ALKYLATION AND THE ACTION OF ALUMINUM HALIDES ON ALKYLBENZENES

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I. INTRODUCTION[1]

The principal reactions of pure alkylbenzenes with aluminum chloride may involve dealkylation (dissociation) and alkylation, and either inter- or intra-molecular rearrangement. Depending on its configuration, the dissociated alkyl radical may undergo isomerization, dehydrogenation to form an olefin, or hydrogenation to form a paraffin. It may also alkylate another molecule of the hydrocarbon, or condense with another alkyl radical. Any or all of these reactions may take place, the extent of each depending on such factors as the particular alkylbenzene used, the amount and quality of the metal halide, the time of heating, and the temperature.

Since it appears, as will be shown later, that the initial reaction is dissociation, followed by re-alkylation, a study of the reactions of alkylbenzenes with aluminum chloride should also include consideration of the changes which occur during the alkylation of benzene or its homologs by the Friedel–Crafts procedure or modifications of it. Any theories which account for the formation of alkylbenzenes may also be applicable to the changes which take place when a hydrocarbon reacts with aluminum chloride.

II. ISOMERIZATION AND ORIENTATION

When alkylbenzenes were first prepared by the Friedel–Crafts reaction, some of the early investigators assumed that the radical entering the ring maintained the same configuration that it had in the alkyl halide. This, in spite of the fact that as early as 1879, it was observed that *n*-propyl bromide was converted into isopropyl bromide when warmed with alumi-

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[1] Discussions of all the various applications of the Friedel-Crafts reaction are to be found in the reviews by Kranzlein (53), Calloway (15), Linstead (56), and Egloff (23). The booklets *Physical Constants of Mononuclear Aromatic Hydrocarbons* by Egloff and Grosse (22) and *The Physical Constants of the Principal Hydrocarbons* by Doss (20) are very convenient sources of references to alkylbenzenes described in the literature, in addition to their usefulness as handbooks of physical constants.

num chloride at 71°C. for several hours (46). For example, toluene and isobutyl bromide were reported as forming *m*- and *p*-isobutyltoluenes (47). The principal product of this reaction was later identified as the *m-tert*-butyltoluene (6), but apparently the para-isomer was overlooked (75).

When the dialkyl homologs of benzene other than dimethylbenzenes are prepared by the Friedel–Crafts procedure, a mixture of meta- and para-isomers is formed with the meta-isomer predominating, rather than an ortho–para mixture as would be expected. In the reaction between the butyl halides and toluene at 0°C., *n*-butyl chloride gave a 75 per cent yield of *m-sec*-butyltoluene and a 25 per cent yield of the para-isomer. With isobutyl bromide, the meta–para ratio of *tert*-butyltoluenes was 70:30. Similar results were obtained using ferric chloride as the condensing agent (75).

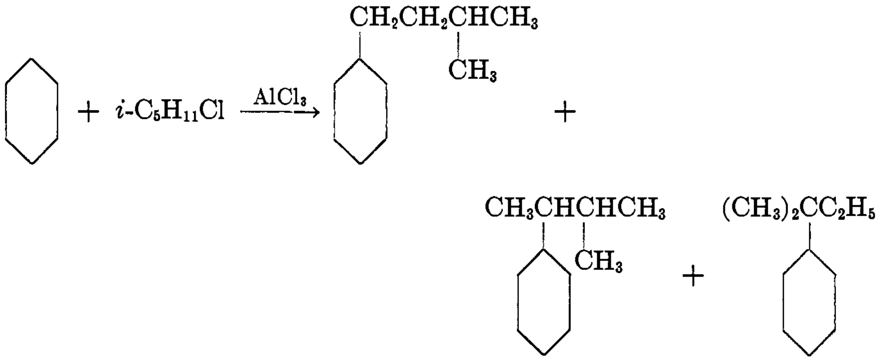
In the syntheses of trialkylbenzenes from benzene, monoalkylbenzenes, or from *m*-dialkylbenzenes by procedures involving the use of aluminum chloride as a catalyst, the principal product has the 1,3,5-configuration rather than the 1,2,4-configuration as would be expected, with the exception of the trimethylbenzenes, and probably the triethylbenzenes under some conditions. In these cases, either the alkyl groups in the meta-position do not exert their usual directing influence, or a 1,2,4-hydrocarbon is first formed and is subsequently rearranged to the 1,3,5-hydrocarbon by the aluminum chloride (61, 72, 81a). In the reaction between an acyl halide and a *m*-dialkylbenzene such as *m*-xylene, the product is a 1,3-dialkyl-4-acylbenzene.

There are conflicting statements in the literature relative to the identity of the propyl radical in the product of the reaction between *n*-propyl halides and benzene. This may be due in part to the different times of heating and different temperatures used by various investigators. At 0°C. the product of the reaction is reported as *n*-propylbenzene, while at higher temperatures a mixture of *n*-propylbenzene and isopropylbenzene results (51, 40).

The reaction between benzene and *n*-propyl formate in the presence of aluminum chloride is noteworthy, for *n*-propylbenzene was reported as the product, even though the reaction mixture stood overnight at room temperature and was subsequently heated to 60°C. (13). *n*-Butyl esters gave *sec*-butylbenzene under similar conditions.

The product from the alkylation of benzene with *n*-octadecyl bromide appears to be *n*-octadecylbenzene. The sulfonamide of the product of the reaction does not depress the melting point of the sulfonamide of *n*-octadecylbenzene prepared by the Wurtz–Fittig reaction or by the reduction of stearophenone (30).

Isoamyl chloride and benzene yielded a mixture of isoamylbenzene, *tert*-amylbenzene, and 2-phenyl-3-methylbutane (52).

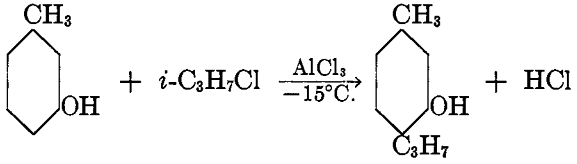


In the furan series, isomerization is even more striking and should be mentioned, even though these data may have no bearing on the alkylation of benzene and its homologs. Methyl 2-furoate and the four butyl chlorides gave methyl 5-*tert*-butyl-2-furoate, but with *n*-amyl chloride and *n*-hexyl chloride there was no isomerization of the alkyl radical (27). When ethyl 5-bromo-2-furoate was alkylated, all alkyl halides containing four or more carbons gave ethyl 4-*tert*-butyl-5-bromo-2-furoate or, in some cases, ethyl-5-*tert*-butyl-2-furoate (27, 29).

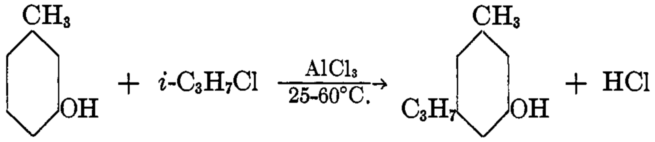
The isomerization of the entering alkyl group is explainable on the basis of Whitmore's theory of intramolecular rearrangements, and the formation of *m*-dialkylbenzenes can be accounted for by Price's mechanism, as will be shown later.

Since the —OH group, small alkyl groups, and halogens are normally ortho–para directing, the products formed when these benzene derivatives are alkylated in the presence of aluminum chloride should have the same orientation as the alkylbenzenes. The 3-methyl-4-*tert*-butylanisole is obtained from *m*-cresyl methyl ether and *tert*-butyl chloride at *low temperatures* (19), and this is the product which would be expected if the ether group and the methyl group exert their normal directing influence.

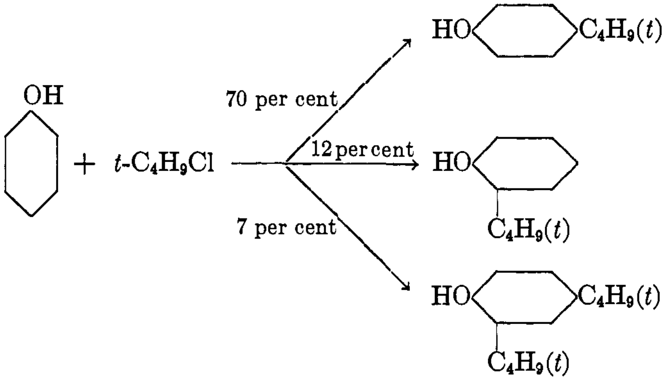
The phenolic group is generally considered as more strongly ortho–para directing than is the methyl group, for in the nitration of *p*-nitrophenol the nitro group enters the nucleus ortho to the hydroxyl group. In the alkylation of *m*-cresol with isopropyl chloride, the hydroxyl group and methyl group should reinforce each other, and the entering isopropyl group would be expected to take the 4-position. Such is the case if the reaction is carried out at −15°C. (31).



If, however, the initial and final temperatures of the reaction are 25° and 60°C., the alkylated phenol has the 1,3,5-configuration.



Phenol itself may be alkylated by means of *tert*-butyl chloride and aluminum chloride. With a mixture of equimolecular quantities of *tert*-butyl chloride and phenol and 1 per cent of aluminum chloride, the products have the normal ortho-para configuration (31).



The initial temperature is 15°C., and is gradually raised to 100°C. *tert*-Butyl alcohol gives similar results (37).

The 1,3-diisopropyl-4-bromobenzene was reported from the reaction of bromobenzene, isopropyl chloride, and aluminum chloride at 0°C. (14).

The methylation of toluene in the presence of aluminum chloride has recently been studied at temperatures ranging from $-3°$ to 106°C. (67a). The data are given in table 1. At the higher temperatures *m*-xylene is the principal product, while at temperatures of $-3°$ to $+18°$C. the ortho-isomer predominates. In only one other case has *o*-xylene been reported in appreciable quantities from the methylation of toluene (42). The ethylation of toluene and *m*-xylene with ethyl bromide and aluminum chloride at $-12°$ to 0°C. yielded mixtures of ethylated hydrocarbons, the composition of which could not be definitely established.

A comparison of the configuration of the products of the alkylation of these three classes of compounds and the experimental conditions under which they are formed shows clearly that the temperature at which the alkylation is carried out is a primary factor in determining the final position taken by the entering group. The nature of the entering alkyl group may also be another important factor, if the view is correct that a 1,4- or a 1,2,4-derivative is first formed and is subsequently rearranged.

III. ALKYLATION

Alkylations of benzene or its homologs by any of the procedures other than the Wurtz-Fittig reaction or the Grignard reaction have the following characteristics in common:

The alkyl radical of the alkylating agent may undergo more or less extensive isomerization in the presence of all of the various catalysts which have been studied,—aluminum chloride, ferric chloride, boron fluoride, hydrogen fluoride, sulfuric acid, and zinc chloride.

TABLE 1

Methylation of toluene (67a)

METHYLATING AGENT + $AlCl_3$	TEMPERATURE	PER CENT XYLENES		
		Ortho	Para	Meta
	°C.	per cent	per cent	per cent
CH_3Br	−3	44.5	27.5	28.0
CH_3Br	5–18	45.6	28.0	26.4
CH_3Br*	−3	49.1	20.4	30.5
CH_3Br	+94	8.4	9.0	83.6
CH_3Cl	0	53.5	19.2	27.3
CH_3Cl	55	12.2	0.7	87.1
CH_3Cl	106	1.8	0.0	98.2

* Plus $AlBr_3$.

Aluminum chloride and ferric chloride usually lead to a mixture of *m*- and *p*-dialkylbenzenes with the meta-isomer predominating. With the other catalysts, an ortho-para mixture is obtained.

When the entering group is ethyl, propyl, or larger, the principal trialkylbenzene is generally the 1,3,5-hydrocarbon, if aluminum chloride is the catalyst. In the presence of sulfuric acid the 1,2,4-hydrocarbon is formed. No 1,2,3-trialkylbenzene has been found among these alkylation products.

In spite of their disadvantages, aluminum chloride and anhydrous ferric chloride are the most generally satisfactory catalysts for those alkylations in which their limitations do not prevent their use. In some cases, ferric chloride gives better yields than does aluminum chloride. Aluminum chloride is a more satisfactory catalyst than aluminum bromide.

In the presence of either aluminum chloride or sulfuric acid, the 1,2,4,5-tetraalkylbenzene is formed almost exclusively with the exception of the tetramethylbenzene and possibly the tetraethylbenzene. The tetraalkylbenzene fraction from the methylation of benzene or toluene is largely the 1,2,3,5-tetramethylbenzene. The 1,2,3,4-tetraalkylbenzenes have been obtained only by means of the Jacobsen reaction.

No alkylbenzenes have been reported which contain more than three butyl groups or more than four isopropyl groups. Hexa-*n*-propylbenzene has been prepared.

It is well known that in the preparation of monoalkylbenzenes by the Friedel–Crafts procedure, varying amounts of higher alkylbenzenes are formed, owing to the fact that a monoalkylbenzene undergoes substitution more readily than does benzene.

A. The preparation of mono- and di-alkylbenzenes

Within the last few years, a number of procedures have been developed for the alkylation of aromatic hydrocarbons by reagents other than alkyl halides and with catalysts other than aluminum chloride. These procedures are for the most part variations of the Friedel–Crafts reaction.

With aluminum chloride as the catalyst, alkyl halides may be replaced by alcohols (38, 40, 67, 67b), olefins (8, 10, 26), paraffins (32b, 63a), inorganic esters (45), and some organic esters (13, 67b) and ethers (67b). In those cases where the orientations of the di-, tri-, and tetra-alkylbenzenes formed have been determined, their configuration is the same as when the standard Friedel–Crafts procedure is used.

