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

Isomerization Accompanying the Alkylation of Benzene with 1-Chloro-3,3- and with 2-Chloro-2,3-dimethylbutane[1]

BY LOUIS SCHMERLING AND J. P. WEST

RECEIVED OCTOBER 23, 1953

Alkylation of benzene with the *t*-hexyl chloride, 2-chloro-2,3-dimethylbutane, in the presence of aluminum chloride or zirconium chloride yields hexylbenzene which is principally the secondary isomer, 2,2-dimethyl-3-phenylbutane (I). When the alkylation is carried out in the presence of ferric chloride or of a nitromethane solution of aluminum chloride, on the other hand, the product is chiefly the *t*-hexylbenzene, 2,3-dimethyl-2-phenylbutane (II). Similarly, alkylation of benzene with the primary chloride, 1-chloro-3,3-dimethylbutane, yields I when aluminum chloride, aluminum bromide or zirconium chloride is used as catalyst, and II when ferric chloride or the nitromethane solution of aluminum chloride is used as catalyst. Treatment of II or of 1,4-bis-(1,1,2-trimethylpropyl)-benzene (IV) in the presence of aluminum chloride results in formation of I. It may be concluded that contrary to general opinion the aluminum chloride-catalyzed alkylation of benzene tends to yield *s*-alkylbenzene rather than *t*-alkylbenzene as the major product. The mechanism of the reaction is discussed.

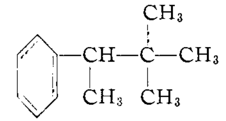
It has long been known that isomerization accompanies the alkylation of benzene with alkyl halides in the presence of aluminum chloride. Indeed, shortly after the discovery of this reaction by Friedel and Crafts,[2] Gustavson[3] reported that the aluminum chloride-catalyzed reaction of *n*-propyl bromide with benzene yields isopropylbenzene. Similarly, the principal product of the reaction of benzene with isobutyl chloride or bromide was found to be *t*-butylbenzene.[4]

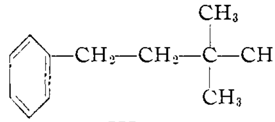
Based on these and similar results, the generalization has been made that alkylation with a primary alkyl halide will yield a secondary alkylbenzene if the alkyl halide contains only primary and secondary carbon atoms, and a tertiary alkylbenzene if it contains a tertiary carbon atom. The extrapolation has even been so made[5] as to give the erroneous conclusion that alkylation of benzene with *n*-butyl chloride yields *t*-alkylbenzene; actually, a mixture of *n*- and *sec*-butylbenzene is produced.

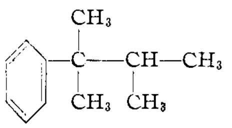
The only alkyl halide which has thus far been shown[6] to undergo carbon skeleton rearrangement (*i.e.*, rearrangement involving migration of a methyl or other alkyl group) during the alkylation of benzene in the presence of aluminum chloride is neopentyl chloride; even with this alkylating agent, the product is 2-methyl-3-phenylbutane rather than 2-methyl-2-phenylbutane (*t*-pentylbenzene). Isobutyl halides and *t*-butyl halides seem to be the only alkyl halides which yield *t*-alkylbenzene as the major reaction product when aluminum chloride is used as catalyst. Not more than about 20% of the pentylbenzene obtained with *t*-pentyl chloride at 25–30° was *t*-pentylbenzene, the remainder being a mixture of isomeric compounds believed to consist chiefly of 1-phenyl-2-methylbutane and 2-methyl-3-phenylbutane.[7] On the other hand, when either aluminum chloride dissolved in nitromethane or ferric chloride was used as catalyst, the product consisted of very pure *t*-pentylbenzene.

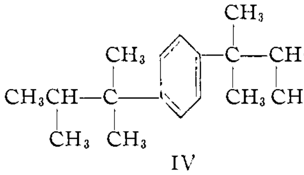
It is the purpose of the present paper to show that the non-formation of *t*-alkylbenzenes as the principal product in the presence of aluminum chloride and certain other Friedel–Crafts catalysts seems to be the general rule rather than the exception.

