[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

# REARRANGEMENTS IN THE FRIEDEL-CRAFTS ALKYLATION OF BENZENE

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### INTRODUCTION

Alkylation by the Friedel-Crafts reaction usually involves rearrangement of the alkyl group. The report that n-octadecyl bromide, with benzene and aluminum chloride, gave n-octadecylbenzene as the principal product (1), was in such contrast to the behavior of the lower alkyl halides, that a further investigation of the effect of chain length on isomerization seemed advisable.

#### HISTORICAL

Alkyl halides and aluminum halides. Shortly after Friedel and Crafts (2) had obtained amylbenzene from amyl chloride with benzene and aluminum chloride, Gustavson (3) found that either isopropyl bromide or *n*-propyl bromide with benzene and aluminum chloride gave isopropylbenzene. Silva (4) confirmed this, using the two propyl chlorides. Heise (5) was the first to offer a derivative as proof of the structure of the propylbenzene obtained. He observed that at  $-2^{\circ}$ , *n*-propyl bromide with benzene and aluminum chloride gave *n*-propylbenzene, identified as its sulfonamide. Genvresse (6) obtained both *n*-propylbenzene and isopropylbenzene by conducting the reaction at reflux temperature. Konowalow (7) found that below 0° *n*-propyl chloride gave *n*-propylbenzene, while from 0° to reflux temperature it gave mixtures of *n*-propylbenzene and isopropylbenzene. More recently it has been shown that at  $-6^{\circ}$ , 60% of the monopropylbenzene was *n*-propylbenzene, and 40% was isopropylbenzene. At  $35^{\circ}$  this ratio was reversed. The relative proportions of the two isomers were determined by fractional crystallization of the diacetamino derivatives (8).

Both isopropyl chloride and *n*-propyl chloride have been found to give 1,3dimethyl-5-isopropylbenzene on reaction with *m*-xylene in the presence of aluminum chloride; the product was identified as its diacetamino derivative (9).

Gossin reported that isobutyl chloride with benzene and aluminum chloride gave a butylbenzene boiling at 166–167°, and a small amount of an alkylbenzene boiling at 152–155°. On the basis of physical properties he decided that the former was isobutylbenzene, while the latter was *t*-butylbenzene (10).<sup>1</sup> These conclusions were shown to be incorrect by Schramm (11), who found that isobutyl chloride and *t*-butyl chloride both gave *t*-butylbenzene. The product was identified as its bromo derivative. He also observed that *n*-butyl chloride gave *s*-butylbenzene, identical with the *s*-butylbenzene prepared from diethylzinc and  $\alpha$ -bromoethylbenzene (12). Whereas Kekulé and Schrötter had found that *n*-propyl bromide when refluxed with aluminum bromide gave isopropyl bro-

<sup>&</sup>lt;sup>1</sup> Kelbe and Pfeiffer, *Ber.*, **19**, 1723 (1886), likewise reported the preparation of isobutyltoluene from isobutyl bromide and toluene with aluminum bromide. They did not prove the structure of the side chain.

mide (13), and had explained Gustavson's results on this basis, Schramm found, that isobutyl chloride did not give *t*-butyl chloride with aluminum chloride. Moreover, since *t*-butyl chloride treated in this way gave butylene and hydrogen chloride, Schramm thought the olefin to be the intermediate in the Friedel-Crafts reaction. Others have reported that the isobutyl group is isomerized to *t*-butyl in reactions with aluminum chloride and benzene (7, 14) or toluene (15).

Estreicher discovered that at  $0^{\circ}$ , *n*-butyl chloride with benzene and aluminum chloride gave a mixture of *n*-butylbenzene and *s*-butylbenzene, while at reflux temperature *s*-butylbenzene appeared to be the only monobutylbenzene formed (16). Shoesmith and McGechen pointed out that Estreicher's identification of his butylbenzenes was not satisfactory. They obtained a mixture of *m*- and *p*-*s*-butyltoluenes from *n*-butyl chloride and toluene with aluminum chloride; the products were identified as their sulfonanilides (17). It has been reported that *n*-butyl chloride gave di-*n*-butylbenzene "as the first product" (18). On the other hand Calloway (19) found that *t*-butylbenzene was formed when *n*-butyl fluoride reacted with benzene and aluminum chloride, but he gave only the boiling point as evidence.

Friedel and Crafts (2) and later Austin (20) did not identify the amylbenzenes they obtained, nor is it clear which amyl chlorides they used. Essner (21) treated amylene hydrochloride and amylene with benzene and aluminum chloride, and in each case obtained a product boiling at  $185-190^{\circ}$ , which he believed to be the same as that obtained by Friedel and Crafts. He claimed to have evidence that the product was not the same as the known amylbenzene (22) or 3-phenylpentane (23); apparently the evidence was the difference in boiling points, for no other data were presented.

n-Amyl chloride with benzene and aluminum chloride "did not yield pure 2-phenylpentane." No experimental data were given (23 a).

Isoamyl chloride reacted with benzene and aluminum chloride to give a mixture of monoamylbenzenes. When this mixture was treated with nitric acid three products were obtained: one nitrated product soluble in alkali, one nitrated product not soluble in alkali, and one portion of the hydrocarbon not attacked by the acid (24). This was explained according to the following scheme.



Although this evidence is not entirely convincing, no better work has been published on this reaction.<sup>2</sup> Other interpretations could be given to the experimental results, though admittedly those advanced by the authors are most reasonable. Neopentyl chloride has been shown to give 2-methyl-3-phenylbutane,

 $(CH_3)_3 CCH_2 Cl \xrightarrow{[AlCl_3]} (CH_3)_2 CHCHC_6 H_5$  $\downarrow \\ CH_3$ 

which was identified as its diacetamino derivative. The yield was not large (24%), and the product was not pure (26).

It has been reported that 1,1-dichloroheptane with benzene and aluminum chloride gave 1-phenylheptane as well as 1,1-diphenylheptane (27). The boiling point of the heptylbenzene did not agree with that of synthetic 1-phenylheptane, however, and it is not likely that this was the product obtained.

Schreiner (28) and Halse (29) prepared a number of tertiary alkylbenzenes from tertiary alkyl chlorides. The configurations of the products were assumed to be the same as those of the reactants.

Seidel and Engelfried (30 a) prepared octadecylbenzene from n-octadecyl bromide with benzene and aluminum chloride. They prepared the sulfonamide of their product, but did not try to establish its structure. Gilman and Turck (1) later showed that this was the sulfonamide of 1-phenyloctadecane.

Kursanoff (31) treated *o*-dichlorocyclohexane with benzene and aluminum chloride and claimed, without much evidence, to have obtained *o*-diphenylcyclohexane, with probably some m- isomer. More recently *o*-dibromocyclohexane has been found to give *p*-diphenylcyclohexane and *m*-diphenylcyclohexane (32). The structures were proved by dehydrogenation with selenium to the known diphenylbenzenes.

Allyl chloride has been reported to give isopropylbenzene (4) and n-propylbenzene (33). Recently it has been found that in the presence of anhydrous aluminum chloride 1,2-diphenylpropane was obtained, while with wet aluminum chloride the products were n-propylbenzene and 9,10-diethylanthracene (34).



Ferric chloride as a catalyst gave 1,2-diphenylpropane and 2-chloropropylbenzene.

It should be noted here that Gilman, Calloway, and Turck (30 b, c) found that a number of substituted furans reacted with *n*-alkyl halides of various chain lengths to give *t*-butyl substituted furans. For example, ethyl 5-bromo-2furoate with *n*-octadecyl bromide and aluminum chloride (1.1 mole) gave a 46%

<sup>2</sup> Gleditsch (25) simply assumed that isoamyl chloride yielded t-amyl compounds.

yield of ethyl 4-t-butyl-5-bromo-2-furoate, as well as 32% of isobutane and 7% of butane. With benzene, *n*-octadecyl bromide and other *n*-alkyl halides have been shown not to undergo such extensive rearrangement using aluminum chloride.