The alkylation of benzene with esters (63) and alcohols (62) may also be accomplished with boron fluoride as the catalyst, and olefins will alkylate with boron fluoride in the presence of sulfuric acid (78). It has been claimed that the use of boron fluoride with sulfuric acid is unnecessary (39), but it has been shown that better yields of alkylbenzenes are obtained when both boron fluoride and sulfuric acid are used (92).

Hydrogen fluoride has been reported as a useful catalytic agent for the alkylation of benzene by olefins and by alkyl halides (76, 14a, 76a).

Most of the investigations of alkylation in the presence of boron fluoride or hydrogen fluoride have been concerned mainly with the formation of mono- and di-alkylbenzenes, and either no attempt was made to prepare trialkylbenzenes, or the fractions containing them were not studied. Trialkylbenzenes formed during alkylation by means of these condensing agents would be expected to have the 1,2,4-configuration, since the dialkylbenzene fraction is an ortho–para mixture with the para-isomer predominating.

A detailed study has been made of the ethylation of benzene, using an excess of ethyl chloride and ethyl bromide with aluminum chloride and aluminum bromide, respectively, under the same experimental conditions, in an effort to compare the efficiency of the two catalysts (88). The aluminum chloride–ethyl chloride combination gave the best yields of hexaethylbenzene and smaller amounts of lower ethylated benzenes. It is suggested that this may be due to the fact that aluminum bromide is more soluble in the ethyl bromide–hydrocarbon mixture and may bring about the dealkylation of some of the hexaethylbenzene formed.

Anhydrous ferric chloride has not been extensively used as a catalyst for the alkylations of aromatic hydrocarbons, although in those instances where its use is recorded, yields are comparable to those obtained with aluminum chloride.

The yields and proportions of *m*- and *p*-*tert*-butyltoluenes from toluene and *tert*-butyl chloride in the presence of ferric chloride are approximately the same as when aluminum chloride is used (75), and in the reaction between *m*-xylene and cyclohexyl bromide better yields were reported with ferric chloride than with aluminum chloride (4). In these two reactions, both metal chlorides have the same orienting influences. The reaction between *tert*-butyl chloride or isobutyl chloride and toluene in the presence of ferric chloride had first been reported as giving only *p*-*tert*-butyltoluene (9).

The yield of *tert*-butylethylbenzene from ethylbenzene and *tert*-butyl chloride is also said to be better with ferric chloride as the catalyst than with aluminum chloride (5). The orientation of the *tert*-butylethylbenzene was not determined.

The ethylation of benzene by ethyl bromide and ferric chloride gives a mixture of mono-, di-, tri-, and tetra-ethylbenzenes, but no effort was made to determine the orientation of the polyethylbenzenes formed (89).

The alkylation of benzene with propylene and isobutylene in the presence of ferric chloride gave good yields of alkylbenzenes (68). Propylene and benzene in equimolecular ratios with 0.3 mole of ferric chloride at room temperature gave a 91 per cent yield of isopropylbenzene. Isobutylene and benzene under the same conditions gave 89 per cent of *tert*-butylbenzene, and 2 moles of isobutylene with 1 mole of benzene gave a 65 per cent yield of *p*-di-*tert*-butylbenzene. It is of interest that only the *p*-dialkylbenzene was reported from the latter reaction, since *tert*-butyl chloride and toluene in the presence of ferric chloride form a meta–para mixture in the ratio of 70:28 (75). The alkylation of benzene with these olefins and aluminum chloride gave smaller yields of the alkylbenzenes.

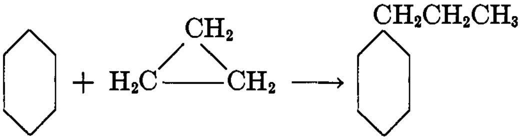
Benzene has been alkylated by ethylene in the presence of hydrogen chloride and beryllium chloride, titanium tetrachloride, zirconium tetrachloride, columbium pentachloride, and tantalum chloride (32a). Temperatures ranged from 75°C. to 200°C. Mixtures of ethylbenzene, diethylbenzene, and the polyethylbenzenes up to hexaethylbenzene were obtained.

Olefins will alkylate benzene in the presence of sulfuric acid in concentrations of 90–96 per cent (39, 39b), as will alcohols in the presence of

70–85 per cent sulfuric acid (48, 58). The dialkylbenzene formed under these conditions is mainly the para-isomer.

These procedures can be used only when the isomerization of the entering radical will not lead to an undesired configuration or to a mixture of isomers.

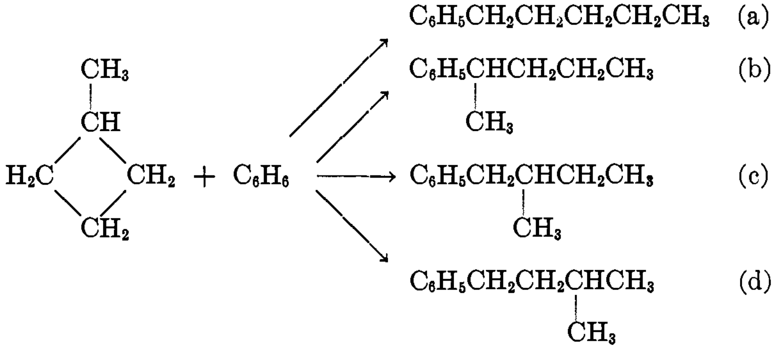
The use of the cycloparaffins and aluminum chloride for the alkylation of benzene has given some interesting results (32). At 0°C. or at 25–30°C., cyclopropane gives *n*-propylbenzene and varying amounts of poly-*n*-propylbenzenes, including hexa-*n*-propylbenzene. There seems to be no doubt as to the identity of this latter hydrocarbon. Cyclopropane and benzene with hydrogen fluoride as a condensing agent also yield *n*-propylbenzene (77).



The formation of *n*-propylbenzene rather than isopropylbenzene from cyclopropane is accounted for as follows (77): "The cyclopropane molecule, being under strain, will be the center of an abnormal electromagnetic field, as indicated by its magnetic susceptibility. This may cause it to add a proton to form a hypothetical and transitory propyl ion. The additional strain may cause the ring to break, and, irrespective of where it breaks, a *n*-propyl positive ion will be formed. The reaction of this ion with benzene will produce *n*-propylbenzene and a proton."

Cyclobutane is reported as reacting readily, presumably to yield *n*-butylbenzene.

Methylcyclobutane could yield four monoamylbenzenes:



A mixture of hydrocarbons was formed, from which isoamylbenzene and 2-phenylpentane were isolated and identified (32). In addition to the products indicated, the reaction could also involve the isomerization of any of these monoamylbenzenes and polyamylbenzenes could also be formed.

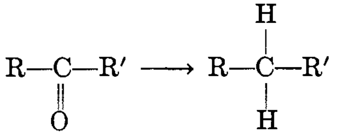
A temperature of 150°C. is required for the reaction of cyclopentane and benzene (32). The products of the reaction are a mixture of amylbenzenes and cyclopentylbenzene. It is probable that *n*-amylbenzene is formed first and is isomerized at the high temperature necessary for the reaction.

Cyclopropane will also alkylate benzene in the presence of sulfuric acid at 0°C. to yield *n*-propylbenzene, but if the temperature is increased to 65°C., the product of the reaction is isopropylbenzene (40). Methylcyclobutane and sulfuric acid at 2–4°C. yield *tert*-amylbenzene (39c).

It is suggested that the methylcyclobutane reacts first with the sulfuric acid to form isoamyl acid sulfate. This ester may be converted into *tert*-amyl acid sulfate, which reacts with benzene to form *tert*-amylbenzene (39c). Cyclopropane may form *n*-propyl acid sulfate.

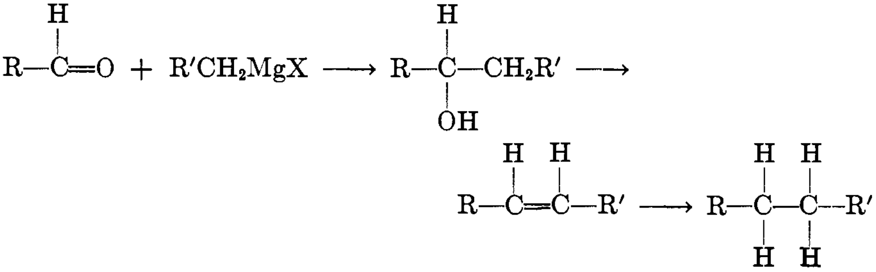
To avoid side reactions as much as possible during the preparation of hydrocarbons by procedures involving the use of aluminum chloride, both the time and temperature of the reaction should be kept at a minimum, and the reaction products should not be left in contact with aluminum chloride any longer than necessary. The value of these precautions is illustrated in the preparation of ethylisopropylbenzene from ethylbenzene and *n*-propyl bromide. The reaction mixture stood at room temperature for 8 days, and the following hydrocarbons were obtained: isopropylbenzene, *m*- and *p*-ethylisopropylbenzenes, *m*-diethylbenzene, and diisopropylbenzene (7).

Hydrocarbons containing normal radicals should be prepared by some other procedure than direct alkylation, with the exception of alkylations with such reagents as cyclopropane. The reduction of a ketone (16) with amalgamated zinc



$$\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}R'} \longrightarrow \mathrm{R{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}R'}$$

where R is aromatic and R′ is aliphatic, is satisfactory if the desired ketone can be readily obtained. Another method makes use of the Grignard reaction



$$\mathrm{R{-}\overset{\overset{H}{|}}{C}{=}O} + \mathrm{R'CH_2MgX} \longrightarrow \mathrm{R{-}\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}{-}CH_2R'} \longrightarrow$$

$$\mathrm{R{-}\overset{\overset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}{-}R'} \longrightarrow \mathrm{R{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}R'}$$

For example, hydrocarbons containing amyl radicals should be prepared by procedures such as these to be certain of the configuration of the amyl radical and to avoid the possibility of mixtures (41, 60).

The Wurtz–Fittig synthesis of hydrocarbons is so well known as to require no comment, but a variation of it should be mentioned. Monoalkylbenzenes may be obtained in 40 to 70 per cent yields from benzyl sodium and an alkyl halide (60). The preparation of amylbenzene proceeds through these steps

$$C_5H_{11}Cl \xrightarrow{\text{Na in } C_6H_6} C_6H_5Na \xrightarrow{C_7H_8} C_6H_5CH_2Na \xrightarrow{C_4H_9Cl} C_6H_5C_5H_{11}$$

By-products in the preparation of ethylbenzene (yield 42 per cent) from benzyl sodium and methyl iodide are pentene, pentane, and decane formed from the amyl chloride used initially, and some liquids boiling at 174–205°C. Benzyl sodium is recommended as an alkylating agent whenever it can be used, but phenyl sodium and alkyl chlorides "are capable of giving high yields of products other than the expected coupling."

Typical procedures for the preparation of dialkylbenzenes are those employed in the preparation of *m*- and *p*-di-*n*-propylbenzenes (3) and the meta- and para-forms of *sec*-butyltoluene and *tert*-butyltoluene (75).

B. The preparation of 1,3,5-trialkylbenzenes

Some of the trialkylbenzenes may be synthesized by the Friedel–Crafts procedure, though in some cases the product is a mixture of 1,2,4- and 1,3,5-isomers.

The formation of the various polymethylbenzenes by the methylation of benzene or its homologs is accounted for in this series of reactions (42):

$$\begin{tikzcd}
 & o\text{-Xylene} \arrow[dr] & & & \\
\text{Toluene} \arrow[ur] \arrow[r] \arrow[dr] & p\text{-Xylene} \arrow[r] & \text{Pseudocumene} \arrow[r] & \text{Durene} \arrow[dr] & \\
 & m\text{-Xylene} \arrow[ur] \arrow[r] & \text{Mesitylene} \arrow[r] & \text{Isodurene} \arrow[r] & \text{Pentamethylbenzene}
\end{tikzcd}$$

This case and one other (67a) are the only instances in which an appreciable amount of *o*-xylene is reported. The methylation of *m*-xylene at 70–80°C. yielded pseudocumene and mesitylene in the ratio of about 4:1. Pseudocumene was formed almost exclusively from *p*-xylene. Mesitylene gave mostly isodurene and pseudocumene gave durene.

Pseudocumene, mesitylene, durene, and isodurene and other polymethylbenzenes result from the methylation of technical xylene with methyl chloride, or by heating technical xylene with aluminum chloride at 130–

140°C. for 8 to 10 hr. (79). The proportions of the isomers in the crude trimethylbenzene fractions average approximately two parts of the 1,2,4-isomer to one part of the 1,3,5-isomer. In the tetramethylbenzene fractions there is 90 per cent of the 1,2,3,5-hydrocarbon (isodurene) and 10 per cent of the 1,2,4,5-hydrocarbon (durene). When the tetramethylbenzenes undergo the Jacobsen reaction, the product is entirely the 1,2,3,4-tetramethylbenzene.

There is some 1,3-dimethyl-4-ethylbenzene in the product of the reaction between *m*-xylene and ethyl bromide (84), and both 1,2,4-triethylbenzene and 1,3,5-triethylbenzene are listed from ethyl chloride and benzene (49). However, in the synthesis of mesitylene and of 1,3,5-triethylbenzene from benzene and methyl or ethyl alcohol, respectively, no mention is made of the presence of the 1,2,4-isomer (49).