Alkylation of benzene with a *t*-hexyl chloride, 2-chloro-2,3-dimethylbutane, in the presence of aluminum chloride at 1° resulted in a 62% yield of hexylbenzene which consisted of the secondary hexylbenzene, 2,2-dimethyl-3-phenylbutane (I), mixed with about 10% of the tertiary isomer, 2,3-dimethyl-2-phenylbutane (II). This unexpected rearrangement also occurred with zirconium chloride. On the other hand, when the reaction was carried out at room temperature in the presence of ferric chloride or of a nitromethane solution of aluminum chloride, the product was the practically pure *t*-hexylbenzene II.


I


III


II


IV

The secondary hexylbenzene I was also the major product of the alkylation of benzene with the primary chloride, 1-chloro-3,3-dimethylbutane, in the presence of aluminum chloride at 2° or at 42° or of zirconium chloride at 85°. None of the primary alkylbenzene, 3,3-dimethyl-1-phenylbutane (III), seemed to be present. Hexane (predominantly 2,3-dimethylbutane) was isolated in 7–15% yield as a by-product of the reaction carried out in the presence of aluminum chloride.

In contrast, the use of ferric chloride or of a nitromethane solution of aluminum chloride as catalyst for the reaction of benzene with the primary chloride at the reflux temperature (83–84°) resulted in 6 and 35% yields, respectively, of hexylbenzene which was chiefly II.

Definite proof that the product obtained by the

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[1] Presented before the Division of Petroleum Chemistry of the American Chemical Society at the Chicago Meeting, September, 1953.

[2] C. Friedel and J. M. Crafts, *Bull. soc. chim.*, [2] **27**, 530 (1877); *Compt. rend.*, **84**, 1392, 1459 (1877).

[3] G. Gustavson, *J. Russ. Phys.-Chem. Soc.*, **10**, 269 (1877); *Ber.*, **11**, 1251 (1878); M. Konowaloff, *J. Russ. Phys.-Chem. Soc.*, **27**, 457 (1895).

[4] (a) J. Schram, *Monatsh.*, **9**, 613 (1888); (b) M. Senkowski, *Ber.*, **23**, 2413 (1890).

[5] N. O. Calloway, *Chem. Revs.*, **17**, 327 (1935).

[6] H. Pines, L. Schmerling and V. N. Ipatieff, THIS JOURNAL, **62**, 2901 (1940).

[7] M. Inatome, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **74**, 292 (1952).

reaction of benzene with the chlorohexanes in the presence of aluminum chloride is I was obtained by synthesizing the hexylbenzene by the reaction of *t*-butylmagnesium chloride with (1-bromoethyl)-benzene. The hexylbenzene which was obtained was shown to be identical with I by its infrared spectrum and by means of crystalline derivatives.

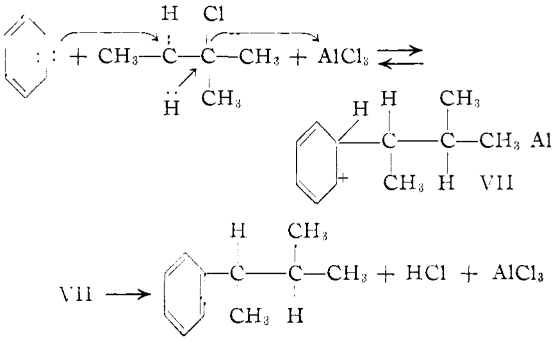
Alkylation of benzene with 2,3-dimethyl-2-butene in the presence of sulfuric acid at ice-bath temperature resulted in a 17% yield of II together with a 25% yield of dihexylbenzene. Since the dihexylbenzene was crystalline, it is probable that its formation was analogous to the formation of crystalline *p*-di-*t*-butylbenzene by the reaction of isobutylene with benzene under similar conditions and that it was 1,4-bis-(1,1,3-trimethylpropyl)-benzene (IV). With hydrogen fluoride as catalyst, the alkylation of benzene with 2,3-dimethyl-2-butene produced II and IV in 50 and 32% yields, respectively.