Alkyl halides and other catalysts. n-Propyl bromide with benzene and hydrogen fluoride gave 88% of isopropylbenzene and 12% of n-propylbenzene in the monopropylbenzene fraction. The products were identified as their sulfonamides, and the ratio of the two isomers was estimated from the melting point of the crude mixture of sulfonamides (35).

Butyl chloride with magnesium and toluene at reflux temperature gave *n*butyltoluene, which, however, was identified only by its physical constants. Similarly, isoamyl chloride was claimed to give *p*-isoamyltoluene (36). *n*-Butyl bromide with toluene and beryllium bromide gave a small yield of butyltoluene, which was not identified (37).

Phenylaluminum halides have been reported to give isopropylbenzene on reaction with *n*-propyl iodide (38); isoamyl iodide gave isoamylbenzene. Duplication of the experiment with *n*-propyl iodide in these laboratories has given a mixture of *n*-propylbenzene and isopropylbenzene, which were identified as their diacetamino derivatives (39).

Alcohols, esters, and other alkylating agents, with various catalysts. Isomerization is common in the reactions of aliphatic alcohols with aromatic hydrocarbons. Secondary and tertiary alcohols condensed with benzene in the presence of aluminum chloride, but primary alcohols did not react (40). Isopropyl alcohol gave isopropylbenzene, and s-butyl alcohol yielded s-butylbenzene. Pentanol-2 was reported to give 2-phenylpentane, while 2-methylbutanol-3 gave 2-methyl-3-phenylbutane. No evidence other than boiling point was given for any of these structures. Isopropyl alcohol and s-butyl alcohol reacted with benzene and toluene to give the unisomerized products. (41). A number of tertiary heptyl alcohols have been shown to react with phenol and aluminum chloride to give t-heptylphenols (42).

Price and Lund (43) alkylated benzene with d-s-butyl alcohol. In the presence of aluminum chloride the product was dl-s-butylbenzene, but when boron trifluoride was used as catalyst the product had optical activity.

Neopentyl alcohol with benzene and aluminum chloride gave a 9% yield of neopentylbenzene (26).

Cycloheptanol with benzene and aluminum chloride yielded largely cycloheptylbenzene, but was to some extent "converted to a six-membered ring" (44). 2,2,4-Trimethylpentanol-2 gave, in addition to the expected *t*-octylbenzene, about 17 to 42% of *t*-butylbenzene (45).

$$(CH_3)_3CCH_2C(CH_3)_2OH \xrightarrow{[C_6H_5]}_{[AlCl_3]} \rightarrow \begin{cases} (CH_3)_3CC_6H_5 \\ + \\ CH_3 \\ (CH_3)_3CCH_2CC_6H_5 \\ \\ (CH_3)_3CCH_2CC_6H_5 \\ \\ CH_3 \end{cases}$$

Toussaint and Hennion (46) alkylated benzene by a number of alcohols in the presence of zinc chloride, sulfuric acid, aluminum chloride, or boron fluoride. It was claimed that primary alcohols gave secondary alkylbenzenes; dodecyl alcohol gave s-dodecylbenzene. No details were given on the identification of the products.

Meyer and Bernhauer (47) alkylated benzene, toluene, phenol, and other aromatic compounds with alcohols in the presence of 80% sulfuric acid at  $65^{\circ}$ . Isopropyl alcohol and *n*-propyl alcohol (8) both gave isopropylbenzene. Isobutyl alcohol and *t*-butyl alcohol both yielded *t*-butylbenzene, identified as its bromo derivative. Both *s*-butyl alcohol and *n*-butyl alcohol gave *s*-butylbenzene. Cyclohexanol yielded cyclohexylbenzene. Other aromatic compounds gave similar results. Nightingale and Smith (48) obtained 1,3-dimethyl-4-s-butylbenzene from *m*-xylene and *s*-butyl or *n*-butyl alcohol with sulfuric acid; *n*butyl alcohol gave only a 6% yield.

Neopentyl alcohol with benzene and sulfuric acid produced *t*-amylbenzene, identified as its diacetamino derivative (26).



Isoamyl alcohol gave *t*-amylbenzene (8). *n*-Amyl alcohol yielded a monoamylbenzene fraction of which 60-65% was 2-phenylpentane and 35-40% was 3-phenylpentane, when treated with benzene and 80% sulfuric acid at  $70^{\circ}$  for six hours. Apparently 1-phenylpentane was absent.

In the presence of boron fluoride, both propyl alcohols gave isopropylbenzene; n-butyl alcohol and s-butyl alcohol yielded s-butylbenzene; and isobutyl alcohol gave t-butylbenzene. Cyclohexylbenzene was obtained from cyclohexyl alcohol. Allyl alcohol yielded allylbenzene. The dialkylbenzenes obtained were shown to be the para isomers. No derivatives of the alkylbenzenes were reported (49).

Esters other than halides have also been used. Triisobutyl borate with xylene and aluminum chloride gave a 90% yield of t-butylxylene (50). Dibutyl sulfate yielded unidentified isomeric butylbenzenes (51). McKenna and Sowa (52) reported that n-propyl formate and n-propyl sulfate, as well as several isopropyl esters, reacted with benzene in the presence of boron fluoride to give isopropylbenzene. n-Butyl phosphate and formate, and several s-butyl esters, yielded s-butylbenzene. Isobutyl formate gave t-butylbenzene. Vinyl acetate reacted violently and gave resinous products. A great many esters did not react. The identification of the propylbenzenes and butylbenzenes was not described.

Bowden (53) alkylated benzene by esters in the presence of aluminum chloride. He identified his alkylbenzenes by means of their diacetamino derivatives. At temperatures up to  $60^{\circ}$ , *n*-propyl sulfite and *n*-propyl formate gave *n*-propylbenzene, with at most only a small proportion of isopropylbenzene. *n*-Butyl oxalate, sulfite, formate, propionate, isobutyrate, valerate, 2-ethylvalerate, benzoate, and stearate, all gave s-butylbenzene. The report on the propyl esters differs from the work of other investigators, but Bowden's proof appears to be conclusive. Nightingale and Carton (9) obtained 5-isopropyl-*m*-xylene from m-xylene with *n*-propyl formate and aluminum chloride. *n*-Butyl acetate has been reported to give *n*-butylbenzene and *n*-butylacetophenone, when treated with benzene and aluminum chloride (54).

Berman and Lowy (55) alkylated benzene with tri-*n*-butyl phosphate in the presence of aluminum chloride, and obtained *s*-butylbenzene. *s*-Butyl acetate gave *s*-butylbenzene. Methylamyl acetate was reported to yield 2-methyl-4-phenylpentane,

$$\mathrm{CH}_{3}\mathrm{COOCH}(\mathrm{CH}_{3})\mathrm{CH}_{2}\mathrm{CH}(\mathrm{CH}_{3})_{2} \xrightarrow{[\mathrm{C}_{6}\mathrm{H}_{5}]}{[\mathrm{AlCl}_{3}]} \xrightarrow{\mathrm{CH}_{3}\mathrm{CH}\mathrm{CH}_{2}\mathrm{CH}(\mathrm{CH}_{3})_{2}} \stackrel{|}{\underset{\mathrm{C}_{6}\mathrm{H}_{5}}{|}} \xrightarrow{\mathrm{CH}_{3}\mathrm{CH}\mathrm{CH}_{2}\mathrm{CH}(\mathrm{CH}_{3})_{2}}$$

but it is doubtful that this was the only product. All of the alkylbenzenes were identified by their physical constants only.