There are also differing statements relative to the products formed in the propylation of benzene (24). Only the 1,3,5-triisopropylbenzene is listed from the reaction of benzene and isopropyl chloride (35). Propylene and benzene give a mixture containing about 75 per cent of 1,3,5-triisopropylbenzene and 25 per cent of the 1,2,4-isomer (8).

Usually the orientation of the trialkylbenzene was determined by oxidizing the hydrocarbon to an acid. In some cases the acid was a dimethylbenzoic acid or a methylphthalic acid, but generally it was trimesic acid or trimellitic acid. In oxidizing a small sample of 1,3,5-hydrocarbon containing a small amount of 1,2,4-isomer, the trimellitic acid could be overlooked during the purification of the trimesic acid. Yields of acids from tetraalkylbenzenes are very poor.

With the various limitations in mind, a variety of 1,3,5-hydrocarbons could be obtained as follows, using aluminum chloride as the condensing agent:

(a) $C_6H_6 + 3\ RCl$

(b) $RC_6H_5 + 2\ RCl$

(c) $R_2C_6H_4 + RCl$

Alcohols (67, 38), olefins (8, 10, 26), some organic esters (13), and some inorganic esters (45) could be substituted for alkyl chlorides with suitable modification of the procedure.

A summary of the reagents used for the preparation of a number of 1,3,5-hydrocarbons as described in the literature is given in table 2.

The 1,3,5-hydrocarbons containing normal radicals, such as tri-*n*-butylbenzene or 1,3-dimethyl-5-*n*-butylbenzene, cannot in general be prepared by procedures involving the use of aluminum chloride.

C. The preparation of 1,2,4-trialkylbenzenes

Prior to 1928, the 1,2,4-hydrocarbons mentioned in the literature, with the exception of pseudocumene, were usually prepared by procedures involving the use of Grignard reagents, or by the reduction of a ketone. Pseudocumene can be obtained from the methylation of benzene with methyl bromide and aluminum chloride at low temperatures (67a), or from *m*-xylene (79).

TABLE 2

Preparation of 1,3,5-trialkylbenzenes

HYDROCARBON	REAGENTS	REFERENCE
1,3,5-Trimethylbenzene	C_6H_6, CH_3OH	(67)
	C_6H_6, CH_3Cl	(42, 79, 67a)
1,3,5-Triethylbenzene	C_6H_6, C_2H_5Cl	(49, 67a)
	C_6H_6, C_2H_4	(26)
1-Methyl-3,5-diethylbenzene	$C_6H_5CH_3$, C_2H_4	(26)
1,3-Dimethyl-5-ethylbenzene	*m*-$C_6H_4(CH_3)_2$, C_2H_4	(26)
	m-$C_6H_4(CH_3)_2$, C_2H_5Br	(84)
1,3,5-Triisopropylbenzene	C_6H_6, C_3H_6	(8)
	C_6H_6, iso-C_3H_7Cl	(74)
1-Methyl-3,5-diisopropylbenzene	Cymene, $AlCl_3$	(72)
Tri-*tert*-butylbenzene	C_6H_6, iso-C_4H_9Cl	(74)
1,3-Dimethyl-5-*tert*-butylbenzene	$C_6H_4(CH_3)_2$, *tert*-C_4H_9Cl	(6)
	$C_6H_4(CH_3)_2$, triisobutyl borate	D.R.P. 184,230
	$C_6H_4(CH_3)_2$, *tert*-C_4H_9OH	(67b)
1,3,5-Tricyclohexylbenzene	C_6H_6, C_6H_{10}	(18)
1,3-Dimethyl-5-cyclohexylbenzene	*m*-$C_6H_4(CH_3)_2$, C_6H_{10}	(11)

In 1928 a method was developed for the preparation of alkylbenzenes from benzene and an alcohol in the presence of 70–80 per cent sulfuric acid at 40–70°C. (58). The hydrocarbon and alcohol were added to the acid. Later it was found that the reaction would proceed readily if 80–85 per cent sulfuric acid was added to the mixture of alcohol and hydrocarbon at room temperature (48). By these procedures, the dialkylbenzene formed is mainly para, and the trialkylbenzene has the 1,2,4-orientation.

This method is subject to one of the limitations already mentioned—namely, the isomerization of the alkyl radical during alkylation. *n*-

Alkylbenzenes have not been prepared by this method, and alcohols above the butyl alcohols are likely to give mixtures. For example, 2-pentanol and benzene could yield a mixture of 2-phenylpentane and 3-phenylpentane. The 1,2,4-hydrocarbons containing normal radicals can best be prepared by other methods, such as the reduction of a ketone or by the use of Grignard reagents.

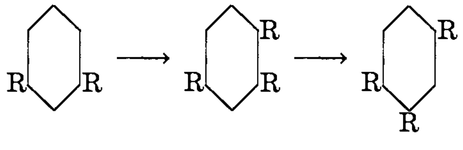
The preparation of 1,2,4-tri-*n*-propylbenzene (3) is a typical procedure by which a tri-*n*-alkylbenzene may be obtained.

D. The tetraalkylbenzenes

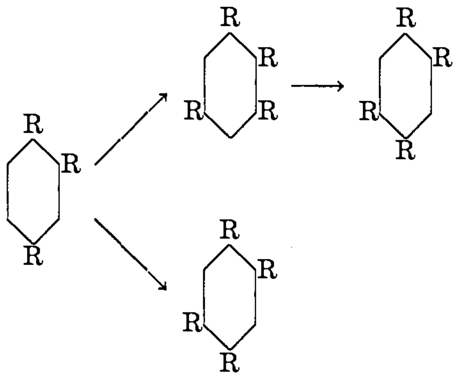
The 1,2,4,5-tetraethylbenzene is the principal product of the reaction between ethyl bromide, benzene, and aluminum chloride at low temperatures (44). A small amount of the 1,2,3,5-isomer is probably formed, but not enough of it could be isolated for positive identification.

The 1,2,4,5-tetraisopropylbenzene is reported from the following reactants: (*1*) benzene, isopropyl alcohol, and concentrated sulfuric acid (48); (*2*) benzene, propylene, and concentrated sulfuric acid, aluminum chloride, or hydrogen fluoride (39, 8, 14a); (*3*) benzene, isopropyl chloride, and aluminum chloride (88). In these reactions, aluminum chloride, hydrogen fluoride, and concentrated sulfuric acid all appear to give the same tetraalkylbenzene. In the case of the tetramethylbenzenes, the 1,2,3,5-hydrocarbon is the principal product.

Since the principal triisopropylbenzene obtained from propylene or isopropyl chloride has the 1,3,5-configuration, the tetraisopropylbenzene formed would be expected to have the 1,2,3,5-configuration as it does in the case of the tetramethylbenzenes, whereas the final product appears to be the symmetrical 1,2,4,5-isomer. If the 1,2,3,5-hydrocarbon is an intermediate product in these alkylations, the formation of the 1,2,4,5-hydrocarbon would require an intramolecular rearrangement involving the migration of an isopropyl group.



In the presence of sulfuric acid as the condensing agent, the trialkylbenzene formed is the 1,2,4-hydrocarbon. The 1,2,4,5-hydrocarbon could be obtained from it by these same changes, or it could be formed directly.



Either type of catalytic agent could lead directly to the symmetrical tetraalkylbenzene through the 1,2,4-hydrocarbon.

It has been reported that a hexapropylbenzene is formed from dipropylbenzene and excess propyl chloride (presumably the normal halide) in the presence of aluminum chloride at room temperature for 40 hr. (88). The melting point of this product is given as 101°C., and the melting point of hexa-*n*-propylbenzene from cyclopropane and benzene is 103°C. (32). Analyses and molecular weight determinations agree with the molecular formula $C_{24}H_{42}$.

In view of the fact that there is more or less isomerization of the *n*-propyl radical during alkylation under these experimental conditions, it would not be surprising if a mixture of poly-*n*-propylbenzenes and polyisopropylbenzenes were obtained from this reaction. An effort to alkylate 1,2,4,5-tetraisopropylbenzene further with isopropyl chloride in the presence of aluminum chloride at temperatures up to 100°C. gave negative results (32).

Ethylmesitylene, 3-ethylpseudocumene, and 5-ethylpseudocumene are prepared through the Grignard reaction from the corresponding bromomesitylene or pseudocumene and diethyl sulfate, or by the reduction of the corresponding acetylmesitylene or pseudocumene (80).

While there is apparently no relation between the mechanism of the Jacobsen reaction and the rearrangements with aluminum chloride, it is of interest to compare the two types of reactions. The Jacobsen reaction is the only means by which 1,2,3,4-hydrocarbons have been obtained.

Trimethylbenzenes do not undergo rearrangement by sulfuric acid or other sulfonating agents.

The polymethylbenzenes above the trimethylbenzenes first undergo sulfonation to form a sulfonic acid and then a methyl group migrates either from one molecule to another or to another position in the same molecule. These reactions are illustrated in chart I (61). It should be noted that in these rearrangements of the polymethylbenzenes, the 1,2,3,4-hydrocarbon is the principal tetraalkylbenzene formed from durene or isodurene. This hydrocarbon has not been obtained either by direct alkylation or by rearrangements by means of aluminum chloride.

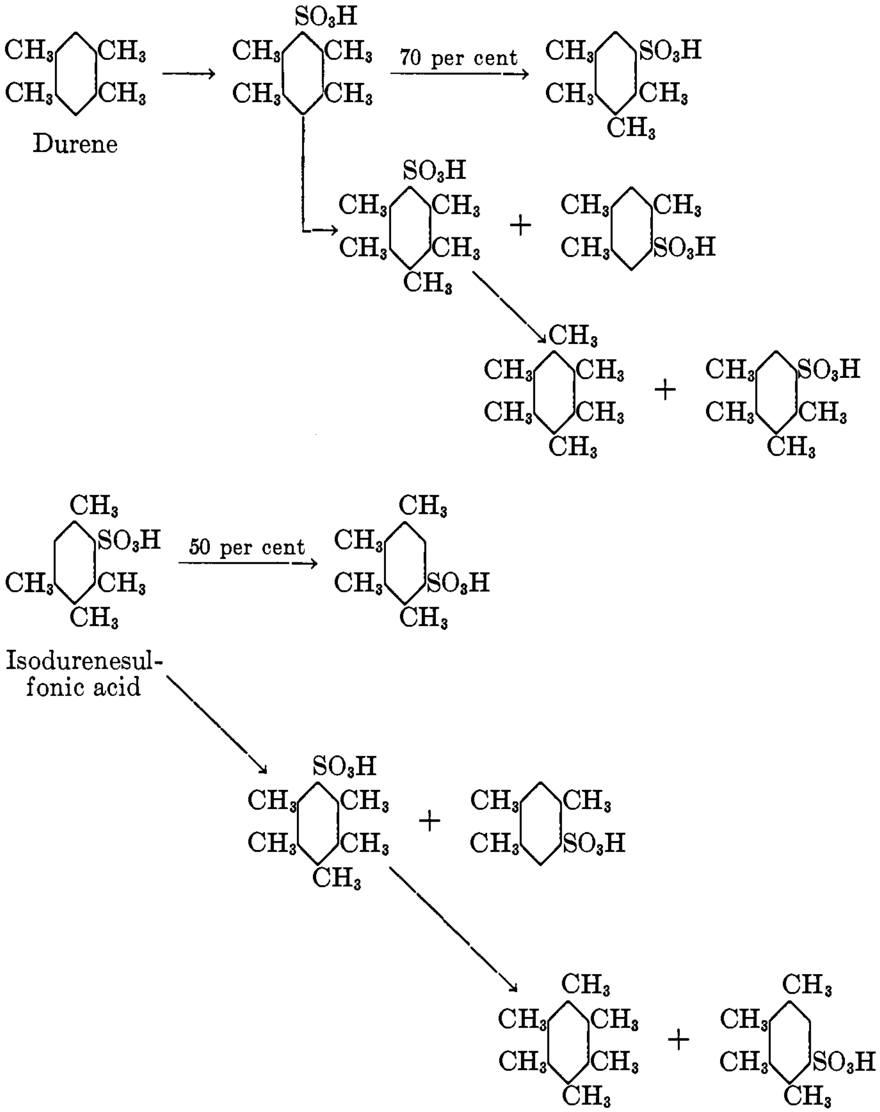


Chart I

Pentamethylbenzene yields hexamethylbenzene and prehnitenesulfonic acid.

When one of the methyl groups of durene and isodurene is replaced by an ethyl group, the changes are much more complex (81). Both 5-ethylpseudocumene and ethylmesitylenesulfonic acid rearrange to 3-ethylpseudocumene in the main reaction. In secondary reactions, 5-ethylpseudocumene gave prehnitene, 1,3-dimethyl-4-ethylbenzene, and pseudocumene.

