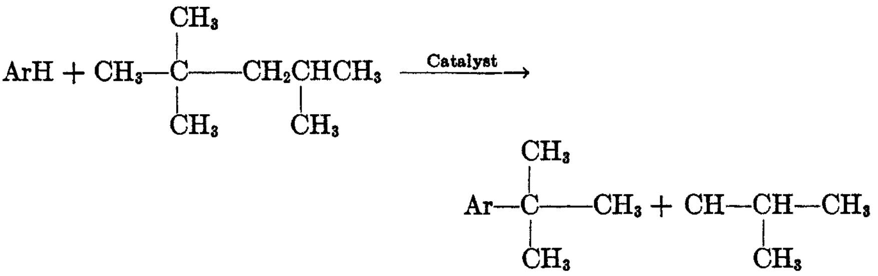
The reaction of various paraffin hydrocarbons with benzene in the presence of catalysts has been described in earlier papers[1, 2]. In the present investigation the reaction of 2,2,4-trimethylpentane with various alkylbenzenes and polynuclear aromatics catalyzed by aluminum chloride has been studied. This particular paraffin was chosen since it has been found to react readily with benzene under mild conditions, and only in one direction—namely, towards the formation of *tert.*-butyl-substituted benzenes and isobutane.[1]

The alkylation reaction can be expressed as follows:



$$\mathrm{ArH} + \mathrm{CH_3{-}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2}\underset{\mathrm{CH_3}}{\mathrm{CH}}\mathrm{CH_3} \xrightarrow{\text{Catalyst}} \mathrm{Ar{-}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_3} + \mathrm{CH{-}}\underset{\mathrm{CH_3}}{\mathrm{CH}}\mathrm{{-}CH_3}$$

Further reaction may result in the formation of aromatic hydrocarbons containing more than one tertiary butyl group per molecule.

In the present investigation the following aromatics were studied: toluene, ethylbenzene, *p*-xylene, biphenyl, naphthalene, fluorene, and pyrene.

With both *toluene* and *biphenyl,* the normal alkylation reaction was found to proceed quite readily (the reaction was particularly rapid in the case of biphenyl) and the yields of isomeric mono tertiary butyl alkylation products were 34 and 35 per cent., respectively, based on the paraffin reacting. Slightly more than one mole of isobutane per mole of the reacting octane was produced in each case.

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[1] GROSSE AND IPATIEFF, *J. Am. Chem. Soc.*, **57,** 2415 (1935).

[2] GROSSE, MAVITY AND IPATIEFF, J. ORG. CHEM., **3,** 137 (1938).

The reactions in the case of *ethylbenzene* and p-*xylene* were complicated by the migration of the alkyl groups[3, 4, 5, 6] giving rise to polyethyl- and polymethylbenzenes, respectively. Although some 2,2,4-trimethylpentane reacted in each case, none of the pure alkylbenzenes formed were isolated from the complex mixtures. The molar ratio of isobutane formed to paraffin reacting (1:1 and 1:3, respectively) indicates that alkylation did occur.

In the case of *fluorene* an interesting hydro-dehydrogenation reaction involving the formation of bifluorenyl and isobutane became predominant.

$$\underset{\text{Fluorene}}{C_{13}H_{10}} + \underset{\text{2,2,4-Trimethylpentane}}{C_8H_{18}} \longrightarrow \underset{\text{Bifluorenyl}}{C_{13}H_9 \cdot C_{13}H_9} + \underset{\text{Isobutane}}{2\ i\text{-}C_4H_{10}}$$

From each mole of 2,2,4-trimethylpentane which reacted, 1.5 moles of isobutane were produced, indicating that more than half of the paraffin reacted according to the indicated equation.

In the case of hydrocarbons with condensed ring systems no alkylated products were obtained. With *naphthalene* and 2,2,4-trimethylpentane, over 80 per cent. of the latter compound was recovered unchanged although 40 per cent. of the naphthalene was converted to higher-boiling products[7]. This result was unexpected in view of the ease with which naphthalene is alkylated with olefins and alkyl halides. With *pyrene*, over 94 per cent. of the paraffin was recovered unchanged.