With hydrogen fluoride and benzene, n-butyl acetate gave s-butylbenzene, identified as its diacetamino derivative, and some acetophenone (56).

Isoamyl ether with benzene and boron fluoride yielded *t*-amylbenzene; *n*-amyl ether gave *s*-amylbenzene. The former was identified as its diacetamino derivative, but no derivative of the secondary amylbenzene was prepared (57). Benzyl *n*-propyl ether gave about 10% of isopropylbenzene and 45% of benzylbenzene when treated with benzene and boron fluoride. Derivatives were not prepared (58).

Olefinic compounds with various catalysts. Compounds with an ethylenic linkage have been widely used as alkylating agents. The reliability of much of the data is questionable, from the point of view of the study of isomerization, but it is probable that in general addition takes place at the double bond, and possibly also at other points. If olefins are involved in the mechanism of the rearrangement of alkyl halides, the olefins should act in much the same way as the halides themselves. It cannot be definitely said that this is the case.

Propylene, as would be expected, gave isopropylbenzene when aluminum chloride (59), boron fluoride (60, 61), hydrogen fluoride (62) or ferric chloride (63) were used as catalysts. *n*-Propylbenzene was not formed.

Isobutylene with xylene and aluminum chloride gave t-butylxylene (64). Ipatieff  $(65)^3$  treated isobutylene with benzene in the presence of phosphoric acid, sulfuric acid, or aluminum chloride, and obtained butylbenzene. Hydrogen fluoride (62) and ferric chloride (63) yielded t-butylbenzene.

Pentene-2 has been condensed with benzene in the presence of hydrogen fluoride, but the product was only tentatively identified as a mixture of 2-phenylpentane and 3-phenylpentane. 2-Methylbutene-2 gave t-amylbenzene (62).

With benzene and sulfuric acid, pentene-1 gave a mixture of 2-phenylpentane and 3-phenylpentane; 2-methylbutene-2 yielded *t*-amylbenzene under these conditions, but gave 2-methyl-3-phenylbutane with aluminum chloride as catalyst.

<sup>3</sup> The product was called "isobutylbenzene" in the Zentralblatt reference (65), but it was probably t-butylbenzene.

The structures were established by preparation of the known diacetamino derivatives (8).

$$CH_{3}(CH_{2})_{2}CH = CH_{2} \xrightarrow{[C_{6}H_{6}]}_{[H_{2}SO_{4}]} \rightarrow \begin{cases} CH_{3}CH_{2}CH_{2}CH_{2}CHCH_{3} \\ C_{6}H_{5} \\ + \\ CH_{3}CH_{2}CHCH_{2}CHCH_{2}CH_{2}CH_{2}CH_{3} \\ C_{6}H_{5} \\ \\ C_$$

Hexene-2 has been reported to give 2-phenylhexane, with benzene and sulfuric acid, but there was no proof of this or of the presence or absence of other isomers (66). Likewise, hexene-3 has been claimed to give 3-phenylhexane when treated with benzene in the presence of hydrogen fluoride,  $H_3BO_2F_2$ , or sulfuric acid. No derivatives were prepared. The boiling point (209-212°) indicated 2-phenylhexane rather than 3-phenylhexane, but this is not wholly reliable evidence (67).

Treatment of fractions of cracked gasolines with benzene and aluminum chloride (68) or ferric chloride (69) gave a series of alkylbenzenes, from amyl to octyl, which were not identified except by physical constants. Tilicheev (70) believed these to be secondary alkylbenzenes, which, while it appears probable, lacks any proof. The "amylene" used was a product boiling at  $30-40^{\circ}$  and containing about 50% of amylene, obtained from paraffin by cracking; "heptylene" was a similar fraction, boiling at 95–98°, and containing 45% of heptylene. With no adequate evidence the products obtained by reaction of these fractions were called 2-phenylpentane, 2-phenylheptane, and so on, up to 2-phenylhexadecane.

Cyclohexylbenzene is formed from cyclohexene with benzene and aluminum chloride (59) or hydrogen fluoride (62). The reaction of 2-cyclohexenylacetic acid with benzene in the presence of aluminum chloride at from 0° to 25° has been reported to give 2-phenylcyclohexylacetic acid (71), but Cook and Goulden (72) obtained a 7% yield of 4-phenylcyclohexylacetic acid in this reaction, and could find no evidence of 2-phenylcyclohexylacetic acid. The product was identified by decarboxylation and dehydrogenation to the known *p*-methylbiphenyl.



This result was confirmed by Nenitzescu and Gavăt (73), who also found that cyclohexylideneacetic acid gave the same product.



1-Cyclopentene-1-carboxylic acid yielded 3-phenylcylopentane-1-carboxylic acid (74), and 2-cyclohexylacrylic acid gave 2-(4-phenylcyclohexyl)propionic acid (73).



Open-chain unsaturated acids have been found by Nenitzescu (75) and his coworkers to show similar isomerizations in their reactions with benzene and aluminum chloride. The phenyl group entered the molecule at the methylene group farthest removed from the carboxyl group. Hexene-2-oic acid-1 was observed to show a shift in the position of the double bond, away from the carboxyl group, in the presence of aluminum chloride; this may explain the other isomerizations noted. The reduction of a double bond in the second example is reminiscent of that noted with allyl chloride (34).

$$\begin{array}{c} \operatorname{CH}_{3}\operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{C}=\operatorname{CHCOOH} & [\operatorname{C}_{6}\operatorname{H}_{6}] \to & \operatorname{CH}_{3}\operatorname{CHCH}_{2}\operatorname{CHCH}_{2}\operatorname{COOH} \\ & & & | & | \\ & & & \operatorname{CH}_{3} & \operatorname{CH}_{3} & \operatorname{CH}_{3} \\ \end{array}$$

$$\begin{array}{c} \operatorname{CH}_{3}\operatorname{CH}=\operatorname{CHCH}=\operatorname{CHCOOH} & [\operatorname{C}_{6}\operatorname{H}_{6}] \to & \operatorname{CH}_{3}\operatorname{CHCH}_{2}\operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{COOH} \\ & & & - & \operatorname{CH}_{3}\operatorname{CHCH}_{2}\operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{COOH} \\ \end{array}$$

In all cases the structures were proved by independent synthesis and mixed melting point observations. The earlier work of Eijkman (76) on this type of reaction indicated that phenylation always took place at the site of the double bond, but in all cases in which his proof of structure was satisfactory, the only alternative would have involved phenylation of a terminal methyl group.<sup>4</sup>

Harmon and Marvel (78) compared the properties of "phenylstearic acid", prepared from oleic acid with benzene and aluminum chloride, with those of synthetic 9-phenylstearic acid and 10-phenylstearic acid. They concluded that phenylstearic acid is a mixture of these two acids. Other isomers may or may not be formed.

<sup>4</sup> Hopff (77) noted phenylation of the terminal methylene group in acrylic acid, with benzene and aluminum chloride.

Cyclopropane reacted with benzene in the presence of aluminum chloride and hydrogen chloride to give *n*-propylbenzene; isopropylbenzene was not detected by derivatization or by examination of the Raman spectra (79). With *m*-xylene and aluminum chloride (9) or ferric chloride (80), cyclopropane gave 1,3-dimethyl-4-*n*-propylbenzene. Hydrogen fluoride and benzene also gave *n*-propylbenzene and no isopropylbenzene (81). Sulfuric acid at 2 to 4° gave *n*-propylbenzene and *n*-propyl alcohol (82), but at 65° the hydrocarbon product was isopropylbenzene (8).