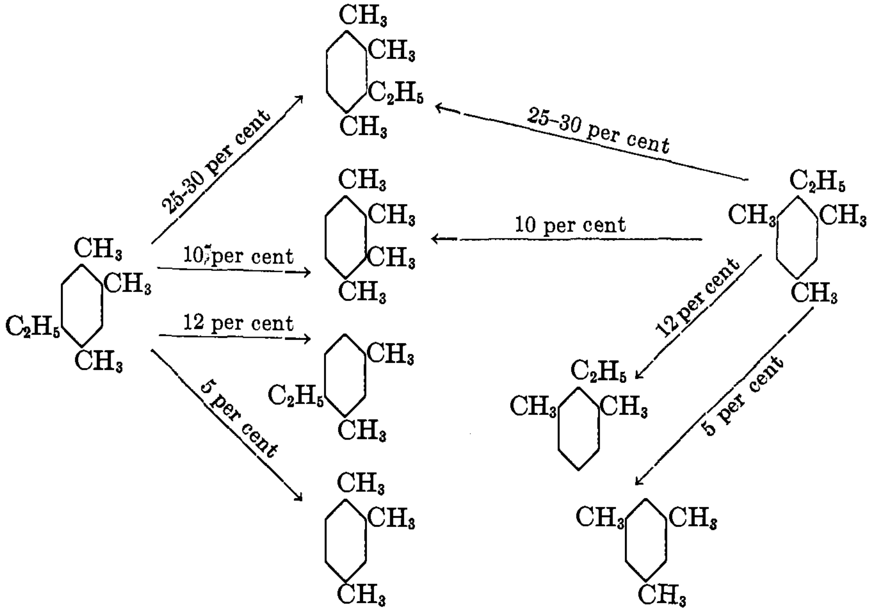


Chart II

Ethylmesitylene gave prehnitene, 1,3-dimethyl-2-ethylbenzene, and mesitylene. These relationships are shown in chart II.

IV. DERIVATIVES OF HYDROCARBONS

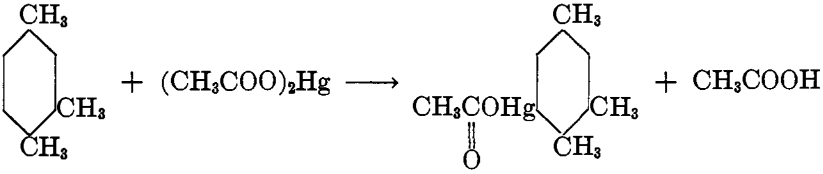
The preparation of suitable derivatives of hydrocarbons for purposes of identification is not as simple as it might first appear. The derivatives should be easily obtained in good yields and in pure form from a small amount of hydrocarbon, they should melt without decomposition, and they should give a definite depression of the melting point when mixed with an isomer.

Unfortunately, compounds which are very similar in structure or are isomers often do not give a marked depression of the melting point, particularly if their melting points are close together. This is especially true of the polyhalogen derivatives of the alkylbenzenes.

Mixtures of polynitro derivatives of isomeric hydrocarbons are more likely to show a definite melting point depression. The preparation of pure polynitro derivatives of some of the alkylbenzenes in good yields is not always readily accomplished, and precautions must be taken to control the temperature of nitration and the composition of the nitrating mixture in order to avoid destruction of any of the alkyl groups, such as large tertiary radicals (4). The trialkylbenzenes in which the radicals are not all the same are likely to yield mixtures of isomeric mono- or di-nitro derivatives, so that complete nitration of the polyalkylbenzenes is carried out whenever possible.

From a 1,2,4-hydrocarbon such as pseudocumene, three mononitro derivatives and three dinitro derivatives are possible. A 1,3,5-hydrocarbon in which all the radicals are the same would yield only one mono- and one di-nitro derivative, but if one radical is different, such as in 1,3-dimethyl-5-ethylbenzene, there are two possible mono- and di-nitro derivatives.

The acetoxymercuri hydrocarbons (82) can be prepared, but the reaction is slow and yields are small.

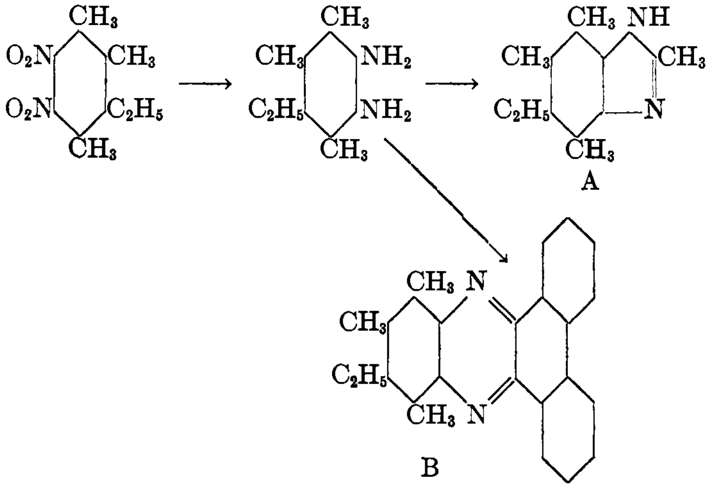


Sulfonation of hydrocarbons and the subsequent conversion of the sulfonic acid to a sulfonamide or substituted amide has been used extensively for purposes of identification, but the reaction is inconvenient for small samples and isomers do not always give satisfactory depressions of the melting point when mixed (81). Concentrated or fuming sulfuric acid causes migration of alkyl groups in alkylbenzenes containing more than three alkyl groups (charts I and II) unless used with great care, and it is possible that radicals larger than methyl might migrate in trialkylbenzenes such as the butyl-*m*-xylenes.

Trialkylbenzenes do not form stable picrates, picrolonates, or styphnates, and the trinitro derivatives of polyalkylbenzenes such as mesitylene and 1,3-dimethyl-5-*tert*-butylbenzene do not form stable addition compounds with naphthalene (19a).

The mono- or di-acetamino derivatives of the monoalkylbenzenes are satisfactory as to ease of preparation and purification and give excellent depressions of the melting point (40a, 41). The polyalkylbenzenes will give mixtures of isomers corresponding to the nitro derivatives mentioned above.

The dinitro derivatives of 1,2,3,4-tetraalkylbenzenes can be reduced to the corresponding diamines, which undergo ring closure with acetic acid to form a benzamidazole (A) or with phenanthraquinone to form a phenanthrophenazine (B).



No ring closure of this type is possible with meta- or para-diamines.

V. BROMINATION IN THE PRESENCE OF ALUMINUM BROMIDE

If benzene, toluene, or the xylenes are treated with excess bromine containing aluminum bromide (bromine containing about 1 per cent aluminum), the hydrocarbon is completely brominated on the ring. If, however, the hydrocarbon contains radicals larger than methyl, these larger radicals are split off as RBr, replaced by bromine, and the ring is completely brominated (see table 3). The reaction is said to be vigorous even at low temperatures and is quantitative.

The statement that bromination of *m*-xylene in the presence of aluminum chloride gives tetrabromo-*p*-xylene (55) is surprising, since *m*-xylene is more stable in the presence of aluminum chloride than is *p*-xylene, and methyl groups in other hydrocarbons are not affected by bromination under these conditions. No experimental details were given in the abstract.

Bromobenzene and aluminum chloride (17) heated on the water bath for 8 hr. yielded a mixture of benzene, the three dibromobenzenes, 1,3,5-tribromobenzene, and some 1,2,4-isomer. *p*-Dibromobenzene yielded benzene, bromobenzene, a mixture of dibromobenzenes, and the 1,2,4- and 1,3,5-tribromobenzenes. The tribromobenzene was mostly the 1,3,5-isomer. Chlorobenzene was not affected by aluminum chloride.

Alkylation of bromobenzene with ethylene in the presence of aluminum chloride (8) yielded a mixture of benzene, ethylbenzene, diethylbenzene, and brominated ethylbenzenes.

VI. THE ACTION OF ALUMINUM CHLORIDE ON ALKYLBENZENES

As early as 1885 the investigators of alkylation and of the reactions between aluminum chloride and pure alkylbenzenes concluded that the reaction was reversible, that radicals were removed from a molecule of a hydrocarbon by the metal halide, and that the radical so removed could alkylate another molecule of the same hydrocarbon or a different hydrocarbon. This early view has proved to be correct.

TABLE 3

Bromination in the presence of aluminum bromide

HYDROCARBON	PRODUCT	REFERENCE
Cymene	Pentabromotoluene	(33)
1,4-Dimethyl-2-ethylbenzene	Tetrabromo-*m*-xylene	(10)
1,3-Dimethyl-5-*tert*-butylbenzene	Tetrabromo-*m*-xylene	(10)
1,2-Dimethyl-4-isopropylbenzene	Tetrabromo-*o*-xylene	(50)
1-Methyl-2-ethyl-3-isopropylbenzene	Pentabromotoluene	(50)
m-Xylene (with aluminum chloride and bromine)	Tetrabromo-*p*-xylene	(55)
Cyclohexylmesitylene	Tribromomesitylene	(11)

A survey of the products formed in the syntheses of alkylbenzenes by the Friedel–Crafts procedure and of the products of the reactions of pure aromatic hydrocarbons with aluminum chloride leads to the following generalizations, although data from the various investigators are not entirely comparable, owing to the use of different experimental conditions, and some of the data are conflicting.

The initial reaction is a dissociation of an alkyl radical followed either by re-alkylation of another molecule of the same hydrocarbon or a different hydrocarbon, or by hydrogenation of the alkyl radical to form a saturated hydrocarbon. The source of this hydrogen is not indicated. There is no evidence for the formation of appreciable amounts of olefins.

In suitable cases the dissociated alkyl radical undergoes isomerization.

The formation, either during alkylation or by warming with aluminum chloride, of a mixture of *m*- and *p*-dialkylbenzenes with the meta-isomer predominating is explainable on the basis of Price's mechanism, as is shown later.

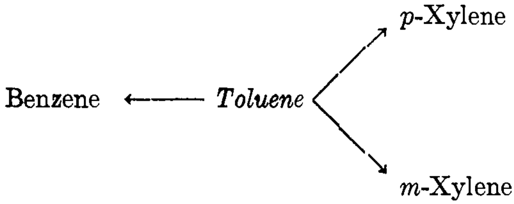
The higher the temperature and the longer the time of heating, the more complex the composition of the mixture becomes, owing to the formation of a variety of benzene homologs in various stages of alkylation, brought about in part by the cleavage of the detached alkyl radicals and some alkylation by the fragments.

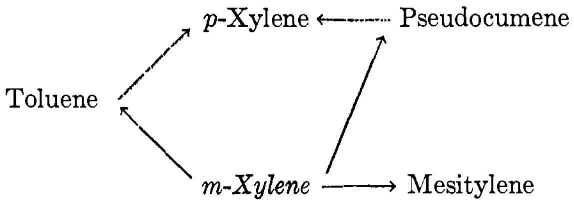
At a given temperature and time of heating, a high concentration of aluminum chloride increases the proportion of dealkylation products, including benzene.

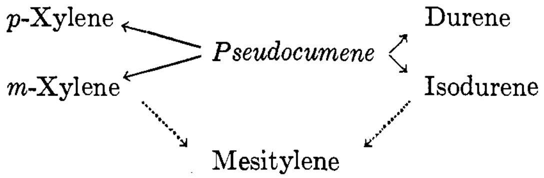
The larger the alkyl radical, the more readily it may be detached from the benzene ring. The bond between the methyl group and the nuclear carbon is the most stable. This is illustrated by the formation of 1-methyl-3,5-diisopropylbenzene from cymene, and of a methyldi-*tert*-butylbenzene, a methyltri-*tert*-butylbenzene and toluene from *p*-*tert*-butyltoluene. Further support for this view is found in the fact that when methylalkylbenzenes are brominated with excess bromine containing aluminum bromide, even at 0°C., all radicals but methyl are lost and the ring is completely brominated (table 3). The 1,2,4-trimethylbenzene appears to be more stable toward aluminum chloride than are other 1,2,4-trialkylbenzenes.

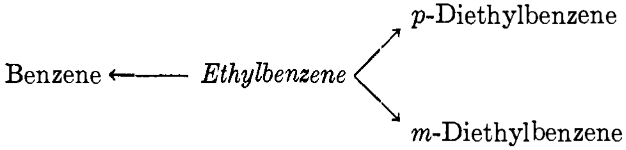
The action of aluminum chloride on the methylbenzenes was studied in detail and independently by several groups of investigators, including Friedel and Crafts, who published their results in 1885 (2, 25, 43).

The products of the reaction between the various methylbenzenes and aluminum chloride at their boiling points were accounted for by the following reactions (2):



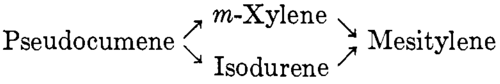






There was no evidence for an *o*-dialkylbenzene in the reaction products.

It was believed that mesitylene was formed indirectly from pseudocumene as indicated by the dotted arrows in the diagram. The formation of *p*-xylene from *m*-xylene through toluene and pseudocumene was accounted for in the same way. From ethylbenzene only *m*- and *p*-diethylbenzenes were identified, with the *p*-diethylbenzene predominating, while with toluene the *m*-xylene was the principal dialkylbenzene. The trialkyl fraction from pseudocumene was mainly mesitylene (1).



An effort was made to determine the amounts of the various products in a more extensive study of the reactions of the polymethylbenzenes and aluminum chloride. The results are summarized in table 4.

From the experiments in which quantities of reactants and reaction products are given, it appears that isodurene and durene are formed in proportions of approximately 2:1 except from pseudocumene where the proportions are reversed under some conditions. In the presence of dry hydrogen chloride, the amounts of de-alkylation products are increased. Much of the mesitylene and pseudocumene was unchanged by the aluminum chloride. No effort was made to determine the proportions of 1,2,4- and 1,3,5-isomers in the trialkyl fractions.