Whereas the data of the previous paper[2] showed the dependancy of the reaction on the structure of the particular paraffin used, the present results extend this conclusion to aromatic hydrocarbons and prove that the structure of the aromatic hydrocarbon is a no less important factor.

EXPERIMENTAL

Apparatus

The reactions were carried out in the Pyrex reaction vessel described in an earlier paper.[1] In one experiment with naphthalene at a temperature above 100°, the materials were sealed in a Pyrex tube and heated in an Ipatieff rotating autoclave.

Sources of Reagents

Merck's reagent grade of sublimed *aluminum chloride* was used without further purification. *Hydrogen chloride* was prepared in our laboratory and stored in small steel cylinders *Toluene* and *ethylbenzene*, from J. T. Baker Chemical Company were C.P. products. p-*Xylene*, *fluorene*, and *pyrene*, from the Gesellschaft für Teer-

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[3] MUNDICI, *Gazz. chim. ital.*, **34,** II, 121 (1904).

[4] HEISE, AND TÖHL, *Ann.*, **270,** 169 (1892).

[5] ANSHÜTZ, *Ann.*, **235,** 182 (1886).

[6] JACOBSEN, *Ber.*, **18,** 342 (1885).

[7] *Cf.* HOMER, *J. Chem. Soc.*, **91,** 1105 (1907).

verwertung, Duisburg-Meiderich, Germany, were pure products with correct melting points. *Naphthalene*, C.P. and *biphenyl*, practical grade, m.p. 67.5–69°, were from the Eastman Kodak Company. *2,2,4-Trimethylpentane* was from Röhm and Haas Company, b.p. 99.37°, m.p. −107.6°, d_4^{20} 0.6920, n_D^{20} 1.3915.

Reaction Products

Condensible gases were collected in dry-ice traps after removal of excess hydrogen chloride in a weighed soda-lime absorber. These liquefied gases were analyzed by low-temperature fractionation in a Podbielniak column and were always found to be chiefly isobutane containing a trace of higher-boiling liquid carried over with the gas stream. Gases not condensed at −78° were collected in a gas bottle over salt water; these consisted almost entirely of displaced nitrogen from the apparatus.

The products remaining in the reaction vessel always separated into two layers. In case the *upper layer* was liquid at room temperature, it was separated, washed thoroughly with water, dried and fractionated in a high-temperature Podbielniak column. It consisted of a mixture of aromatic hydrocarbons along with any unchanged 2,2,4-trimethylpentane. The quantity of the latter was determined by shaking the appropriate fractions (in a volume ratio of 1:1) first with 100% sulfuric acid, then with acid containing 15% of free sulfur trioxide until the residual hydrocarbon gave no reaction with nitrating mixture.

TABLE I

IDENTIFICATION OF HYDROCARBONS

HYDROCARBON	DERIVATIVE OR METHOD OF IDENTIFICATION
Benzene	Melting point; *m*-dinitrobenzene
m-Diethylbenzene	2,4,6-Trinitro-1,3-diethylbenzene
Durene	Mixture melting point
m-tert.-Butyltoluene	2,4,6-Trinitro-3-tert.-butyltoluene
p-tert.-Butylbiphenyl	Mixture melting point; C and H analysis
Bifluorenyl	C and H analysis

The *lower layers* were carefully treated with water, the resulting oil was extracted with ether, and distilled. These oils distilled over a wide range, and considerable material remained as residue at 350°. The higher fractions varied in color from yellow to orange and were unsaturated to permanganate solution.

In the reactions where solid aromatic hydrocarbons were used, the upper layers were solid or partially solid at room temperature. In these cases the reaction mixture was first steam-distilled. Any gas evolved during the steam distillation was collected and analyzed. The solid and liquid products were dried and fractionated, the higher-boiling material being distilled under reduced pressure.

The methods used for identifying individual hydrocarbons in narrow boiling fractions are indicated in Table I.

The quantities of starting materials and recovered products as well as the conditions used in each experiment are recorded in Table III.

1. Reaction of 2,2,4-timethylpentane with toluene.—A mixture of toluene (41.4 g.) and aluminum chloride (6.0 g.) was heated by means of a boiling water bath. This was mechanically stirred, while a second mixture consisting of toluene (41.4 g.) and 2,2,4-trimethylpentane (51.4 g.) was introduced dropwise over a period of 3 hours.