Methylcyclobutane with aluminum chloride and hydrogen chloride catalysts gave isoamylbenzene and an unidentified fraction which was probably 2-phenylpentane (79). With sulfuric acid the product was *t*-amylbenzene (82).



Cyclopentane did not react with benzene in the presence of sulfuric acid (82), but with aluminum chloride and hydrogen chloride it gave unidentified amylbenzenes, and cyclopentylbenzene (79).

Isoöctane reacted with benzene and aluminum chloride to give t-butylbenzene and isobutane, with small amounts of n-butane (83, 84). Toluene, biphenyl, and other aromatics reacted similarly. Phenol and aluminum chloride reacted with t-octylphenol to give t-butylphenol (85).

Alkylating catalysts may cause alkylbenzenes to rearrange. It has recently been reported that 1,3-dimethyl-4-*n*-propylbenzene with aluminum chloride at  $55^{\circ}$  for three hours gave the unchanged hydrocarbon, but at  $85-90^{\circ}$  for four hours yielded what appeared to be a mixture of 4-*n*-propylxylene and 5-isopropylxylene. When the reactants were held at 100° for four hours, a product definitely identified as 5-isopropylxylene was obtained (9). This is in contrast to the early work of Heise and Töhl (86), who found, that *n*-propylbenzene with aluminum chloride and hydrogen chloride at 100° for six hours gave benzene, *n*-propylbenzene, and *m*- and *p*-di-*n*-propylbenzenes. The products were identified as their sulfonamides. Baddeley and Kenner (87) likewise found no rearrangement of the *n*-propyl group in the treatment of *p*-di-*n*-propylbenzene with aluminum chloride at 100° for twenty-two hours. Identification was accomplished by means of the acetamino derivatives.

The reactions of butylxylenes with aluminum chloride and ferric chloride have given interesting rearrangements; 1,3-dimethyl-4-*n*-butylbenzene at 100° for four hours gave 1,3-dimethyl-5-*s*-butylbenzene, identified as its trinitro derivative. Surprisingly, 1,3-dimethyl-4-*s*-butylbenzene yielded 1,3-dimethyl-5-*t*-butylbenzene when warmed with aluminum chloride for  $2\frac{1}{2}$  hours. Isobutylxylene gave a complex mixture (48). In the presence of ferric chloride, 1,3-dimethyl-4-isobutylbenzene yielded the expected 1,3-dimethyl-5-*t*-butylbenzene, and the other butylxylenes reacted as described in the case of aluminum chloride (80). Bodendorf (88) condensed propionaldehyde with benzene and aluminum chloride, and obtained n-propylbenzene, but gave no details concerning the identification of the product. Similarly he claimed that butyraldehyde gave n-butylbenzene, while isobutyraldehyde gave isobutylbenzene, but with no adequate proof.

*Conclusion*. This study of the isomerization accompanying alkylation shows that the subject requires further and more careful study, for many of the important orienting experiments may be at fault because the products were not properly identified. Boiling point, density, and refractive index are not always sufficient to differentiate between isomers. If, however, we examine the more decisive experiments we can draw a few general conclusions. Primary alkyl compounds give both primary and secondary alkylbenzenes, and higher temperatures favor the formation of the latter. Secondary alkyl compounds give secondary and never primary, alkylbenzenes. Isoalkyl compounds apparently have little tendency to form isoalkylbenzenes, and give largely tertiary alkylbenzenes instead. Tertiary alkyl compounds yield only tertiary alkylbenzenes.

To explain these results we might assume a series of eliminations and additions of hydrogen halide to the alkyl group (75), although in the absence of benzene (or other aromatic compound) this reaction may not take place readily under the mild conditions generally used for Friedel-Crafts reactions (11). Since pentene-1 did not yield any 1-phenylpentane (8) in reaction with benzene and sulfuric acid, and since primary alkyl halides do give some 1-phenylalkanes, it may be supposed that it is the alkyl halide that actually reacts, and not the olefin, although there is, unfortunately, a paucity of information on olefin reactions in which aluminum chloride is the catalyst.

With *n*-hexyl bromide, which has been shown to give 1-phenylhexane, 2-phenylhexane, and 3-phenylhexane (89), the reactions involved would be, according to this mechanism,



# DISCUSSION OF EXPERIMENTAL RESULTS

Hexyl bromide and benzene. Hexyl bromide reacted readily with benzene and aluminum chloride at low to moderate temperatures to give good yields of hexylbenzene. Fractional crystallization of the diacetamino derivatives of the product showed that 1-phenylhexane and 3-phenylhexane were present, and indicated, not so satisfactorily, that 2-phenylhexane had also been formed. It was later shown by use of the sulfonamides that 2-phenylhexane was actually present. The three hexylbenzenes were synthesized for purposes of comparison; derivatives were prepared of each, and mixed melting point depressions were observed, in order to eliminate possibility of error, in so far as was practicable.<sup>5</sup> There remains the chance that the carbon skeleton of the hexyl group rearranged, but it is not probable that in the presence of considerable amounts of other isomers the derivatives of the three isomers found could have been obtained so readily, and with no indication of any other hexylbenzene.

For instance, if all seventeen possible hexylbenzenes and all 3,057 possible dodecylbenzenes were formed in this reaction and in the reaction with dodecyl bromide described below, the odds against isolating the five derivatives obtained are four million to one. On the other hand, if only one other hexylbenzene and one other dodecylbenzene formed, the odds against our experiments falling into the pattern obtained are 3.33 to one. The actual chances fall somewhere between these two figures.

Dodecyl bromide and benzene. A preliminary study of the reaction of n-dodecyl bromide with benzene and aluminum chloride indicated that this alkyl bromide behaved as did octadecyl bromide. When, however, the five normal secondary dodecylbenzenes were synthesized, and derivatives of these were compared with those of the reaction product, it was found that 1-phenyldodecane and 6-phenyl-dodecane were both present. Attempts to identify definitely any other isomers did not succeed. There is reason to believe, however, that all six normal dodecylbenzenes were in the product.

Other long-chain alkyl bromides. Tetradecyl bromide reacted with benzene and aluminum chloride to give a mixture of tetradecylbenzenes. As with dodecyl and octadecyl bromides, the product was shown to contain the normal primary alkylbenzene, 1-phenyltetradecane. Similarly, hexadecyl bromide yielded a product containing 1-phenylhexadecane. It is believed that in both cases, all of the possible normal secondary alkylbenzenes were also formed. The octadecylbenzene obtained by Gilman and Turck (1) from *n*-octadecyl bromide with benzene and aluminum chloride was likewise not pure 1-phenyloctadecane, as they supposed, but undoubtedly contained the eight secondary phenyloctadecanes as well. The cause of their error lay in their method of preparing the sulfonamide, and this aspect is discussed in the following section.

Derivatization of alkylbenzenes. Turck (91) used the procedure described by Seidel and Engelfried (30a) for the preparation of the sulfonamide of octadecylbenzene. In this procedure the alkylbenzenesulfonic acid in ether is shaken

<sup>&</sup>lt;sup>5</sup> There are 14 other possible hexylbenzenes, few of which are known (cf. 90).

with saturated aqueous sodium chloride, and the sodium alkylbenzenesulfonate precipitates and is filtered off for use in preparation of the sulfonamide. We have found that while this is satisfactory for 1-phenylalkanes, the secondary alkylbenzenes in general do not give precipitates, for the sodium salts of the sulfonic acids prepared from them are quite soluble in ether. An exception to this rule is 2-phenyldodecane, which after standing for a short time gave the expected sodium salt. With hexylbenzene and heptylbenzene even the sodium sulfonate of the 1-phenylalkane was sufficiently soluble so that the reaction product containing the three normal alkylbenzenes did not give a precipitate of the sodium sulfonate in this procedure. Pure 1-phenylhexane or 1-phenylheptane did give precipitates, however.