When technical xylene is refluxed with aluminum chloride at temperatures of 130–140°C., the crude trimethylbenzene fraction contains pseudocumene and mesitylene in proportions averaging 2:1 (79). The crude tetramethylbenzene fraction consists of approximately 90 per cent isodurene and 10 per cent durene. This would indicate that pseudocumene and isodurene are more stable in the presence of aluminum chloride than are their isomers. No evidence has been found for the presence of any

1,2,3-trimethylbenzene or any 1,2,3,4-tetramethylbenzene among the products of the methylation of benzene or its homologs, or of the demethylation products of penta- and hexa-methylbenzenes, by the action of aluminum chloride.

TABLE 4

The polymethylbenzenes and aluminum chloride (43)

HYDROCARBON	CONCENTRATION OF $AlCl_3$	TEMPERATURE	TIME	PRODUCTS*
	per cent	°C.		
$C_6(CH_3)_6$	50	190–200		$C_6H(CH_3)_5$ Durene } large amounts Isodurene Mesitylene, *pseudocumene*, *m*-xylene, toluene, benzene
$C_6(CH_3)_6$ (+HCl)	10	164		Same products but larger amounts of benzene and toluene
$C_6H(CH_3)_5$	50	50–55	14 days	Mostly unchanged hydrocarbon, some *isodurene*, and some hexamethylbenzene
$C_6H(CH_3)_5$ (+HCl)	20	100–110	Sealed tube; 4 hr.	*Isodurene* and some durene
Pseudocumene	12	169		Benzene, toluene, *m*- and *p*-xylenes, durene, *isodurene*
Pseudocumene	10	15–25	8 weeks	Much durene; no mention of isodurene
Pseudocumene (+HCl)	10	150–160	6 hr.	Benzene, toluene, *m*-xylene, mesitylene, *durene*, isodurene
Mesitylene (+HCl)	10	150–160		Benzene, toluene, *m*-xylene, durene, *isodurene*
m-Xylene	20	139		Toluene, pseudocumene, mesitylene, durene

* The principal isomer is given in italics.

The proportions of the tetraalkyl isomers and trialkyl isomers formed in these experiments are about the same as for the methylation of benzene with methyl chloride (42).

No detailed study has been made of the action of aluminum chloride on pure tetraalkylbenzenes. The tetramethylbenzenes are only mentioned as yielding trimethylbenzenes and xylenes (25) or lower methylated benzenes (43).

The action of aluminum chloride on several alkylbenzenes at 100°C. or over (36) is summarized in table 5.

With regard to the identity of the propyl radical in the reaction products from *n*-propylbenzene, it is maintained that di-*n*-propylbenzenes are obtained along with unchanged *n*-propylbenzene. To substantiate this view, strontium and barium salts of the sulfonic acids and the sulfamides of the reaction products were prepared and this statement made: "These compounds agree with those described by Spica and R. Meyer as characteristic of *n*-propylbenzene." No mention is made of melting points of mixtures of derivatives of any of the reaction products from *n*-propylbenzene with a derivative of an authentic sample of *n*-propylbenzene or of isopropylbenzene.

To determine the effect of aluminum chloride on the xylenes under the experimental conditions for their formation, the three isomers were warmed with aluminum chloride at 55°C. for 10 min. while hydrogen chloride was passed through the mixture (67a). The *o*-xylene yielded 18.7 per cent *m*-xylene and 81.6 per cent unchanged *o*-xylene. The *p*-xylene yielded 0.6 per cent *o*-xylene, 37.1 per cent unchanged *p*-xylene, and 64.3 per cent *m*-xylene. Under these conditions the ortho-isomer is more stable toward aluminum chloride than is the para-isomer.

TABLE 5

Alkylbenzenes and aluminum chloride (36)

ALKYLBENZENE	TIME	TEMPERATURE	PRODUCTS IN ADDITION TO BENZENE
	hours	*°C.*	
o- and *p*-xylenes	5		Mostly *m*-xylene, pseudocumene, mesitylene
m-Xylene			Toluene, mesitylene, pseudocumene
Ethylbenzene	10	100	*m*- and *p*-diethylbenzenes, triethylbenzene
Isopropylbenzene	4–6	100–150	Propane, *m*- and *p*-diisopropylbenzenes
n-Propylbenzene	6	100	*m*- and *p*-di-*n*-propylbenzenes
n-Butylbenzene	5		*m*- and *p*-dibutylbenzenes

The action of aluminum chloride on cymene has been carefully studied at temperatures from 60–150°C. and with varying amounts of aluminum chloride (72). Propane, diisopropyl, benzene, toluene, *m*-xylene, and 1-methyl-3,5-diisopropylbenzene were isolated from the reaction products. There was some evidence that small amounts of *p*-xylene and some 1,2,4-hydrocarbon were present, but they could not be isolated.

At the higher temperatures the amount of propane and the amount of the fractions boiling below 145°C. increased, but the amount of trialkylbenzene fraction remained nearly constant.

In another series of experiments, carried out under these same experimental conditions but with amounts of aluminum chloride varying from 10 to 50 per cent, the benzene fraction increased with increasing amounts of aluminum chloride and the toluene fraction decreased.

TABLE 6

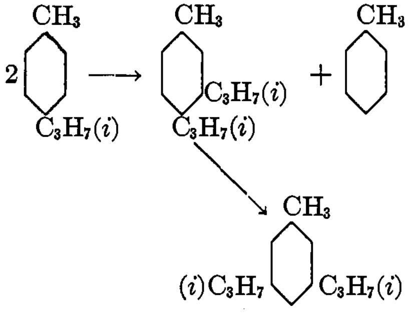
p-tert-Butyltoluene and cymene with aluminum chloride (54)

	p-tert-BUTYLTOLUENE		*p*-CYMENE	
	Grams	Per cent	Grams	Per cent
Total amount of hydrocarbon	150*		50	
Total reaction time, hours	5		240	
Temperature, °C	20–35		20–35	
Unchanged hydrocarbon	27.5	18.4	18	36
Gas	27.5	18.4†		
Benzene			2	4
Toluene	43	29.8	8	16
Xylenes				
Disubstituted toluene	10.8	7.2	11	22
Trisubstituted toluene	9.1	6		
Higher fractions and residue	31.6	21.3	7.6	15.2

* Three runs of 50 g. of hydrocarbon and 44.5 g. of aluminum chloride.

† Isobutane.

It is suggested that 1-methyl-3,4-diisopropylbenzene may be formed first and then rearranged to the 1,3,5-isomer.



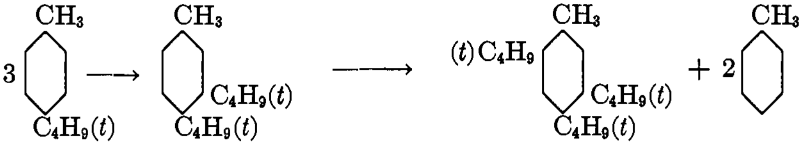
The 1,3,5-hydrocarbon was oxidized to trimesic acid. There was some qualitative evidence for the presence of trimellitic acid, but none of it could be isolated.

In another investigation, both cymene and *p-tert*-butyltoluene were subjected to the action of aluminum chloride under carefully controlled conditions (54). The results are summarized in table 6.

Analyses and molecular weight determinations of the trialkylbenzene fraction corresponded to a dibutyltoluene. Nitration did not yield a pure trinitro derivative, and oxidation products were indefinite. The 1,3,4-configuration is suggested for this methyldibutylbenzene, even though the 1,3,5-configuration is more probable.

Oxidation products of the tetraalkylbenzene fraction from *p-tert*-butyltoluene indicate that this hydrocarbon has the 1,2,4,5-configuration. In this connection it should be noted that the tetramethylbenzene formed during the methylation of commercial xylene is largely the 1,2,3,5-hydrocarbon.

In conformity with the suggested configurations, the formation of the principal products isolated could be accounted for as follows:



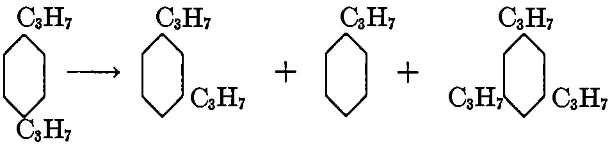
The products from cymene and aluminum chloride were the same as those reported previously. The oxidation of the diisopropyltoluene with nitric acid yielded 5-methylisophthalic acid. It is of interest to note that no propane, and apparently no tetraalkylbenzene, was obtained from cymene, and no *m*-dialkylbenzene was reported from either cymene or *p-tert*-butyltoluene. There was no evidence to indicate the formation of olefins from either cymene or *p-tert*-butyltoluene.

The formation of a tetraalkylbenzene from *p-tert*-butyltoluene and not from cymene may imply that the larger radicals such as *tert*-butyl form the more highly alkylated benzenes more readily than do the smaller radicals. The percentage of toluene is correspondingly higher. In this case, there was ample opportunity for the formation of polyalkylated benzenes from cymene, for the time of the reaction was 240 hr. as compared with 5 hr. for *p-tert*-butyltoluene.

Cumene heated with aluminum chloride at 150°C. gave a 2.7 per cent yield of toluene and 26.5 per cent yield of xylenes (59). This is attributed to the decomposition of the isopropyl group.

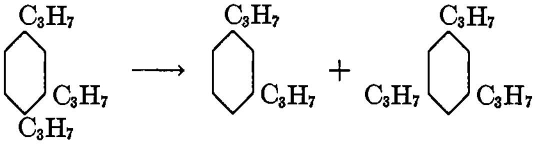
The reaction between the *m*- and *p*-di-*n*-propylbenzenes and the 1,2,4-tri-*n*-propylbenzene in the presence of aluminum chloride has been extensively studied for the purpose of establishing the mechanism for the formation of the reaction products (3).

The *m*- and *p*-di-*n*-propylbenzenes were warmed on a steam bath with aluminum chloride for 22 hr. The para-compound gave 11 per cent *n*-propylbenzene, 15 per cent of the *m*-di-*n*-propylbenzene, and 11 per cent of 1,3,5-tri-*n*-propylbenzene, in addition to unchanged hydrocarbon and residue. The dialkyl fraction from *m*-di-*n*-propylbenzene was mainly unchanged hydrocarbon with small amounts of para-isomer.



A disulfonamide (m.p. 195°C.) of the *m*-di-*n*-propylbenzene and a sulfonamide (m.p. 105°C). of the *p*-di-*n*-propylbenzene were made. The reaction products from *p*-di-*n*-propylbenzene formed sulfonamides having these same melting points, but there is no record of melting points of mixtures of these derivatives. The conclusions as to the configuration of the migrating propyl group were based on the melting points of the above-mentioned sulfonamides, and on earlier work with the propylbenzenes (36).

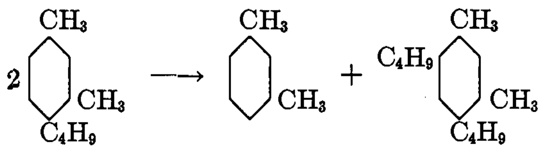
The 1,2,4-tri-*n*-propylbenzene and aluminum chloride at 100°C. for 4 hr. yielded approximately 30 per cent of *m*-di-*n*-propylbenzene and 30 per cent of 1,3,5-tri-*n*-propylbenzene in addition to about 10 per cent of higher alkylated benzenes. The trialkyl fraction on oxidation yielded nearly pure trimesic acid.



That a *n*-propyl group, migrating in the presence of aluminum chloride at 100°C., should maintain its identity is questionable. By analogy with the behavior of the *n*-butyl group when 1,3-dimethyl-4-*n*-butylbenzene is warmed with aluminum chloride, the predicted product from 1,2,4-tri-*n*-propylbenzene and aluminum chloride would be 1,3-dimethyl-5-isopropylbenzene. No derivatives were made of the 1,2,4-tri-*n*-propylbenzene or of its rearrangement products.

The principal changes involved when the 1,3-dimethyl-4-butylbenzenes are warmed with aluminum chloride (66, 81a) are shown in chart III, and experimental data are given in table 7. The other products of the reaction are *m*-xylene and, presumably, higher alkylated benzenes. The hydrocarbons boiling above the trialkylbenzenes would not yield a fraction of constant boiling point.

The formation of the by-products would involve the dealkylation of one hydrocarbon molecule and alkylation of another by the detached radical. The 1,3-dimethyl-4-*tert*-butylbenzene could yield *m*-xylene and a di-*tert*-butyl-*m*-xylene.



The identity of the 1,3-dimethyl-5-*tert*-butyl- and 5-*sec*-butyl-benzenes formed by rearrangement of the 1,3,4-hydrocarbons was established by means of the melting points of mixtures of their trinitro derivatives with trinitro derivatives of the same hydrocarbons synthesized directly by the Friedel–Crafts procedure, and by means of cooling curves of the hydrocarbons. The 1,3-dimethyl-5-*tert*-butylbenzene formed by rearrangement of the 4-*sec*-butyl or 4-*tert*-butyl hydrocarbon did not depress the freezing point of a sample of 1,3-dimethyl-5-*tert*-butylbenzene which had been synthesized by the Friedel–Crafts procedure and refluxed with aluminum chloride.