Heating was continued for 5 hours. Throughout the entire 8 hours, a slow, continuous stream of dry hydrogen chloride was introduced.

The progress of the reaction, which proceeded gradually, could be followed by observing the rate at which condensible gas was formed.

Low-temperature Podbielniak fractionation of the condensed gas showed the following composition (% by volume): isobutane 90.5%, *n*-butane 5.8%, above butane 3.7%.

High-temperature Podbielniak fractionation of the upper layer gave 17.3 grams of a fraction boiling at 185–190° at 747 mm. and having n_D^{20} 1.4928. Intensive nitration of this material gave a liquid which crystallized on the addition of absolute alcohol. Repeated crystallization gave beautiful pale-yellow crystals having a strong odor of musk and melting at 96–96.5°. The melting point of 2,4,6-trinitro-3-*tert.*-butyltoluene is 96–97°.[8]

Anal. Calc'd for $C_{11}H_{13}N_3O_6$: N, 14.84. Found: N, 14.35.

These results establish the presence of appreciable quantities of *m*-*tert.*-butyltoluene in this fraction. The remainder of this fraction probably consists of the *p*-isomer.[9]

TABLE II

CHARACTER OF LOWER LAYER

FRACTION	BOILING RANGE, °C.	VOLUME, CC.	n_D^{20}	REMARKS
1	70–132	5.4	1.4827	Saturated to $KMnO_4$. Colorless; aromatic hydrocarbons.
2	132–204	1.0	1.5019	Decolorizes $KMnO_4$ slowly. Yellow; aromatic hydrocarbons.
3	204–368	5.6	1.5799	Decolorizes $KMnO_4$ rapidly. Orange.
Residue		(1.86 g.)		Black

The character of the lower layer is indicated by the data on the oil obtained by treatment of the material with water and extraction with ether (Table II).

2. Reaction of 2,2,4-trimethylpentane with biphenyl.—During a period of 2 hours, 45.6 g. of 2,2,4-trimethylpentane was allowed to fall dropwise into a mechanically-stirred mixture of 123.2 g. of molten biphenyl and 5.3 g. of aluminum chloride, heated in a water bath at 90–95°. A slow, continuous stream of hydrogen chloride was introduced. Reaction proceeded as rapidly as the paraffin was added and the heating and stirring was discontinued 10 minutes after the addition was complete. The major portion of unchanged biphenyl was then steam distilled from the reaction mixture.

The condensed gas (25.5 g.) showed the following composition by low temperature Podbielniak fractionation (% by volume): isobutane 95.5%, butylenes 0.7%, above butane 3.8%. A small quantity of gas (1.2 g.) liberated during the steam distillation was evidently butane, as it was paraffinic and showed a carbon index of 3.9.

The oily residue (80 g.) from the steam distillation was fractionated at diminished pressure to yield 30 g. of biphenyl; 4 g. of intermediate fraction boiling at 100–122°/2

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[8] BAUR, *Ber.*, **24**, 2836 (1891).

[9] *Cf.* SHOESMITH AND MCGECHEN, *J. Chem. Soc.*, **1930**, 2231–6.

TABLE III

DESTRUCTIVE ALKYLATION

Aromatics with 2,2,4-Trimethylpentane. Catalyst: Aluminum Chloride + Hydrogen Chloride