It has been indicated that the *p*-*t*-dodecyltoluenes obtained by the alkylation of toluene with propylene tetramer in the presence of sulfuric acid may be isomerized to *m*-*sec*-dodecyltoluenes by treatment with aluminum chloride.[8] Similarly, the action of aluminum chloride on II at room temperature resulted in a 70% yield of substantially pure I. Furthermore, the monohexylbenzene which was obtained in 52% yield by the reaction of the crystalline dihexylbenzene IV with benzene in the presence of aluminum chloride at room temperature also consisted of I of at least 98% purity. On the other hand, the reaction of IV in the presence of ferric chloride resulted in a 41% yield of monohexylbenzene which was principally II. It is again obvious that aluminum chloride favors the formation of a secondary alkylbenzene, whereas ferric chloride yields the tertiary isomer.

Alkylation of benzene with *t*-pentyl chloride in the presence of aluminum chloride at ice temperature resulted in a somewhat lower (43% instead of 52%) yield of pentylbenzene than had been obtained[7] at room temperature. Infrared analysis of the product indicated that it consisted of 2-methyl-3-phenylbutane (V) mixed with not more than 15% of *t*-pentylbenzene (VI). A similar mixture was obtained by the reaction with isopentyl bromide under the same conditions; infrared analysis showed that no isopentylbenzene was present. The formation of a mixture of isopentylbenzene, V and VI by the alkylation of benzene with isopentyl chloride was reported in an early investigation in which side-chain nitration of the products was used to determine their structures.[9]

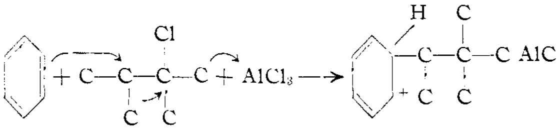
The Alkylation Mechanism

It is obvious that any mechanism offered to explain the alkylation of benzene with *t*-alkyl halides in the presence of aluminum chloride must show why the product is not the expected *t*-alkylbenzene. At first thought it would seem obvious that the mechanism cannot involve the intermediate formation of *t*-alkyl cations since these are the most stable and should yield the corresponding *t*-alkylbenzene. The formation of the product can be explained without using carbonium ions by assuming that the reaction occurs by way of a concerted molecular nucleophilic displacement reaction[10]



The driving force for elimination of the chlorine atom is the reaction with a molecule of aluminum chloride to form $AlCl_4^-$. It is suggested that substitution takes place at the secondary carbon atom rather than the tertiary atom because backside attack by the approaching phenyl group is more difficult at a tertiary carbon atom.

Alkylation with the tertiary hexyl chloride may be similarly indicated



VIII

$$\text{VIII} \longrightarrow \text{I} + HCl + AlCl_3$$

The displacement may be a bimolecular reaction (S_N2) involving the reaction of the alkyl chloride with a complex of benzene and aluminum chloride[10] or of benzene with a complex of the alkyl chloride and the catalyst.[11] However, such a displacement mechanism involves two simultaneous S_N2 displacements, *i.e.*, two Walden inversions on adjacent carbon atoms. The benzene displaces a hydride ion from one carbon atom and the hydride ion displaces the chloride ion from the adjacent carbon atom. Since the bulky entering and leaving groups are adjacent, reaction by this mechanism seems unlikely.

Moreover, it was pointed out[11] that while alkylation with primary alkyl chlorides is probably a bimolecular displacement reaction, alkylation with *t*-alkyl halides is more likely a carbonium ion reaction in view of the ease with which *t*-alkyl ions are believed to be formed in the presence of catalysts of the Friedel–Crafts type. If this quite reasonable assumption be accepted, the formation of the *sec*-alkylbenzenes from *t*-alkyl chlorides may be explained by assuming that the mechanism involves the intermediate formation of the *t*-alkylbenzene by reaction with the *t*-alkyl ion, followed by isomerization of this intermediate.