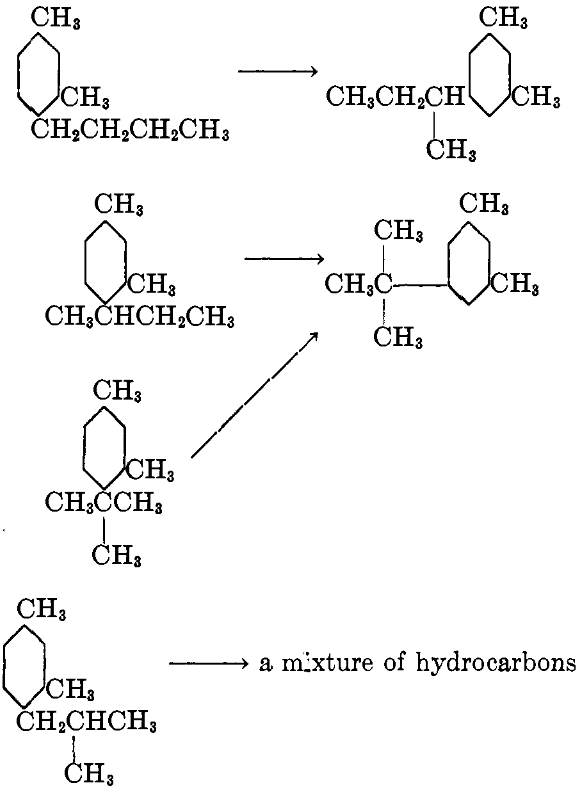


Chart III

In view of the fact that 1,3,5-hydrocarbons synthesized by the Friedel-Crafts procedure and having radicals up to propyl are reported as containing variable amounts of the 1,2,4-isomer, the question may arise as to whether or not the rearrangement products from 1,3-dimethyl-4-butylbenzenes may contain small amounts of unchanged 1,3,4-hydrocarbon. There is some qualitative evidence for the presence of a small amount of 1,2,4-hydrocarbon in the trialkyl fraction from *p*-cymene (72), but even though relatively large amounts (10 g.) of oxidation product were obtained, not enough of any other acid could be isolated for identification. At the present time there seems to be no satisfactory method for the detection of small amounts of 1,2,4-hydrocarbon in a sample of 1,3,5-hydrocarbon, especially when only small amounts of material are available.

TABLE 7

1,3-Dimethyl-4-butylbenzenes and aluminum chloride (66)

HYDROCARBON		$AlCl_3$	TIME	*m*-XYLENE FRACTION	1, 3, 5-FRACTION			RESIDUE*
Name	Amount				Amount	$n_D^{25°}$	Melting point of trinitro derivative	
	gms.	*gms.*	*hours*	*grams*	*gms.*		*°C.*	*grams*
1,3-Dimethyl-4-*n*-butylbenzene.....	37	8	4	3.5	7	1.4928	97	15.5
1,3-Dimethyl-4-*sec*-butylbenzene...	37	8	2.5	3.5	16	1.4938	113	6
1,3-Dimethyl-4-*tert*-butylbenzene...	48	10	3.25	3	15	1.4935	113	9
1,3-Dimethyl-4-isobutylbenzene....	50	10	3	4				40
1,3-Dimethyl-4-isobutylbenzene....	30	7	2	2				26

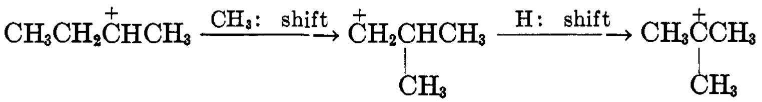
* Includes all fractions which would not yield a constant-boiling cut.

If it may be assumed that the aluminum chloride leads to the formation of butyl ions, the isomerization of the *n*-butyl radical may be interpreted in terms of Whitmore's (91) theory of intramolecular rearrangements, as follows:

$$\mathrm{(CH_3)_2C_6H_3C_4H_9 \xrightarrow{AlCl_3} (CH_3)_2C_6H_3^- + CH_3CH_2CH_2\overset{+}{C}H_2}$$

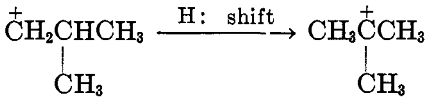
$$\mathrm{CH_3CH_2CH_2\overset{+}{C}H_2 \xrightarrow{H:\ shift} CH_3CH_2\overset{+}{C}HCH_3}$$

The isomerization of the *sec*-butyl radical from 1,3-dimethyl-4-*sec*-butylbenzene could take place similarly:



$$\mathrm{CH_3CH_2\overset{+}{C}HCH_3 \xrightarrow{CH_3:\ shift} \overset{+}{C}H_2\underset{\underset{CH_3}{|}}{C}HCH_3 \xrightarrow{H:\ shift} CH_3\underset{\underset{CH_3}{|}}{\overset{+}{C}}CH_3}$$

On this basis, the 1,3-dimethyl-4-isobutylbenzene would be expected to yield readily 1,3-dimethyl-5-*tert*-butylbenzene.



$$\overset{+}{C}H_2\underset{\underset{CH_3}{|}}{C}HCH_3 \xrightarrow{\text{H: shift}} CH_3\underset{\underset{CH_3}{|}}{\overset{+}{C}}CH_3$$

The product of this reaction, however, appears to be a mixture of *m*-xylene and other hydrocarbons.

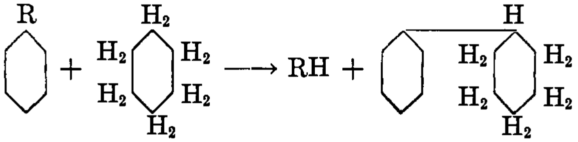
The products from the reaction of alkylbenzenes and some of the cycloparaffins in the presence of aluminum chloride furnish evidence as to the relative stability of some of the different types of alkyl groups.

When an alkylbenzene and either cyclohexane or decahydronaphthalene are warmed with aluminum chloride in the presence of hydrogen chloride at 80°C. for 3 to 4 hr., the alkyl group is split off to yield a paraffin hydrocarbon, the cycloparaffin furnishing the necessary hydrogen (39a).

TABLE 8

Alkylbenzenes, cycloparaffins, and aluminum chloride (39a)

AROMATIC HYDROCARBON USED	PARAFFIN FORMED		
	Kind	From cyclohexane	From decahydronaphthalene
		per cent yield	*per cent yield*
Toluene	None	0	0
Ethylbenzene	None	0	0
Isopropylbenzene	Propane	33	53
sec-Butylbenzene	Butane	35	71
tert-Butylbenzene	Isobutane	61	94
sec-Amylbenzene	Isopentane	60	



Other compounds are formed, among them di- and tri-alkylbenzenes and alkylcycloparaffins.

There is a marked difference in the ease with which the alkyl groups are cleaved from the benzene ring, as indicated by the yield of paraffin hydrocarbon (table 8).

Methyl and ethyl groups are not split off under these conditions. Of the two secondary radicals, the isopropyl group is held more firmly, and the tertiary butyl group is more easily detached than is the secondary butyl group. No experiments are reported in which *n*-alkylbenzenes were used.

The transfer of alkyl groups from one aromatic hydrocarbon molecule to another is illustrated by experiments with approximately 10 per cent solutions of alkylbenzenes in benzene at the boiling point of the solution (12). The data are summarized in table 9.

The results with *p*-cymene are a further indication that the methyl group is more firmly held to the benzene ring than are the larger radicals.

This transfer of alkyl groups to another ring is also illustrated by the alkyl phenols. *p*-*tert*-Butylphenol refluxed with aluminum chloride in benzene solution gave phenol and a 70 per cent yield of *tert*-butylbenzene (83).

TABLE 9

The transfer of alkyl groups (12)

HYDROCARBON		$AlCl_3$	BENZENE	PRODUCT	
Name	Quantity			Name	Quantity
	grams	*grams*	*grams*		*grams*
m- and *p*-xylenes	100	10	1000	No toluene	
Diethylbenzene	85	20	850	Ethylbenzene	70
Cymene	100	20	1000	Toluene	41
				Isopropylbenzene	85
Polyisopropylbenzenes	65	15	650	Isopropylbenzene	49
Di-*p*-*tert*-butylbenzene	5	0.35	50	*tert*-Butylbenzene	6.5
Polyamylbenzene	11	1	110	*tert*-Amylbenzene	3

Phenol and 4-(1,1,3,3)-tetramethobutylphenol yielded *p*-*tert*-butylphenol. This latter reaction appears to involve dissociation and cleavage of the octyl group and alkylation by the two four-carbon fragments.

VII. THEORIES

It has long been recognized that the Friedel–Crafts reaction is reversible, and that reactions between a pure alkylbenzene and aluminum chloride may involve both dealkylation and re-alkylation by the detached radical. Most investigators who have studied possible mechanisms to account for variety and types of products formed in a Friedel–Crafts synthesis are agreed that at present no one theory is adequate to explain all of the changes which take place when a hydrocarbon is synthesized by a procedure in which aluminum chloride is used as the catalyst, or when a pure alkylbenzene reacts with aluminum chloride.

From the data assembled by the various investigators and interpreted in terms of modern concepts of atomic structures and organic reactions, the following general conclusions may be drawn:

Aluminum chloride forms addition compounds with alkyl halides of the type R:X:$AlCl_3$, but these are unstable for the most part, in contrast to the stable addition compounds formed with acyl halides.

Aluminum chloride and benzene or alkylbenzenes form unstable addition compounds of uncertain composition, which may or may not be essential to the reaction.

These addition compounds may form ternary compounds in which alkylation takes place.

From extensive conductivity studies of the system benzene–ethyl bromide–aluminum bromide, Wertyporoch (88) concludes that "the classical Friedel–Crafts reaction is dependent on the formation of an ionized ternary complex. In the ethyl bromide molecule, the union between C_2H_5 and Br is loosened through salt formation, and likewise the carbon–hydrogen bond in the benzene combined in the cation, and stabilization can take place through the formation of ethylated benzenes with the elimination of hydrogen bromide." Subsequent studies by other investigators have substantiated this view in effect.

It is perhaps unfortunate that in the physicochemical studies of the reaction it was necessary to substitute aluminum bromide or gallium chloride for aluminum chloride in order to obtain satisfactory results, owing to the fact that aluminum chloride is difficultly soluble in aromatic hydrocarbons. The above conclusions are therefore based on the assumption that aluminum chloride behaves similarly.

Gustavson made an extensive study of the nature of addition compounds of aluminum chloride with aromatic hydrocarbons (34). A few typical examples of the many compounds which he reported as isolated are

$Al_2Cl_6 \cdot C_6H_4(CH_3)_2$ $\qquad$ $Al_2Cl_6 \cdot C_6H_3(C_2H_5)_3 \cdot 3C_6H_2(C_2H_5)_4$
$Al_2Cl_6 \cdot C_6H_3(C_2H_5)_3 \cdot 6C_6H_6$ $\qquad$ $Al_2Cl_6 \cdot C_6H_3(C_2H_5)_3 \cdot C_6H_6$

Most of these complexes are described as unstable. From observations of a series of alkylations involving the use of the addition compound $Al_2Cl_6 \cdot C_6H_3(C_2H_5)_3$, he concluded that it and other addition compounds such as $Al_2Cl_6 \cdot C_6(C_2H_5)_6$ and $Al_2Cl_6 \cdot C_6H_4(CH_3)_2$ catalyzed alkylations and were recovered unchanged. These addition compounds were therefore described as having enzyme-like properties. This view was erroneous, and a detailed study of freezing point diagrams of mixtures of aluminum bromide with benzene, toluene, and *p*-xylene has shown that addition compounds of the composition which Gustavson ascribed to them are not formed (57). Aluminum bromide was used rather than aluminum chloride in the freezing point experiments because of the slight solubility of aluminum chloride in the hydrocarbons. However, the observations as to the formation of addition compounds are of some value as qualitative evidence, for it is generally believed that aluminum halides do form complexes with aromatic hydrocarbons.

According to the recent work of Norris and Rubinstein (67a), toluene and aluminum bromide at room temperature and in the presence of hydrogen bromide form an oily complex the composition of which approximates $Al_2Br_6 \cdot 6C_6H_5CH_3$. This complex is easily decomposed and loses toluene in a vacuum, probably forming a more stable complex of the composition $Al_2Br_6 \cdot C_6H_5CH_3$. These complexes were not formed in the absence of hydrogen bromide. When aluminum chloride and hydrogen chloride were substituted for the bromides at 80–90°C., a mixture of hydrocarbons resulted and a pure complex could therefore not be obtained. Analyses of the complex indicated that the ratio of Al_2Cl_6 to hydrocarbon was 1:6.

There are little comparable data available to indicate the extent to which the presence of hydrogen halides affects the reactions of alkylbenzenes with aluminum halides. The data cited above indicate that the hydrogen halides promote complex formation, and there is some evidence that hydrogen chloride increases the amounts of some of the dealkylation products.

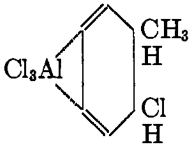
Early investigators, among them Friedel and Crafts (25), suggested that alkylation proceeded as follows:

$$C_6H_6 + AlCl_3 \rightarrow C_6H_5AlCl_2 + HCl$$

$$C_6H_5AlCl_2 + RCl \rightarrow C_6H_5R + AlCl_3$$

Later it was found that organoaluminum compounds of this type are not formed under the experimental conditions for alkylation, and compounds such as $C_6H_5AlCl_2$ do not yield hydrocarbons readily when added to alkyl halides.

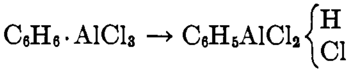
Schaarschmidt (71) thought that the aluminum chloride became attached to the nucleus by residual valences, and that the alkyl halide added to this complex to form a dihydrobenzene intermediate product



which lost hydrogen chloride and later aluminum chloride.