AROMATIC	TIME, HRS.	TEMP., °C.	MAXIMUM PRESSURE, ATM.	QUANTITIES OF MATERIALS CHARGED								RECOVERED STARTING MATERIALS				HYDROGEN CHLORIDE		REACTING AROMATIC		(DIFF.) PARAFFIN		MOLAR RATIO OF REACTING MATERIALS PARAFFIN AROMATIC	GAS, GRAMS (HYDROCARBON PORTION)	UPPER LAYER, GRAMS	LOWER LAYER, GRAMS	REACTION PRODUCTS AND APPROXIMATE YIELDS, GRAMS
				Aromatic		Paraffin		Aluminum Chloride		Hydrogen Chloride		Aromatic		Paraffin												
				Grams	Moles	Grams	Moles	Grams	Moles	Grams	Moles	Grams	Moles	Grams	Moles	Grams	Moles	Moles	%	Moles	%					
Toluene	8	96	1	82.8	0.90	51.4	0.45	6.0	0.045	1.25	0.034	51.5	0.56	9.7	0.085	0.27	0.007	0.34	38	0.365	81	1.1	25.4	90.2	24.5	*i*-Butane, 22.1; *n*-butane, 1.4; monobutyltoluene, 17.3; (*m-tert.*-butyltoluene. identified).
Ethylbenzene	7	100	1	95.4	0.90	51.4	0.45	6.0	0.045	2.02	0.055	34	0.32	18	0.16	1.19	0.033	0.58	64	0.29	64	0.50	20.7	108.4	23.8	*i*-Butane, 18.9; *n*-butane, 0.0; diethylbenzene, 20; benzene, 20; (no individual alkylation prod. definitely identified).
p-Xylene	22.5	100	1	85.0	0.80	45.6	0.40	5.35	0.040	1.10	0.030	42*	0.40	27.5	0.24	0.27	0.007	0.40	50	0.16	40	0.40	13.21	101.82	19.11†	*i*-Butane, 12.1; toluene, 9.6; trimethylbenzene, 9.1; (durene identified; no individual alkylation prod. definitely identified).
Biphenyl	2.2	90–95	1	123.2	0.80	45.6	0.40	5.3	0.040	0.67	0.018	87	0.57	1.8	0.016	0.22	0.006	0.23	29	0.38	95	1.7	26.7	—	—	*i*-Butane, 24.9; isomeric monobutylbiphenyls, 28.5.
Fluorene	22	95–100	1	90.8	0.55	31.2	0.27	3.64	0.027	1.09	0.030	65	0.39	16.6	0.15	0.65	0.018	0.16	29	0.13	47	0.81	11.75	—	—	*i*-Butane, 10.8; bifluorenyl isolated; (no alkylation products identified).

Naphthalene	7	100	1	155.8	1.22	69.4	0.61	8.2	0.061	0.15	0.004	—	—	57.8	0.51	0.12	0.003	—	—	0.10	17	—	0.9	—	—	Butanes, 0.7; (no alkylation products).
Naphthalene	15 2	125 150	(Sealed tube)	104.3	0.82	46.5	0.41	4.5	0.034	<1.0	<0.03	62.1	0.49	35.6	0.31	—	—	0.33	40	0.10	23	0.30	>2	—	—	*i*-Butane >2; β,β′-binaphthyl identified; (no alkylation products identified).
Pyrene	20	100	1	50.5	0.25	28.5	0.25	3.32	0.025	0.56	0.015	—	—	26.8	0.24	0.18	0.005	—	—	0.01	6	—	0.08	—	—	*i*-Butane, 0.08.

* Includes isomerized xylene (*i.e.* *m*-xylene).

† Black solid.

mm.; 28.5 g. of a water-white liquid boiling at 122–125°/2 mm., n_D^{20} 1.5757; 8 g. of yellow, viscous liquid boiling at 125–162°/2 mm., n_D^{20} 1.5714; and 8.5 g. of a dark-brown, solid residue.

The fraction distilling at 122–125°/2 mm. crystallized to a white solid on standing for several days at −30°, but again liquefied on warming to room temperature. By low-temperature crystallization from pentane, 27% of this fraction was obtained as a white, crystalline solid, which, after several crystallizations from absolute alcohol, melted sharply at 53.1°. A photomicrograph of a single crystal is shown in Figure I.

The well-developed flat prisms show double refraction with straight extinction; their symmetry is probably not greater than rhombic.

Anal. Calc'd. for $C_{16}H_{18}$: C, 91.43; H, 8.57. Found: C, 91.21; H, 8.82.

This compound proved to be identical with a compound synthesized from *p*-bromo-*tert.*-butylbenzene and phenyllithium and is therefore identified as p-tert.-*butylbiphenyl*. The yield by this latter reaction was poor (about 5%), the chief products being *tert.*-butylbenzene, biphenyl, and a high-boiling resinous material. The synthetic compound melted at 51–2° and this melting point was not depressed by addition of the crystalline alkylation product.