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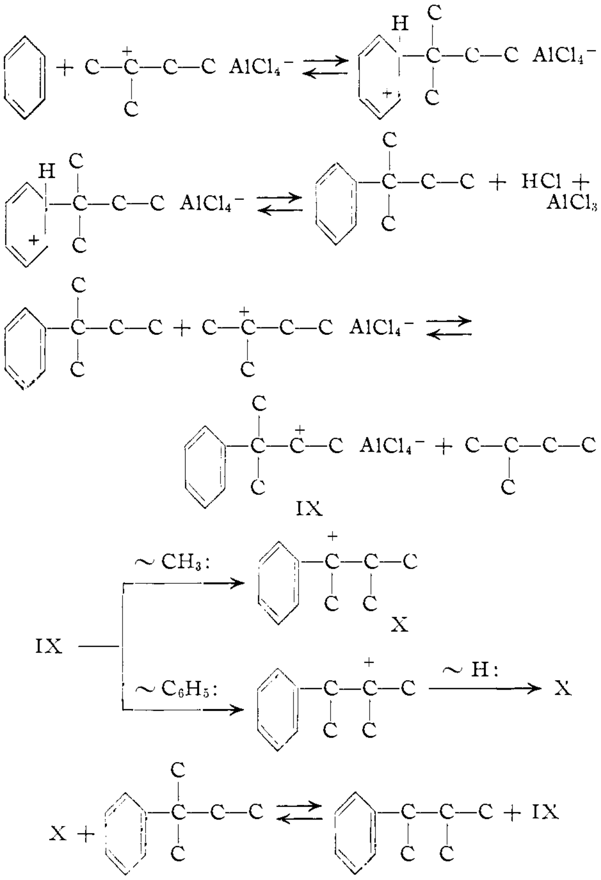
[8] H. S. Bloch and G. L. Hervert, paper presented before the Division of Petroleum Chemistry of the American Chemical Society at the Chicago Meeting, Sept., 1953.

[9] M. Konwaloff and J. Egoroff, *J. Russ. Phys.-Chem. Soc.*, **30**, 1031 (1898).

[10] L. Schmerling, *Ind. Eng. Chem.*, **45**, 1447 (1953).

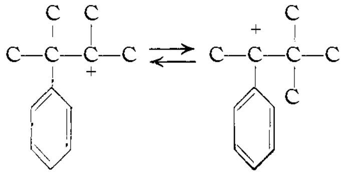
[11] H. C. Brown, L. P. Eddy, W. J. Wallace, M. Grayson and K. L. Nelson, *ibid.*, **45**, 1462 (1953).



IX starts a new cycle and the reaction resulting in the formation of isopentane is a chain-initiating reaction only.

Isomerization of IX to X occurs because the latter (a benzyl cation) is the more stable, being stabilized by resonance involving the benzene ring. Hence, secondary alkylbenzenes are the preferred products when possible.

Similarly, for the alkylation with 2-chloro-2,3-dimethylbutane, the following isomerization may be involved.

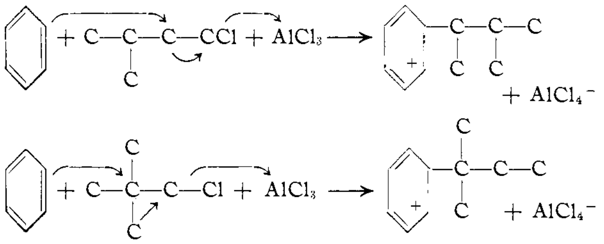


It is to be expected that abstraction of the hydride ion from the tertiary carbon atom of the hexylbenzene takes place more readily than abstraction of one of the hydrides from the secondary carbon atom of the *t*-pentylbenzene; this explains why zirconium chloride yields chiefly the *sec*-hexylbenzene (I) and the *t*-pentylbenzene (VI).