It is probable that the reason that the sulfonamides of only the 1-phenylalkanes were found in the cases of dodecyl-, tetradecyl-, hexadecyl-, and octadecylbenzenes prepared by the Friedel-Crafts reaction, was that the secondary alkylbenzenes were lost at this point in the preparation of the derivative.

The diacetamino derivatives, whose method of preparation was described by Ipatieff and Schmerling (92), were found to be useful in the identification and separation of the hexylbenzenes. In the case of the dodecylbenzenes, however, crystalline derivatives could not be obtained with acetic anhydride and the amino derivative. When  $\beta$ -naphthalenesulfonyl chloride was substituted for the acetic anhydride, a very convenient series of derivatives was obtained, which complemented the series of sulfonamides and made possible the identification of 6-phenyldodecane in the mixture of dodecylbenzenes. The derivative was



probably a mixture of the ortho and para isomers.

No satisfactory way has been found of estimating the proportions of the isomers in the hexylbenzene or dodecylbenzene produced from the alkyl bromides with benzene and aluminum chloride. Even with hexylbenzene, our fractional distillation did not separate the isomers efficiently. The crude separation achieved did not indicate a great preponderance of any of the isomers.

A comparison of the yields of ether-insoluble sodium sulfonates obtained from 1-phenyldodecane and from Friedel-Crafts dodecylbenzene indicated that 1-phenyldodecane and 2-phenyldodecane together make up about 40% of the latter. Here again, no great preponderance of any one isomer was indicated.

### EXPERIMENTAL

Alkylation of benzene. Benzene and aluminum chloride (B. and A. reagent) were mixed in a 3-necked flask equipped with a stirrer and a reflux condenser to which a drying-tube and an outlet for hydrogen halides were attached. The alkyl bromide was added slowly through a dropping-funnel and the mixture was stirred. Table I gives the conditions of the reactions and the results obtained.

Identification of alkylbenzenes. The sulfonamide of the hexadecylbenzene obtained in experiment 1 melted at  $97^{\circ}$ , and did not depress the melting point of the sulfonamide of synthetic 1-phenylhexadecane. The sulfonamide of the tetradecylbenzene obtained in experiment 2 melted at  $97.5^{\circ}$ , and did not depress the melting point of the sulfonamide of synthetic 1-phenyltetradecane. The sulfonamide of the dodecylbenzene obtained in experiment 3 melted at  $97.5^{\circ}$ , and did not depress the melting point of the sulfonamide of synthetic 1-phenyltetradecane.

The products of reaction in experiment 4 were fractionated by distillation. After removal of the solvent the lowest-boiling fraction distilled at  $100^{\circ}$  at 43 mm., or  $205-208^{\circ}$  at 1

			Br	BENZENE		A	ICI:				AL	KYLBE	NZENES	
T. NO	ALKYL BROMIDE	G.	MOLES	cc.	ES	G.	MOLES	темр. °C.	TIME HR.	в.р.°С.	PRESS.		YIELD	
EXE					MOI						мм.	G.	MOLES	%
1	n-Hexadecyl	30.5	0.10	77	0.85	2.0	0.015	Room 50–53	$26.5 \\ 4$	211–228	13	11.6	0.038	38.4
2	n-Tetradecyl	16.6	0.06	45	0.50	1.2	0.009	Room 45–55	$\frac{34}{4}$	170–179	6	10.3	0.038	62.6
3	$n ext{-}\mathrm{Dodecyl}$	16.5	0.066	45	0.50	1.3	0.01	Room 40–50	34 4	144–151	5	6.8	0.027	41.7
4	$n ext{-}Dodecyl$	80.7	0.324	265	2.98	7.0	0.052	0-23	48	_	—			—
5	$n ext{-}Dodecyl$	16.6	0.066	45	0.50	1.3	0.01	Room	35	200 - 218	43	8.4	0.038	57
								40–60	4.5				ļ	
6	$n ext{-Heptyl}$	17.7	0.10	77	0.85	2.0	0.015	Room	34	129–133	37	8.0	0.046	46
_								40-50	4					
7	n-Hexyl	16.5	0.10	77	0.85	2.0	0.015	Room 50	45 4	213-223	atm.	8.7	0.054	53.6
8	n-Hexyl	19.8	0.12	92	1.03	2.4	0.018	0	20	210-213	atm.	8.1	0.050	41.5
9	<i>n</i> -Hexyl	82.5	0.50	380	4.38	10	0.075	0-23	48	200-227	atm.	60.1	0.37	74
10	n-Hexyl	82.5	0.50	380	4.38	10	0.075	0	49	200-227	atm.	56.9	0.35	70
11	n-Hexyl	90.8	0.55	365	4.21	11	0.083	0	40			_		
12	n-Octadecyl	16.6	0.05	38	0.43	1.0	0.008	Room	34	205-215	6	7.9	0.024	48.2
								4060	4					

TABLE I Friedel-Crafts Alkylations

atm. The yield was 3.4 g;  $n_D^{20}$  1.4233;  $d_2^{20}$  0.752. This may be a mixture of dodecenes (93). The second portion boiled at 185-190° at 33 mm., or 194-203° at 46 mm.;  $n_D^{20}$  1.4810;  $d_2^{20}$  0.857. The yield was 4.8 g. (5.5%). This fraction was nitrated and reduced (92), and the monoamine was treated with  $\beta$ -naphthalenesulfonyl chloride. Fractional crystallization of the resulting derivative gave a product which melted at 127°. A mixed melting point with the  $\beta$ -naphthalene sulfonamide of 6-phenyldodecane was 127-128°. A third fraction boiled at 190-195° at 34 mm.;  $n_D^{20}$  1.4821;  $d_2^{20}$  0.858; yield 11.3 g. (11.9%). The sodium sulfonate obtained from this was soluble in ether. A fourth portion distilled at 195-201° at 35 mm.; yield 11.7 g. (12.4%). The undistilled residue weighed 5.9 g.

In the fifth experiment the product was sulfonated with fuming sulfuric acid in a carefully standardized procedure. The yield of sodium sulfonate insoluble in ether was 16.7%. The same procedure gave a 41% yield with pure 1-phenyldodecane. Since the only two *n*-dodecylbenzenes giving ether-insoluble sodium sulfonates were 1-phenyldodecane and

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2-phenyldodecane, it was concluded that about 40% of the Friedel-Crafts product consisted of these two dodecylbenzenes.

The sodium sulfonates of the heptylbenzene obtained in experiment 6 and of the hexylbenzenes obtained in experiments 7 and 8 were soluble in ether.

The hexylbenzene from experiment 9 was fractionated in a small, jacketed column. The first portion distilled at 200-205° and weighed 2.8 g;  $n_{\rm D}^{\rm m}$  1.4875;  $d_{\rm m}^{\rm m}$  0.861. The diacetamino derivative after several recrystallizations melted at 201°, and did not depress the melting point of the diacetamino derivative of 3-phenylhexane. The third portion boiled at 207.5-210° and weighed 12.1 g;  $n_{\rm D}^{\rm m}$  1.4886;  $d_{\rm m}^{\rm m}$  0.860. From this was obtained a diacetamino derivative which melted at 172°. In mixture with the diacetamino derivative of 2-phenylhexane (m.p. 178°), it melted at 175-178°. The fourth fraction, boiling at 210-215°, and weighing 10.9 g. ( $n_{\rm D}^{\rm m}$  1.4885;  $d_{\rm m}^{\rm m}$  0.860), gave a diacetamino derivative similar to that obtained from the third fraction. The sixth fraction, which distilled above 220°, weighed 4.9 g.;  $n_{\rm D}^{\rm m}$  1.4924;  $d_{\rm m}^{\rm m}$  0.867. The diacetamino derivative of 1-phenylhexane.