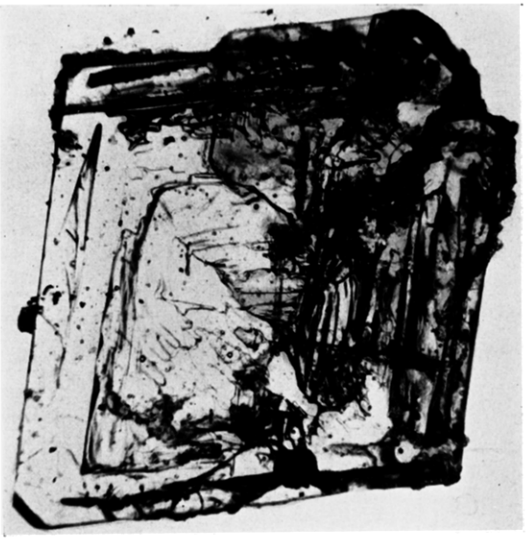

FIGURE I.—*p-tert.*-BUTYLBIPHENYL. MAGNIFICATION 24×

The liquid alkylation product as obtained by distillation is most likely a mixture of isomeric *tert.*-butylbiphenyls. It corresponds to 35% of the reacting 2,2,4-trimethylpentane.

3. Reaction of 2,2,4-trimethylpentane with fluorene.—A mechanically-stirred mixture of 2,2,4-trimethylpentane (31.2 g.), fluorene (90.8 g.) and aluminum chloride (3.64 g.) was heated at a temperature of 95–100°, while a slow continuous stream of dry hydrogen chloride was introduced. Gas evolution was slow, and was apparently complete after 22 hours. At the end of this time the mixture was steam-distilled.

The following composition of the condensed gas (10.65 g.) was indicated by low-temperature Podbielniak fractionation (% by volume): isobutane 91.5, isopentane

5.3, above pentane 3.2. The gas from the steam distillation (1.0 g.) was paraffinic, and had a carbon index of 4.1.

The liquid portion of the steam distillate was identified as unchanged 2,2,4-trimethylpentane, the solid as unchanged fluorene.

The residue from the steam distillation amounted to 25.3 g. of a hard, black solid, which dissolved completely in benzene. It was distilled under diminished pressure to give 2.9 g. of unchanged fluorene; 0.7 g. of an intermediate yellow, liquid fraction distilling at 155–210°/0.2 mm.; 6.8 g. of a clear, red-brown resin boiling at 210–240°/0.2 mm.; and 14.8 g. of residue, consisting of a hard brownish-black resin which deposited crystals from benzene solution.

The fraction boiling at 210–240°/0.2 mm. crystallized readily from benzene, giving, after several crystallizations, pure, white, fine needles melting at 230.2° to 230.7°. The compound is sparingly soluble in benzene. Its composition corresponds to *bifluorenyl.*

Anal. Calc'd for $C_{26}H_{18}$: C, 94.50; H, 5.50.
Found: C, 94.6; H, 5.51.

4. Reaction of 2,2,4-Trimethylpentane with ethylbenzene, p-*xylene, naphthalene, and pyrene.*—Data on the conditions of the attempted reaction of 2,2,4-trimethylpentane with each of these four aromatic hydrocarbons are included in Table III.

ACKNOWLEDGMENT

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SUMMARY

2,2,4-Trimethylpentane has been caused to react with various aromatic hydrocarbons with the use of aluminum chloride as catalyst.

1) With *toluene* and with *biphenyl,* the destructive alkylation reaction occurred, giving isobutane and about 35 per cent. of the mono *tert.*-butyl aromatic. *m-tert.*-Butyltoluene and *p-tert.*-butylbiphenyl have been definitely identified.

2) With *ethylbenzene* and p-*xylene* the alkylation reaction was complicated by migration of the ethyl and methyl groups, giving polyethyl and polymethyl aromatics.

3) *Fluorene* and 2,2,4-trimethylpentane underwent a hydrodehydrogenation reaction, giving bifluorenyl and isobutane.

4) In the case of the polynuclear aromatic hydrocarbons, *naphthalene* and *pyrene,* no alkylation could be established and substantially all of the paraffin could be recovered unchanged.