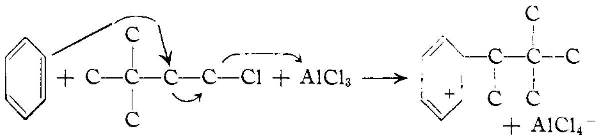
Postulation of the isomerization of the alkylbenzene has the advantage that it shows why *t*-alkyl chlorides yield *sec*-alkylbenzenes with aluminum chloride but not with nitromethane solutions of aluminum chloride; the former is a very active catalyst for the isomerization of saturated hydrocarbons, while the latter does not seem to be a sufficiently strong acid to cause isomerization of paraffins or cycloparaffins even at 70°.[12] Similarly, zirconium chloride which produced I with the *t*-hexyl chloride is a good isomerization catalyst for saturated hydrocarbons.[13] On the other hand, ferric chloride which yielded II is not an isomerization catalyst at the moderate temperatures employed in the alkylation.

Furthermore, the step which initiates the isomerization chain explains the formation of the small amount of paraffin corresponding to the alkyl chloride which is often obtained as by-product in the alkylation of benzene.

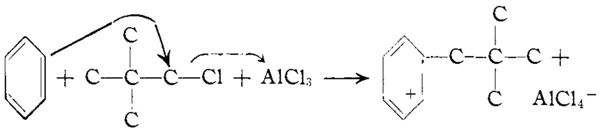
More information is necessary in order to decide whether alkylation with a primary alkyl halide containing (1) a tertiary carbon atom and a secondary carbon atom (*e.g.*, isopentyl chloride) or (2) a *gem*-dimethyl group (*e.g.*, neopentyl chloride or 1-chloro-3,3-dimethylbutane) in the presence of aluminum chloride proceeds by a displacement (S_N) mechanism or by a carbonium ion mechanism (S_E). The former mechanism may be illustrated by



(Isomerization of the intermediate *t*-pentylbenzene yields 2-methyl-3-phenylbutane)



Besides being subject to the objection that it involves two Walden inversions on adjacent carbon atoms, this mechanism seems unlikely because it does not explain the fact that there is formed little or none of the primary alkylbenzene (*e.g.*, isopentylbenzene, neopentylbenzene and 3,3-dimethyl-1-phenylbutane, respectively) which would be expected by the direct displacement of the chlorine in the three chlorides by the benzene; for example, alkylation with neopentyl chloride



While isopentylbenzene (which contains a relatively easily abstracted hydrogen atom attached to a tertiary carbon atom) might be expected to isomerize to 2-methyl-3-phenylbutane, both neopentylbenzene and 3,3-dimethyl-1-phenylbutane are stable and would be isolated.

The carbonium ion mechanism involves rearrangement to *t*-alkylcarbonium ions, and hence formation of *t*-alkylbenzenes which isomerize to yield the final product

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(12) L. Schmerling, *Ind. Eng. Chem.*, **40**, 2072 (1948).

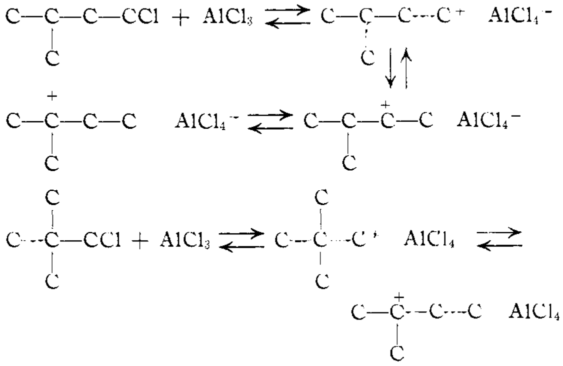
(13) Unpublished results, these laboratories.