TABLE II	
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PREPARATION OF KETONES

$\begin{array}{c} \text{ketone} \\ n\text{-}C_{15}H_{31}COC_6H_5nC_1_3H_{27}COC_6H_5nC_1_3H_{27}COC_6H_5nC_1_3H_{27}COC_6H_5nC_1_3H_{27}COC_6H_5nC_1_3H_{27}COC_6H_5nC_1_3H_{27}COC_6H_5nC_1_3H_{27}COC_6H_5nC_1_3H_{27}COC_6H_5$	<u>ا مع</u>	PRESS.	N B °C	VIELD <sup>4</sup> CZ	SEMICAR-	ANALYSIS		
REJONE	B.F. C.	MM.	al.F, C.	TIELD 70	M.P. °C.	N FOUND	N CALC'D	
$n-C_{15}H_{31}COC_6H_5$			56	67	88	11.25	11.26	
$n-C_{13}H_{27}COC_6H_5$	206	5	52	45	97 <sup>6</sup>	12.41	12.16	
$n-C_{11}H_{23}COC_6H_6$	187	5	42.5	64	94.5-95	13.60	13.24	
$n-C_9H_{19}COC_6H_5^c$	168	<b>5</b>	35-36	82.8	124	15.0	14.53	
$n-C_6H_{13}COC_6H_5^d$	173	34				—		
$n-C_{5}H_{11}COC_{6}H_{5}$	160	33	-	73.8	131°			
$n-C_4H_9COC_6H_5$	161	67	-	44				
$n-C_{3}H_{7}COC_{6}H_{5}$	110	10		82.51				
$n-C_2H_5COC_6H_5$	212-215	atm.		32.3	—	-		

<sup>a</sup> Yield is based on acid used.

<sup>b</sup> Sabatier and Maihle, Compt. rend., 158, 834 (1914) reported 75°.

<sup>c</sup> Anal. Cale'd for C<sub>16</sub>H<sub>24</sub>O: C, 82.70; H, 10.4. Found: C, 82.32; H, 10.70.

<sup>d</sup> Krafft, Ber., 19, 2987 (1886). Observed  $n_{D}^{20}$  1.5068.

<sup>e</sup> Schroeter, Ber., 40, 1603 (1907).

<sup>f</sup> Based on butyryl chloride.

The hexylbenzene from experiment 11 was fractionated through a jacketed column (94) and divided into a number of (2-cc.) portions. The thirteenth fraction gave the diacetamino derivative of 1-phenylhexane mixed with what appeared to be that of 2-phenylhexane. Fraction 14 (b.p. 210°;  $n_{\rm D}^{20}$  1.4879) gave a sulfonamide which melted at 82°. The mixed melting point with the sulfonamide of 2-phenylhexane was 82-83°.

The octadecylbenzene from experiment 12 yielded a sulfonamide which melted at 99-100°, and which did not depress the melting point of the sulfonamide prepared by Turck from synthetic 1-phenyloctadecane (1).

Preparation of synthetic hydrocarbons. The synthetic hydrocarbons were prepared solely for the purpose of obtaining the melting points of their derivatives, and of obtaining samples for mixed melting point determinations. No particular efforts were made to remove small amounts of impurities which would not interfere with this purpose. The physical constants should for this reason not be taken as the constants of the pure hydrocarbons. The 1phenylalkanes were each prepared in two ways: by the Clemmensen reduction of the appropriate alkyl phenyl ketone, and by the Wurtz-Fittig reactions. In each case the sulfonamides of both products were prepared, and were shown to be identical by the method of mixed melting points. The results are shown in Tables II, III, and IV. The ketones were prepared from the acid chlorides and benzene, with aluminum chloride. They were reduced by a modification of the Clemmensen method (95). The Wurtz-Fittig reactions were carried out in about 35 cc. of benzene, per 5 g. of sodium. Hexylbenzene and heptylbenzene prepared by this method were very impure, since the two symmetrical coupling products distilled at very nearly the same temperature as the alkylbenzene in each case.

The secondary alkylbenzenes were prepared in three steps: (a) the reaction of a ketone with a Grignard reagent to give a tertiary carbinol, (b) dehydration of the carbinol with

KETONE	ALKYLBEN- ZENE	E OF DUCTION	LD %	в.р. °С.	PRESS.	$n_{\rm D}^{\rm t}$	$d_{20}^{t}$	MOLECULAR REFRACTION	
		TIME	VIE1					FOUND	CALC'D
n-C <sub>15</sub> H <sub>31</sub> COC <sub>6</sub> H <sub>5</sub>	n-Hexa- decyl	29 hr.	29.6	202-213	7	1.480227.5	0.85827.3	100.2	100.2
$n-C_{13}H_{27}COC_6H_5$	n-Tetra- decyl	—	58	188–189	6	1.483524.8	0.85723.6	91.53	90.96
$n-C_{11}H_{23}COC_6H_5$	n-Dodecyl		31	164	4	$1.4857^{20}$	$0.859^{24.2}$	82.00	81.72
$n-C_6H_{13}COC_6H_5$	n-Heptyl			240-244	atm.	$1.4842^{31.5}$	$0.959^{27}$	58.8	58.63
$n-C_5H_{11}COC_6H_5$	n-Hexyl	12	51.8	220-222	atm.	1.488020	0.86120	54.34	54.02

TABLE III REDUCTION OF KETONES

# TABLE IV

WURTZ-FITTIG REACTIONS

	ALKYLBEN-	R	Br	BR BEN	OMO- ZENE	so	DIUM	% <b>G</b>	°C	SS. MM.	n <sup>t</sup> p	d <sup>t</sup>	MOLE REFRA	CULAR
NO.		G.	MOLES	G.	MOLES	G.	ATOMS	VIEI	B.P.	PRE			FOUND	CALC'D
1	n-Hexa- decyl	15.3	0.05	8.7	0.055	5	0.217	26.4	230 - 232	14	1.479327.5	0.85725.4	100.0	100.2
2	n-Tetra- decyl	13.6	0.05	8.7	0.055	5	0.217	33.6	193	7	1.482226	—		—
3	n-Do- decyl	16.2	0.065	11.5	0.073	6.35	0.276	38.1	164	5	1.483220	0.85424	82.13	81.72

60% sulfuric acid to produce the olefin, and (c) reduction of the olefin with sodium and alcohol. The results are given in Tables V, VI, and VII. A description of the preparation of 2-phenyldodecane will be sufficient to show the methods used.

Decyl bromide was prepared from *n*-decyl alcohol by heating with 48% hydrobromic acid and concentrated sulfuric acid (96); boiling point 152-155° at 66 mm.;  $n_p^{20}$  1.4551 (97). To the Grignard reagent prepared from 23.7 g. of decyl bromide (0.107 mole), 2.6 g. of magnesium, and 100 cc. of ether, 12.8 g. of acetophenone (0.106 mole) was added slowly at 0°. The product was hydrolyzed with ammonium chloride solution, separated, washed with dilute sodium carbonate solution, and finally with water. It was dried over sodium sulfate and distilled *in vacuo*. This yielded 14 g. (50%) of 2-phenyldodecanol-2.

Fourteen grams (0.053 mole) of 2-phenyldodecanol-2 and 20 g. of 60% sulfuric acid (98) were warmed on a water-bath until the upper layer became clear. The upper layer was then separated, washed with water, then with dilute sodium carbonate solution, and dried over calcium chloride. The yield was 10.7 g. (82.2%) of 2-phenyldodecene.