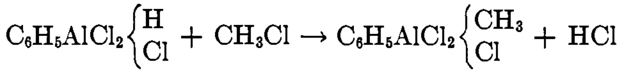
Prins (70) disproved this idea by treating dihydrobenzene with aluminum chloride. The extensive resinification which took place is not observed in a Friedel–Crafts synthesis. Furthermore, if such a dihydrobenzene complex is formed, it would be expected to take up bromine readily, but on titration with bromine only a small amount was absorbed.

Schröter (73) believed that the hydrocarbon and the aluminum chloride formed a complex which rearranged to form in effect the hydrochloride of an organometallic compound:



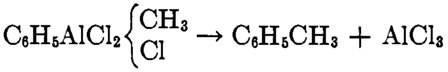
$$C_6H_6 \cdot AlCl_3 \rightarrow C_6H_5AlCl_2\left\{\begin{matrix}H\\Cl\end{matrix}\right.$$

When an alkyl halide was added, the hydrogen was exchanged for a radical,



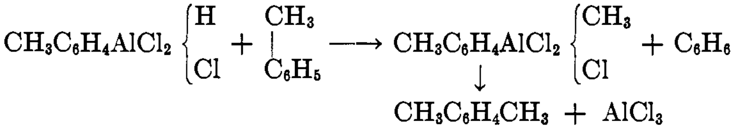
$$C_6H_5AlCl_2\left\{\begin{matrix}H\\Cl\end{matrix}\right. + CH_3Cl \rightarrow C_6H_5AlCl_2\left\{\begin{matrix}CH_3\\Cl\end{matrix}\right. + HCl$$

and the double molecule so formed yielded toluene:



$$C_6H_5AlCl_2\left\{\begin{matrix}CH_3\\Cl\end{matrix}\right. \rightarrow C_6H_5CH_3 + AlCl_3$$

In the same manner, toluene could form benzene and xylene:



$$\begin{matrix} CH_3C_6H_4AlCl_2\left\{\begin{matrix}H\\ \\Cl\end{matrix}\right. + \begin{matrix}CH_3\\|\\C_6H_5\end{matrix} \longrightarrow & CH_3C_6H_4AlCl_2\left\{\begin{matrix}CH_3\\ \\Cl\end{matrix}\right. + C_6H_6 \\ & \downarrow \\ & CH_3C_6H_4CH_3 + AlCl_3 \end{matrix}$$

Prins expressed the reaction as an interchange of ions. Under the influence of aluminum chloride, benzene could form a phenylchloroaluminic acid. The alkyl halide likewise formed a methylchloroaluminic acid and the two complexes reacted by an interchange of ions:

$$(C_6H_5AlCl_3)^-H^+ + (AlCl_4)^-CH_3^+ \rightarrow (C_6H_5AlCl_3)^-CH_3^+ + H^+(AlCl_4)^-$$

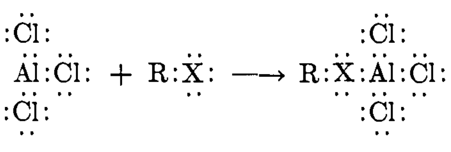
Toluene and aluminum chloride could form two types of complexes

$$(CH_3C_6H_4AlCl_3)^-H^+ \quad \text{and} \quad (C_6H_5AlCl_3)^-CH_3^+$$

and by an exchange of cations, benzene and xylene were formed.

With the development of the electronic conception of valence and its application to the structures of organic molecules, these earlier theories were interpreted in terms of electronic structures.

The ability of aluminum chloride to form a complex with alkyl halides is thought to be due to the fact that in the aluminum chloride molecule the aluminum atom has only six electrons in its outer shell. It can coördinate with an unshared pair of electrons in another molecule to form a complex.



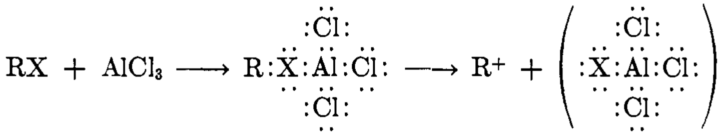
$$\begin{matrix} :\ddot{Cl}: & & & & & :\ddot{Cl}: \\ \ddot{Al}:\ddot{Cl}: & + & R:\ddot{X}: & \longrightarrow & R:\ddot{X}: & \ddot{Al}:\ddot{Cl}: \\ :\ddot{Cl}: & & & & & :\ddot{Cl}: \end{matrix}$$

These complexes were expected to have a polar character, and this proved to be true, for solutions of aluminum halides in alkyl halides are conducting.

It would follow by analogy that boron fluoride and boron chloride, which also have an outer shell of six electrons, should catalyze alkylations by means of alkyl halides, but they do not do so (90). It has already been mentioned that boron fluoride does catalyze alkylations by means of alcohols, olefins, and esters. Anhydrous ferric chloride, which has the same electronic configuration in its outer shell as does aluminum chloride, appears to be a satisfactory catalyst for alkylations.

In the reaction between benzyl chloride and toluene in the presence of ferric chloride, there is no evidence for the formation of an addition compound of ferric chloride and the hydrocarbon either formed or used (85). When ferric chloride is added to benzene, there is no evidence of a reaction, but heat is developed when an olefin is added to the mixture (68).

Dougherty (21) expressed the reaction as follows:



$$RX + AlCl_3 \longrightarrow R:\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}:\underset{:\underset{\cdot\cdot}{Cl}:}{\overset{:\overset{\cdot\cdot}{Cl}:}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{Al}}}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \longrightarrow R^+ + \left(:\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}:\underset{:\underset{\cdot\cdot}{Cl}:}{\overset{:\overset{\cdot\cdot}{Cl}:}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{Al}}}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\right)^-$$

$$C_6H_6 + AlCl_3 \rightarrow C_6H_6 \cdot AlCl_3 \rightarrow (C_6H_5AlCl_3)^-H^+$$

$$(C_6H_5AlCl_3)^-H^+ + R^+(XAlCl_3)^- \rightarrow (C_6H_5AlCl_3)^-R^+ + H^+(XAlCl_3)^-$$

$$H^+(XAlCl_3)^- \rightarrow HX \cdot AlCl_3 \rightarrow HX + AlCl_3$$

The reaction proceeds toward completion by the formation of the volatile halogen acid. The alkylbenzene so produced may in turn form an ionizing complex which will undergo further alkylation.

In an attempt to find an answer to the many questions which arose in connection with these various theories, Wertyporoch (90, 88, 87) used conductivity measurements in an extensive study of the system hydrocarbon–metal halide–alkyl halide. Aluminum bromide was substituted for aluminum chloride because of the slight solubility of the latter in benzene.

The principal questions which he attempted to answer were: (*1*) Does aluminum chloride form an addition compound with alkyl halides which may be either an ester of the acid $HAlCl_4$ or a molecular compound? (*2*) Is an intermediate product formed with benzene and the aluminum halide, which is independent of the alkyl halide? (*3*) Do the $AlCl_3 \cdot RX$ and $AlCl_3 \cdot C_6H_6$ compounds, if formed, react with each other through an interchange of ions, or do they form a ternary compound?

For purposes of comparison, the behavior of aluminum bromide in ether solution was first investigated. For an approximately 0.5 *M* solution of aluminum bromide (20 per cent) in ether solution the mol conductivity is = 0.1. The conductivity is thought to be due to the solvate formation of complexes analogous to those formed in solutions of lithium ethyl in zinc diethyl. Wertyporoch regarded the complexes as Al_2Br_6 and Al_4Br_{12}, changed by solvation into complexes of the type

$$[Al(C_2H_5)_2O]_n[AlBr_6] \quad \text{and} \quad [Al(C_2H_5)_2O]_n[AlBr_4]_3$$

respectively. These complexes are present in very small concentrations.

Carefully purified ethyl bromide is practically non-conducting, K being equal to 3×10^{-9} for the specific conductivity. On the addition of aluminum bromide, the conductivity increases with increasing concentrations to about $K = 1.206 \times 10^{-4}$ for a 20 per cent solution of aluminum bromide.

The conducting ternary complex formed when benzene is added to a solution of aluminum bromide in ethyl bromide is precipitated as a dark heavy oil by the addition of a large excess of benzene or saturated hydrocarbon. The supernatant liquid contains hydrogen bromide, but is non-conducting. If the precipitated oil is redissolved in ethyl bromide, its conductivity is unchanged. If aluminum bromide in ethyl bromide is treated with the corresponding amount of hexaethylbenzene instead of with benzene, the solution has the same final conductivity value as when benzene is used.

The question as to the nature of the conducting complexes was studied by means of transference experiments. For a solvate of $AlBr_3$, aluminum should concentrate at the cathode. For a solvate of Al_2Br_6, there should be a migration of aluminum to both anode and cathode, and for Al_4Br_{12}, three atoms of aluminum should migrate to the anode and one to the cathode. In solutions of aluminum bromide in ethyl bromide, the aluminum accumulates at the anode, indicating that a salt $Al(AlBr_4)_3$ is present. This is further confirmed by other transference experiments in the presence of hexaethylbenzene.

From these experimental data Wertyporoch concludes that simple alkyl halides form compounds with aluminum halides in which there is an equilibrium between a "pseudo" salt and an ionized solvate. The fact that stable addition products of the alkyl halide and aluminum bromide cannot be isolated should not be interpreted as disproving the existence of such complexes, since there are many cases in which an unstable intermediate product catalytically active and present in small amounts cannot be isolated.

Since it was not possible to prove directly that the reaction may proceed as an interchange of ions,

$$(C_6H_5 \cdot AlCl_3)^-H^+ + (AlCl_4)^-CH_3^+ \rightarrow (C_6H_5 \cdot AlCl_3)^-CH_3^+ + (AlCl_4)^-H^+$$

conductivity measurements were used further in an effort to determine if a benzene–aluminum bromide solution has a salt-like character. It is known that the oily complex compounds which result from aluminum bromide and benzene or toluene in the presence of hydrogen bromide conduct well; $K = 10^{-2}$. This holds only for the oil itself. The saturated layer over the oily complex, a very dilute solution of aluminum bromide, is not noticeably conducting.

Benzene has a very small specific conductivity at 25°C.; $K = 1 \times 10^{-13}$. On the addition of aluminum bromide in concentrations up to 20 per cent there is no noticeable increase in conductivity.

The fact that aluminum halides do not form conducting complexes with benzene is interpreted by Wertyporoch as excluding those reaction mechanisms which involve an exchange of ions, but this does not exclude the possible formation of a non-conducting complex between benzene and the aluminum halide.

Transference experiments with a solution of aluminum bromide, ethyl bromide, and benzene show that for approximately four atoms of aluminum, one migrates to the cathode and three to the anode, and that hexaethylbenzene formed or added becomes five times as concentrated at the cathode as at the anode, and also that about four molecules of the hydrocarbon (hexaethylbenzene) and one mole of aluminum migrate to the cathode. This leads to a formula

$$[\mathrm{Al(C_2H_5Br)}_n\mathrm{(C_{18}H_{30})_4}][\mathrm{AlBr_4}]_3$$

for the ternary compound, in which aluminum has a coördination number of four and "*n*" corresponds to a not yet established number of ethyl bromide molecules forming the solvate.

Wertyporoch therefore suggests that the reaction involves first the formation of an ionized complex salt with the aluminum chloride and the alkyl halide. This complex salt may then add to the aromatic hydrocarbon to form a strongly conducting ternary complex in the cation of which the reaction proper takes pace. The nuclear carbon–hydrogen bond and the carbon–halogen bonds are weakened in this complex cation. Stabilization takes place with the elimination of the volatile halogen acid and the formation of ethylated benzenes. The manner in which the reaction proceeds in the cation of the postulated ternary compound is as yet unexplained.

Wertyporoch considers the Friedel–Crafts reaction as corresponding to the general scheme of organic reactions such as halogenation or nitration, or molecular rearrangements, which may proceed through the formation of an addition product, decomposition of this addition product, and finally the formation of a stable compound by the elimination of water, halogen acid, etc.

The conductivity studies were extended to include a number of other alkyl chlorides and aluminum chloride, the results of which are given in table 10 (88).

It is suggested that the magnitude of the specific conductivity for chlorocyclohexane and the propyl chlorides as compared with ethyl chloride may be due to the loss of hydrogen chloride from the alkyl halides to form olefins, which form strongly conducting complexes with aluminum chloride.

The changes in conductivity on the addition of the alkylated benzenes,—hexaethylbenzene, propylbenzene, and isopropylbenzene,—to the solutions of the corresponding alkyl chlorides and aluminum chloride paralleled those already described in detail for the aluminum bromide–ethyl bromide–hydrocarbon experiments, except that the final conductivity value was reached more rapidly. The addition of cyclohexane to chlorocyclohexane in the presence of aluminum chloride had no effect on the conductivity.

In a kinetic study of the reaction between *n*-propyl chloride and benzene in the presence of aluminum chloride or gallium chloride, Ulich and Heyne (86) substantiated in effect most of the views of Wertyporoch, and concluded that the reaction involves the formation of the $MCl_3 \cdot C_3H_7Cl$ complex, which is in equilibrium with complexes formed between the metal chloride and benzene and the reaction products.