TABLE I

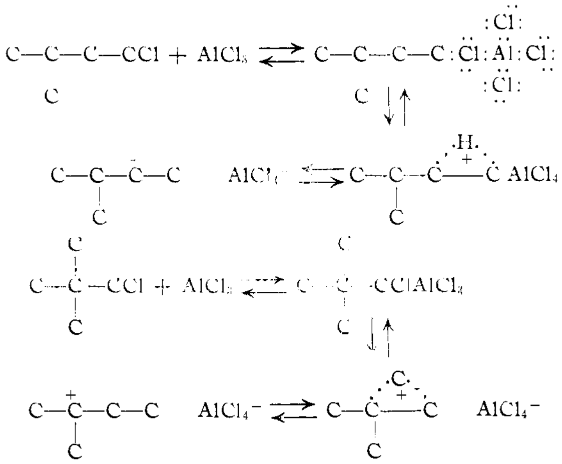
ALKYLATION OF BENZENE

Method	Reactants, moles C_6H_6	Reactants, moles Alk. agt.	Catalyst Kind	Catalyst g.	Ave. temp., °C.	Duration, hr.	Monoalkylbenzene Composition	Yield, %
			With 2-chloro-2,3-dimethylbutane					
A	1.54	0.15	$AlCl_3$	3	1	1	90% I, 10% II	62
R	0.46	.14	$ZrCl_4$	3	85	8	85% I, 15% II	62
E[a]	0.41	.03	$AlCl_3$[b]	1[b]	29	1	98% II, 0% I	62
A	1.54	.14	$FeCl_3$	3	28	..[c]	100% II	71
			With 1-chloro-3,3-dimethylbutane					
A	5.15	1.02	$AlCl_3$	20	2	4	100% I	49[d]
A	2.56	0.50	$AlCl_3$	10	42	1	85% I, 15% II	53[e]
A	1.67	.33	$AlBr_3$	5	2	4	95% I, 5% II	47
R	1.54	.33	$ZrCl_4$	8	85	2	85% I, 15% II	56
R	1.60	.25	$AlCl_3$[f]	3[f]	83	2	6% I, 94% II	35
R	1.02	.20	$FeCl_3$	5	84	2	10% I, 90% II	6
			With 2,3-dimethyl-2-butene					
A	2.56	0.48	H_2SO_4	80	2	2	100% II	17[g]
A	2.05	0.38	HF	70	...[h]	1	100% II	50[i]
			With 2,3-dimethyl-2-phenylbutane (II)					
E	0.13	0.06	$AlCl_3$	3	22	4	100% I	70
			With 1,4-bis-(1,1,2-trimethylpropyl)-benzene (IV)					
E	0.17	0.03	$AlCl_3$	1	22	4	98% I, 2% II	52
E	0.17	0.03	$FeCl_3$	1	22	4	6% I, 94% II	41
			With 2-chloro-2-methylbutane					
A	5.18	1.13	$AlCl_3$	20	1	3	85% V, 15% VI	43
R	1.55	0.35	$ZrCl_4$	3	89	8	15% V, 85% VI	71
A	1.50	0.43	BF_3	..[j]	33	2	100% VI	28
			With 1-bromo-3-methylbutane					
A	5.15	1.00	$AlCl_3$	10	1	3	85% V, 15% VI	7[k]

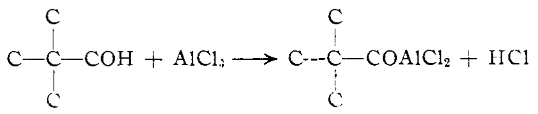
[a] Not shaken. [b] Dissolved in 2 g. of nitromethane. [c] The solution of chlorohexane in benzene was added at 0° during 2 hours after which the temperature was permitted to rise to 28° during 1.5 hours. [d] Also 7% hexane identified as principally 2,3-dimethylbutane by its boiling point and by photobromination to crystalline 2,3-dibromo-2,3-dimethylbutane. [e] Also 15% hexane shown by infrared analysis to consist of 94% 2,3- and 6% 2,2-dimethylbutane. [f] Dissolved in 5 g. of nitromethane. [g] Also 25% IV. [h] Not determined. Carried out in copper flask immersed in ice-water. [i] Also 32% IV. [j] Not determined. Boron fluoride was bubbled into the flask during the addition of the *t*-pentyl chloride. [k] The infrared spectrum of the recovered pentyl bromide indicated that it contained no 2-bromo-3-methylbutane.