### TABLE V

KETONE	GRIGNARD	%	с:	. MM.	m <sup>2</sup> 0	<i>4</i> 20	M.R.ª	ANAL	.ysis <sup>b</sup>
	FROM	VIEL	B.P. °	PRESS	" D	20	FOUND	с	H
Acetophe- none	Decyl bro- mide	50	174- 177	7	1.4914	0.911	83.52	82.78	11.94
n-Nonyl phe- nyl ketone	Ethyl bro- mide	82	168	5	1.4954	0.920	83.22	82.90	11.59
n-Propyl phenyl ke- tone	Octyl bro- mide	50.2	170	4	1.4940	0.917	83.39	82.42	11.77
n-Butyl phe- nyl ketone	Heptyl bro- mide	62	166- 168	5	1.4961	0.922	83.10	82.32	11.39
n-Amyl phe- nyl ketone	Hexyl bro- mide	66	169– 170	6	1.4947	0.921	83.12	82.84	11.51
Acetophe- none	Butyl bro- mide	52.9	120	10	1.5084	0.963	55.46	80.72	10.41
Propiophe- none	Propyl bro- mide	72.4	134	27	1.5100	0.966	55.1		
	KETONE Acetophe- none n-Nonyl phe- nyl ketone n-Propyl phenyl ke- tone n-Butyl phe- nyl ketone n-Amyl phe- nyl ketone Acetophe- none Propiophe- none	KETONEGRIGNARD REAGENT FROMAcetophe- noneDecyl bro- miden-Nonyl phe- nyl ketoneEthyl bro- miden-PropylOctyl bro- miden-Propyl phenyl ke- toneOctyl bro- miden-Butyl phe- nyl ketoneHeptyl bro- miden-Amyl phe- nyl ketoneButyl bro- midenonebro- midenonebro- midePropiophe- noneButyl bro- midePropiophe- nonebro- mide	KETONEGRIGNARD REAGENT FROMSQ G G GAcetophe- noneDecyl bro- mide50n-Nonyl phe- nyl ketoneEthyl bro- mide82n-Propyl phenyl ke- toneOctyl bro- mide50.2n-Butyl phe- nyl ketonebro- mide62n-Amyl phe- nyl ketonebro- mide66n-Amyl phe- nyl ketoneButyl bro- mide52.9nonebro- mide52.9Propiophe- nonePropyl bro- mide72.4	KETONEGRIGNARD REAGENT FROMSQ Nonyl phe- noneDecyl Docyl Do Nonyl phe- bro- mide Nyl ketone50 D 174- 177 mide 82168 168 168 168 mide nonen-Nonyl phe- nyl ketoneDecyl bro- mide50.2 170 168 mide 166169- 170 170 170 miden-Amyl phe- nyl ketoneHexyl bro- mide66 169- 170 170 170 170 170 mide120 120Propiophe- nonePropyl bro- mide72.4 134	KETONEGRIGNARD REAGENT FROMSQ GSQ G <b< td=""><td>KETONE<math>GRIGNARDREAGENTFROM<math>S_{P}</math> Q</math></td><td>KETONE<math>GRIGNARDREAGENTFROM<math>S_{2}</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> <math>G</math> 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$GRIGNARDREAGENTFROMS_{2}GG$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

# PREPARATION OF TERTIARY CARBINOLS

 $^{a}$  Molecular refraction calc'd for  $C_{18}H_{20}O$  is 83.45; for  $C_{12}H_{18}O$  it is 55.42.

<sup>b</sup> Cale'd for C<sub>18</sub>H<sub>30</sub>O: C, 82.39; H, 11.53. Cale'd for C<sub>12</sub>H<sub>18</sub>O: C, 80.87; H, 10.17.

<sup>c</sup> Conant and Carlson, J. Am. Chem. Soc., 54, 4084 (1932).

<sup>d</sup> Yéramian, Compt. rend., 173, 362 (1921).

# TABLE VI Dehydration of Carbinols

	ormud	%		PRESS.		120	M.R.ª	ANALYSES	
CARBINOL	OLEFIN"	VIELD	B.P. C.	мм.	n D	20	FOUND	с	н
2-Phenyldodecanol-2	2-Phenyldodecene	82.2	160-162	5	1.5003	0.873	82.38	88.20	11.63
3-Phenyldodecanol-3	3-Phenyldodecene	89	165	7	1.5025	0.880	81.98	88.38	11.83
4-Phenyldodecanol-4	4-Phenyldodecene	84.5	153 - 154	5	1.5011	0.876	82.16	88.84	11.86
5-Phenyldodecanol-5	5-Phenyldodecene	85	156 - 157	6	1.5034	0.881	82.08	88.14	11.67
6-Phenyldodecanol-6	6-Phenyldodecene	77	161	9	1.5025	0.875	82.47	88.48	11.67
U U			192	33					
2-Phenylhexanol-2	2-Phenylhexene	87.8	125-130	42	1.5230	0.899	54.16	89.82	10.26
3-Phenylhexanol-3	3-Phenylhexene	76	125-130	56	1.5236	0.895	54.68		
-	-		206-217	atm.					

<sup>a</sup> Molecular refraction; calc'd for  $C_{18}H_{28}$  is 81.20; for  $C_{12}H_{18}$  is 53.54.

<sup>b</sup> Calc'd for C<sub>18</sub>H<sub>28</sub>: C, 88.46; H, 11.54.

Calc'd for C<sub>12</sub>H<sub>16</sub>: C, 89.95; H, 10.05.

<sup>e</sup> Yéramian, Compt. rend., 173, 362 (1921).

<sup>d</sup> The position of the double bond was not ascertained.

Ten and seven-tenths grams of 2-phenyldodecene (0.043 mole) was dissolved in 80 cc. of absolute alcohol, and the solution was treated with 8.7 g. of sodium. The product was hydrolyzed, acidified, extracted with petroleum ether, separated, washed, and dried over calcium chloride. There was obtained 8.5 g. (78.8%) of 2-phenyldodecane.

Since it was thought possible that 60% sulfuric acid might cause rearrangement of the hydrocarbon during dehydration, 2-phenylhexanol-2 was reduced to 2-phenylhexane with hydrogen iodide, and the product was compared with the 2-phenylhexane obtained by the usual method.

Three and one-quarter grams of red phosphorus, 1.1 g. of iodine, and 54 cc. of glacial acetic acid were warmed for one-half hour. To this mixture was added 1.1 cc. of water, followed by 16.9 g. (0.095 mole) of 2-phenylhexanol-2. The mixture was refluxed gently for five hours. It was filtered, diluted with water, extracted with ether, washed with sodium bisulfite, then with dilute sodium carbonate, and finally with water. It was dried over calcium chloride, and distilled; boiling point 62-67° at 4 mm.;  $n_{2}^{20}$  1.4960;  $d_{22}^{20}$  0.866; M.R. 54.7 (calc'd 54.0). The acetamino derivative of this 2-phenylhexane melted at 76° and gave

AT KVI BENZENE	YIELD	B B °C	PRESS.	20	<i>4</i> 20	M.R.ª	ANALYSES <sup>b</sup>	
	%	мм.		<sup>78</sup> D	20	FOUND	С	н
2-Phenyldodecane	78.8	161	7	1.4800	0.854	81.98	88.18	12.37
3-Phenyldodecane	80.7	171	13	1.4845	0.861	81.94	87.30	12.26
_		151	5					
4-Phenyldodecane	78	164	17	1.4855	0.861	82.1	88.20	12.26
5-Phenyldodecane	83	158	7.5	1.4880	0.863	82.24	87.25	11.77
6-Phenyldodecane	82	153	6	1.4885	0.860	82.62	87.70	11.97
-		190	35					
2-Phenylhexane	86.2	208.7 - 210	741	1.4873	0.861	54.26	89.15	11.09
3-Phenylhexane <sup>c</sup>	48	200-203.5	atm.	1.4894	0.863	54.36	88.67	11.04

TABLE VII

PREPARATION OF SECONDARY ALKYLBENZENES

<sup>a</sup> Calc'd for C<sub>18</sub>H<sub>30</sub>: M, 81.7. Calc'd for C<sub>12</sub>H<sub>18</sub>: M, 54.02.

<sup>b</sup> Calc'd for C<sub>18</sub>H<sub>80</sub>: C, 87.73; H, 12.27. Calc'd for C<sub>12</sub>H<sub>18</sub>: C, 88.84; H, 11.16.

<sup>c</sup> Levene and Marker, J. Biol. Chem., 93, 749 (1931).

no depression of the melting point when mixed with the acetamino derivative of the other 2-phenylhexane.

Preparation of derivatives. Sulfonamides. The sulfonamides of the 1-phenylalkanes and of 2-phenyldodecane were prepared according to the directions of Turck (91). The other sulfonamides could not be conveniently prepared in this way. It was found better to neutralize the acids with calcium oxide, extract the calcium alkylbenzenesulfonate with water, and decompose with sodium carbonate. The solution was evaporated and the sodium alkylbenzenesulfonate was extracted with alcohol. The alcohol was evaporated to give the dry salt. This was treated with phosphorus pentachloride and then with ammonia to give the sulfonamide. Acetamino. The procedure of Ipatieff and Schmerling (92) was used to prepare the acetamino and diacetamino derivatives of the hexylbenzenes.  $\beta$ -Naphthalenesulfonamides. The monoamino derivatives were prepared and isolated by the method of Ipatieff and Schmerling (92). The amine was dissolved in benzene, and treated with half its weight of  $\beta$ -naphthalenesulfonyl chloride. The benzene was removed by distillation, and the residue was dissolved in petroleum ether. The solution was shaken with 10% aqueous sodium hydroxide; methanol was added to break the emulsion. The petroleum ether layer was separated, dried over sodium sulfate, filtered, and heated in an open flask on the steam-bath until a thick gel formed. Acetone was added and the precipi-

ALKYLBENZENE	DERIVATIVE	м.р. °С.	N found	N calc'd
Hexadecyl-(1)	Sulfonamide	97	3.67	3.67
Tetradecyl-(1)	44	97.5-98	4.29	3.96
Dodecyl-(1)	" "	97.5	4.35	4.30
Dodecyl-(2)	"	99	4.25	4.30
Dodecyl-(3)	" "	56	4.38	4.30
Dodecyl-(4)	**	60	4.26	4.30
Heptyl-(1)	" (	90.5	5.52	5.49
Hexyl-(1)	" "	86	5.75	5.81
Hexyl-(2)	"	83	6.01	5.81
Hexyl-(3)	"	63	5.95	5.81
Dodecyl-(3)	$\beta$ -Naphthalene	103	3.12	3.10
	sulfonamide			
Dodecyl-(4)	""	112 - 112.5	3.26	3.10
Dodecyl-(5)	""	107-107.5	3.34	3.10
Dodecyl-(6)	"	128	3.41	3.10
Hexyl-(1)	Acetamino	91	6.32	6.39
Hexyl-(2)	"	76	6.48	6.39
Hexyl-(3)	"	127	6.43	6.39
Hexyl-(1)	Diacetamino	200-202	10.08	10.13
Hexyl-(2)	"	178	10.43	10.13
Hexyl-(3)	"	199–201	10.47	10.13

# TABLE VIII Derivatives of Alkylbenzenes

TABLE IX Mixed Melting Points of Derivatives

Α	м.р. °С.	В	м.р. °С.	A + B M.P. ℃.
	SU	LFONAMIDES		<u> </u>
1-Phenyloctadecane	99–100	1-Phenylhexadecane	97	96
1-Phenyltetradecane	97.5-98	1-Phenylhexadecane	97	94
1-Phenyltetradecane	97.5-98	1-Phenyldodecane	97.5	93
2-Phenyldodecane	99	1-Phenyldodecane	97.5	82-95
3-Phenyldodecane	56	4-Phenyldodecane	60	44-47
1-Phenylhexane	86	2-Phenylhexane	83	6266
1-Phenylhexane	86	3-Phenylhexane	63	50
2-Phenylhexane	83	3-Phenylhexane	63	51
	DIACETAN	MINO DERIVATIVES		
1-Phenylhexane	200-202	2-Phenylhexane	178	135-17
1-Phenylhexane	200-202	3-Phenylhexane	199-201	145-15
2-Phenylhexane	178	3-Phenylhexane	199-201	165-16
	<b>β-ΝΑΡΗΤΗΑ</b> Ι	LENE SULFONAMIDES		
3-Phenyldodecane	103	4-Phenyldodecane	112-112.5	103-10
3-Phenyldodecane	103	5-Phenyldodecane	107-107.5	81-87
4-Phenyldodecane	112-112.5	5-Phenyldodecane	107-107.5	98-10
4-Phenyldodecane	112-112.5	6-Phenyldodecane	128	97-11
······································		143		

tate was filtered off. The sodium salt so obtained was decomposed by suspending it in ether and treating the suspension with dilute hydrochloric acid. The ether solution was washed, dried over sodium sulfate, filtered, and evaporated nearly to dryness. The residue was treated with petroleum ether and set aside to crystallize. The product was recrystallized from petroleum ether, alcohol, or aqueous alcohol. The yield was about 10%. Nitrogen analyses showed the products to be the  $\beta$ -naphthalene-sulfono-dodecylanilides,  $\beta$ -C<sub>10</sub>H<sub>7</sub>SO<sub>2</sub>NHC<sub>6</sub>H<sub>4</sub>C<sub>11</sub>H<sub>25</sub>. The orientation of the amine was not determined. These are the derivatives referred to in Table VIII as the  $\beta$ -naphthalenesulfonamides.

*Mixed melting points*. Melting points were observed for mixtures of various pairs of the above derivatives. The results are shown in Table IX. The observations show clearly that the conclusions drawn concerning the identity of the alkylbenzenes were justified, for in only one instance did mixtures of isomers fail to give a distinct lowering of the melting point.

#### SUMMARY

Normal hexyl bromide has been shown to give 1-phenylhexane, 2-phenylhexane, and 3-phenylhexane, when treated with benzene in the presence of aluminum chloride. Under the same conditions, *n*-dodecyl bromide yielded a mixture of dodecylbenzenes, in which 1-phenyldodecane and 6-phenyldodecane have been identified.

Derivatives of synthetic primary and secondary n-hexyl- and n-dodecylbenzenes have been prepared, and the structures of the Friedel-Crafts alkylation products have been established by the method of mixed melting points. A study of the melting points of known mixtures showed that this method was reliable in the cases in which it was applied.

Among the products of the reaction of n-tetradecyl bromide with benzene and aluminum chloride, 1-phenyltetradecane has been identified. n-Hexadecyl bromide under these conditions gave some 1-phenylhexadecane, and n-octadecyl bromide gave some 1-phenyloctadecane.

It may be concluded from present findings, that under mild conditions benzene reacts with a normal primary alkyl bromide in the presence of aluminum chloride to give a mixture of alkylbenzenes, in which the phenyl group is very probably attached to each one of the carbon atoms in the alkyl residue. The evidence obtained does not indicate any appreciable amount of branching of the alkyl chain under the experimental conditions used.

AMES, IOWA

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