A possible objection to this carbonium ion mechanism, the intermediate formation of primary carbonium ions, may be overcome by substituting nonclassical ions.[14]



While there is some question as to whether alkylation with these primary alkyl chlorides is an S_E or an S_N reaction, it seems quite probable that the alkylation of benzene with primary alcohols (at least) in the presence of aluminum chloride is a bimolecular displacement reaction.[10] For example, with neopentyl alcohol, the product is neopentylbenzene[6] rather than either *t*-pentylbenzene or 2-methyl-3-phenylbutane



$$C{-}C(C)_2{-}COH + AlCl_3 \longrightarrow C{-}C(C)_2{-}COAlCl_2 + HCl$$

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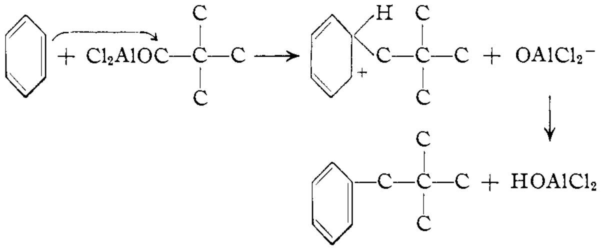
[14] *Cf.* S. Winstein and B. K. Morse, THIS JOURNAL, **74**, 1133 (1952).

TABLE II

PHYSICAL PROPERTIES OF THE HEXYLBENZENES

	Alkylbenzene	B.p.,		B.p. at 760 mm.,			Mol. ref.		Analyses, %			
									Calcd.		Found	
		°C.	Mm.	°C.[a]	$n^{20}D$	d^{20}_4	Calcd.	Obsd.	C	H	C	H
(I)	$PhCHMeCMe_3$[b]	105	31	205[c]	1.4954	0.8745	54.05	54.17	88.82	11.18	88.92	11.21
(II)	$PHCMe_2CHMe_2$[d]	66	4.3	210[e]	1.4995	0.8843	54.05	53.96	88.82	11.18	88.80	11.16
(IV)	$Ph(CMe_2CHMe_2)_2$	138	6.0	294[f]	....	....	...	...	87.73	12.27	87.40	12.38

[a] Calculated from boiling point under reduced pressure using Lippincott nomograph, *Ind. Eng. Chem.*, **38**, 320 (1946). [b] R. C. Huston and S. A. Kaye, THIS JOURNAL, **64**, 1577 (1942), report b.p. 205–207° (760 mm.), $n^{25}D$ 1.4942, d^{25}_4 0.8763 for the product prepared by the alkylation of benzene with 3,3-dimethyl-2-butanol (pinacolyl alcohol) in the presence of added hydrogen chloride and aluminum chloride. [c] B.p. determined in Cottrell reboiler (J. H. Bruun and M. M. Hicks-Bruun, *Bur. Standards J. Research*, **6**, 871 (1931), 74.6° (10 mm.) and 204.4° (743.8 mm.). [d] R. C. Huston, W. B. Fox and M. N. Binder, *J. Org. Chem.*, **3**, 251 (1938), report b.p. 209–210° (745 mm.), $n^{20}D$ 1.4988, d^{20}_4 0.8814 for the product prepared by the alkylation of benzene with 2,3-dimethyl-2-butanol in the presence of aluminum chloride. [e] B.p. in Cottrell reboiler, 81.0° (10 mm.) and 212° (745.6 mm.). [f] M.p. 92–93°.



Experimental

Materials.—1-Chloro-3,3-dimethylbutane was synthesized by the condensation of *t*-butyl chloride with ethylene in the presence of aluminum chloride.[15] 2-Chloro-2,3-dimethylbutane was prepared by bubbling hydrogen chloride through 2,3-dimethyl-2-butene dissolved in *n*-pentane at −78°; b.p. 42–43° (68 mm.), 109–110° (760 mm.), $n^{20}D$ 1.4191. 2,3-Dimethyl-2-butene was obtained by fractionating the hexene formed by dehydrochlorinating 1-chloro-3,3-dimethylbutane by passing it over soda lime at 300–350°; b.p. 72–73°, $n^{20}D$ 1.4128.

Procedures.—Three general procedures were used, resulting in the data summarized in Table I.

Method A.—A solution of the alkylating agent in about one-third of the total amount of benzene used was added slowly to a stirred mixture of the remainder of the benzene and the catalyst. Stirring was continued for about 0.5–1.0 hour after all of the mixture had been added, after which the product was permitted to stand for about 10 minutes and the upper layer was separated from the catalyst layer, washed with dilute alkali and with water, dried over anhydrous potassium carbonate and distilled. The fractions were analyzed by means of their infrared spectra.[16]

Method E.—The mixture of reactants and catalyst was shaken mechanically in an erlenmeyer flask and the product was worked up as described for method A.

Method R.—The mixture of reactants and catalyst was heated under reflux and the product treated in the usual manner.

The properties of the alkylbenzenes and of their derivatives are shown in Tables II and III, respectively.

Synthesis of 2,2-Dimethyl-3-phenylbutane.—A solution of 90 g. (0.5 mole) of (1-bromoethyl)-benzene in 50 cc. of ether was added during three hours to the ice-cooled Grignard reagent prepared by the reaction of 92 g. (1.0 mole) of *t*-butyl chloride (dissolved in 200 cc. of dry ether) and 20 g. (0.8 mole) of magnesium stirred with 200 cc. of dry ether. The product was stirred at 0–1° for 0.5 hour and then permitted to warm to 15° during an additional 0.5 hour. Water was slowly added to the stirred product, the ether layer was separated, washed, dried, and distilled. There was obtained 11 g. (12% yield), b.p. 50–51° (1 mm.), $n^{20}D$ 1.4950. Refluxing over sodium removed impurities and yielded product (b.p. 70–70° at 74 mm., 202–202° at 760 mm., $n^{20}D$ 1.4950), the infrared spectrum of which indicated that it consisted of substantially pure I. It yielded a diacetamido derivative melting at 222–225°; a mixture of this derivative with that (m.p. 225–226°) of the hexylbenzene prepared by the condensation of 1-chloro-3,3-dimethylbutane with benzene in the presence of aluminum chloride also melted at 222–225°.

TABLE III

DERIVATIVES OF THE HEXYLBENZENES

Compound	M.p., °C.	Nitrogen, % Calcd.	Found
Of 2,2-dimethyl-3-phenylbutane (I)			
Diacetamido[a]	225–226	10.14	10.25
Monoacetamido[a]	134–135	6.38	6.43
Semicarbazone[b]	225–226[d]	16.07	15.62
Dinitrophenylhydrazone[c]	178–179[e]	14.57	13.77
Of 2,3-dimethyl-2-phenylbutane (II)			
Diacetamido[a]	Oil	...	...
Monoacetamido[a]	116–117[f]	...	...
Semicarbazone[b]	209–210[d]	16.07	15.84
Dinitrophenylhydrazone[c]	184–185[e]	14.57	13.95

[a] Prepared by the procedure of V. N. Ipatieff and L. Schmerling, THIS JOURNAL, **59**, 1056 (1937). [b] Semicarbazone of the methyl hexylphenyl ketone (presumably methyl 4-hexylphenyl ketone) prepared by the reaction of the alkylbenzene with acetyl chloride in the presence of aluminum chloride using the procedure described by H. Pines, A. Weizmann and V. N. Ipatieff, *ibid.*, **70**, 3859 (1948). [c] 2,4-Dinitrophenylhydrazone of the methyl hexylphenyl ketone. [d] Mixed m.p. of 1:1 mixture of derivatives of I and II, 195–196°. [e] Mixed m.p. of 1:1 mixture of derivatives of I and II, 176–177°. [f] R. C. Huston and W. T. Barrett, *J. Org. Chem.*, **11**, 657 (1946), report 118–119°.

RIVERSIDE, ILLINOIS

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[15] L. Schmerling, THIS JOURNAL, **67**, 1152 (1945).

[16] The authors are indebted to Mr. Edmond Baclawski, Physics Division, Universal Oil Products Company, for the infrared absorption analyses of the alkylbenzenes.