TABLE 10

Conductivities of alkyl chlorides and aluminum chloride (88)

CHLORIDE	$K \times 10^{-7}$		
	Specific conductivity	0.08 mole $AlCl_3$ per liter	0.2 mole $AlCl_3$ per liter
Ethyl chloride	0.03	180	380
Chlorocyclohexane	0.03	650	1800
Propyl chloride	0.03	3180	14400
Isopropyl chloride	0.03	3300	14000

Since aluminum chloride is difficultly soluble, Ulich and Heyne suggested that reaction may proceed slowly on the surface of the solid aluminum chloride. The reaction products dissolve aluminum chloride better than does carbon disulfide, so that a liquid phase results which contains aluminum chloride in the form of a molecular compound with the reaction products. The aluminum chloride so dissolved has a high catalytic activity and may catalyze the reaction with the $AlCl_3 \cdot C_3H_7Cl$ complex.

Gallium chloride proved to be more satisfactory than aluminum chloride in these experiments, because it is readily soluble in carbon disulfide and other solvents of low dielectric constant, forming a homogeneous system. The course of the reaction was followed by measuring at constant pressure the volume of hydrogen chloride evolved. Carbon disulfide was used as the solvent in all the experiments. These authors represent the reaction as taking place in three steps

$$GaCl_3 + C_6H_6 \rightarrow GaCl_3 \cdot C_6H_6$$

$$C_3H_7Cl + GaCl_3 \cdot C_6H_6 \rightarrow GaCl_3 \cdot C_3H_7Cl + C_6H_6$$

$$GaCl_3 \cdot C_3H_7Cl + C_6H_6 \rightarrow C_6H_5C_3H_7 + GaCl_3 + HCl$$

but it seems more reasonable that the alkyl halide–gallium chloride addition compound should be formed directly from the two reactants

$$C_3H_7Cl + GaCl_3 \rightarrow C_3H_7Cl \cdot GaCl_3$$

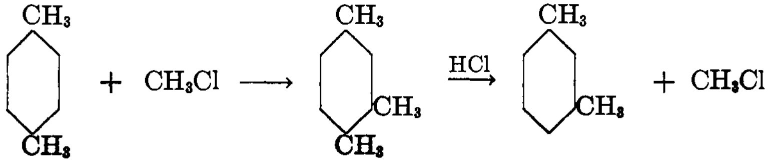
The equilibrium constant was derived for the formation of the complex.

$$\frac{dx}{dt} = K'[GaCl_3 \cdot C_3H_7Cl][C_6H_6]$$

For a large excess of one of the reactants, either benzene or propyl chloride, and a constant amount of gallium chloride, the reaction is of the first order.

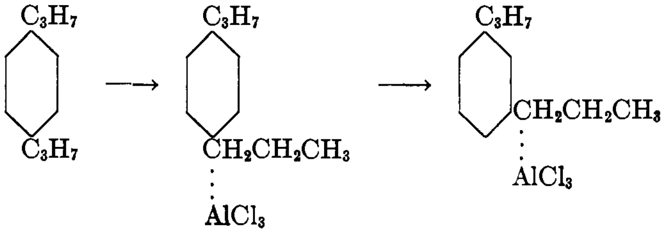
Another physicochemical approach to the problem was made by Fairbrother (24). Powdered aluminum chloride, activated by being exposed to a stream of deuterons, was mixed with inactive aluminum chloride and immediately brought into contact with benzene and *tert*-butyl chloride. A complete interchange of chlorine atoms occurred, the chlorine which formed hydrogen chloride having a radioactivity equal to that of the chlorine which was combined in the final reacting mixture. The radioactivities of the silver chloride from the evolved hydrogen chloride and from the hydrogen chloride obtained from the reaction mixture do not differ by 10 per cent. This leads again to the conclusion that the first step in the reaction is the ionization, by means of aluminum chloride, of the covalent C—Cl bond, with the formation of the negative ion $[AlCl_4]^-$ and the positive carbonium ion, R^+. Such a process constitutes "activation" of the aliphatic chloride, in that the ion pair is more reactive in the complex than in the unionized chloride and the final product. A small amount of aluminum chloride will thus serve to activate a large amount of alkyl halide.

To account for the predominance of *m*-dialkylbenzenes in the mixtures of meta- and para-isomers formed in the synthesis of dialkylbenzenes, and for the conversion of a *p*-dialkylbenzene into the meta-isomer, Baddeley and Kenner (3) agreed with Anschutz (2) that a 1,2,4-hydrocarbon could be formed, and subsequently dealkylated to yield the meta-isomer:



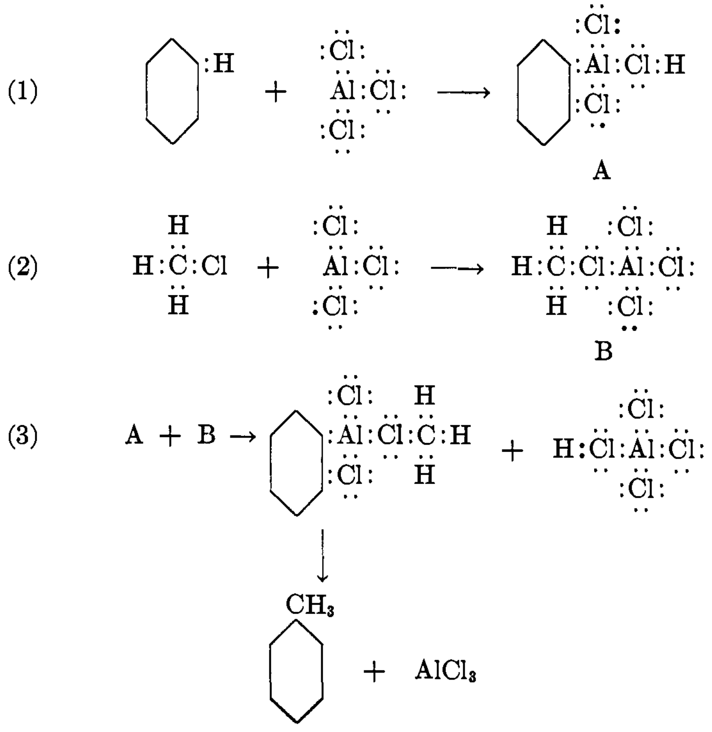
This hypothesis would involve isomerization of the alkyl group in suitable cases, such as the *p*-di-*n*-propylbenzene with which they worked. These investigators concluded that their experimental evidence (no isomerization of the migrating radical) from *p*-di-*n*-propylbenzene and from 1,2,4-tri-*n*-propylbenzene did not substantiate this view.

As an alternative, it was suggested that the rearrangement is a form of the Wagner–Meerwein rearrangement, with the migrant a complex of aluminum chloride and a propyl radical.

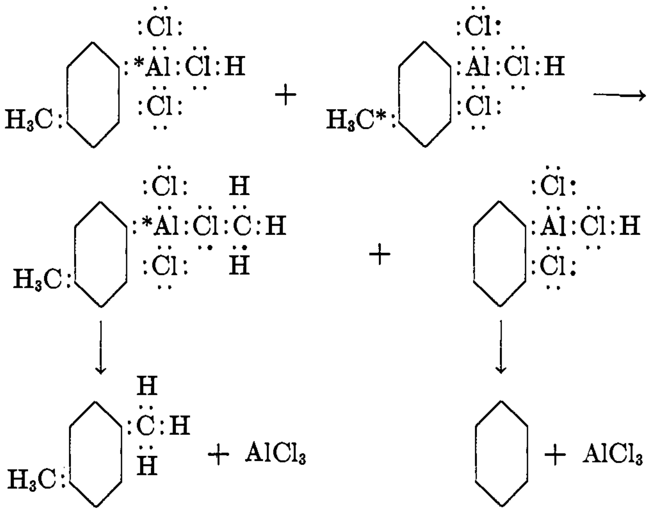


The relative stability of *m*-di-*n*-propylbenzene is accounted for by the assumption that the aluminum chloride may attach itself to the benzene ring para to one of the alkyl groups.

The essentials of some of these theories have been expressed in terms of electronic structures (23).

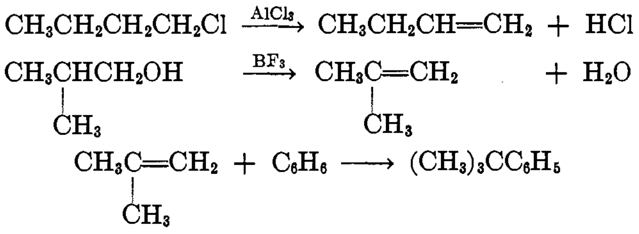


The formation of benzene and *p*-xylene from toluene may occur in the same way.



The asterisks correspond to a shift of an electron doublet which makes the methyl group positive relative to the aromatic nucleus.

Alkylation by means of alcohols, esters, and alkyl halides in the presence of aluminum chloride or boron fluoride has usually been interpreted as involving first the formation of an olefin and subsequent addition of the aromatic hydrocarbon to the olefin according to Markownikoff's rule. This accounted for the isomerization of a normal radical to a secondary radical, or of a radical such as isobutyl to tertiary butyl.

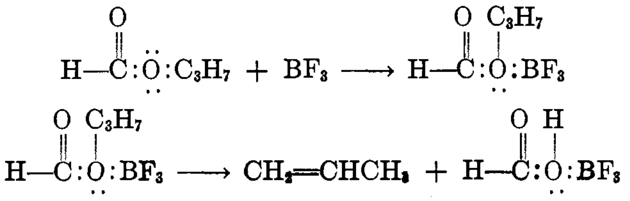


$$CH_3CH_2CH_2CH_2Cl \xrightarrow{AlCl_3} CH_3CH_2CH{=}CH_2 + HCl$$

$$CH_3\underset{\substack{|\\ CH_3}}{C}HCH_2OH \xrightarrow{BF_3} CH_3\underset{\substack{|\\ CH_3}}{C}{=}CH_2 + H_2O$$

$$CH_3\underset{\substack{|\\ CH_3}}{C}{=}CH_2 + C_6H_6 \longrightarrow (CH_3)_3CC_6H_5$$

For the alkylation of benzene with *n*-propyl formate in the presence of aluminum chloride, McKenna and Sowa proposed that the boron fluoride coördinated with the oxygen of the ester.



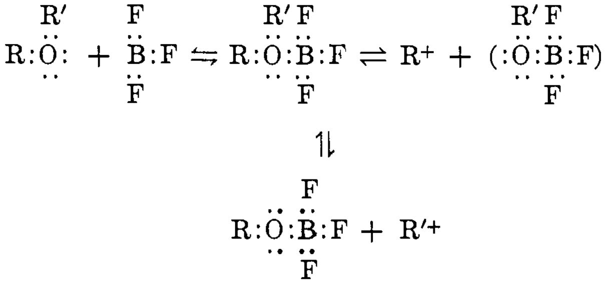
$$H{-}\overset{\substack{O\\ \|}}{C}{:}\overset{..}{\underset{..}{O}}{:}C_3H_7 + BF_3 \longrightarrow H{-}\overset{\substack{O\\ \|}}{C}{:}\underset{..}{\overset{\substack{C_3H_7\\ |}}{O}}{:}BF_3$$

$$H{-}\overset{\substack{O\\ \|}}{C}{:}\underset{..}{\overset{\substack{C_3H_7\\ |}}{O}}{:}BF_3 \longrightarrow CH_2{=}CHCH_3 + H{-}\overset{\substack{O\\ \|}}{C}{:}\underset{..}{\overset{\substack{H\\ |}}{O}}{:}BF_3$$

It should be mentioned that this reaction leads to the formation of isopropylbenzene, whereas when aluminum chloride is the catalyst, the product is reported as *n*-propylbenzene (13).

Bowden (13) pointed out that such a mechanism is not applicable to alkylating agents which contain methyl or benzyl radicals, such as methyl sulfate, methyl alcohol, or benzyl alcohol, in which olefin formation is impossible.

In connection with a discussion of alkylation by means of alcohols with boron fluoride as a catalyst, Price (69) has expressed alkylation in general terms applicable to the different alkylating agents which have been used successfully with the various catalysts already mentioned.



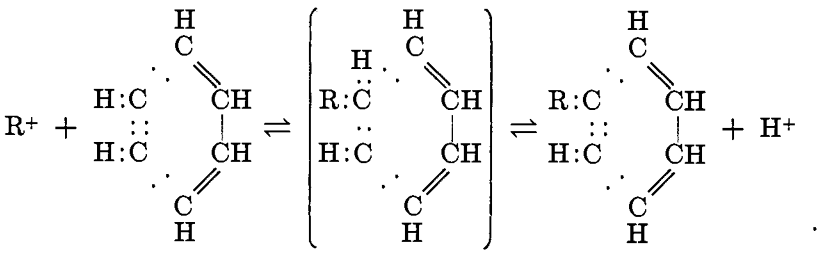
$$R\!:\!\overset{R'}{\underset{\cdot\cdot}{\ddot{O}}}\!: + \overset{F}{\underset{\cdot\cdot}{\ddot{B}}}\!:\!F \leftrightarrows R\!:\!\overset{R'}{\underset{\cdot\cdot}{\ddot{O}}}\!:\!\overset{F}{\underset{\underset{F}{\cdot\cdot}}{\ddot{B}}}\!:\!F \rightleftharpoons R^{+} + (:\!\overset{R'}{\underset{\cdot\cdot}{\ddot{O}}}\!:\!\overset{F}{\underset{\underset{F}{\cdot\cdot}}{\ddot{B}}}\!:\!F)$$

$$\upharpoonleft\downharpoonright$$

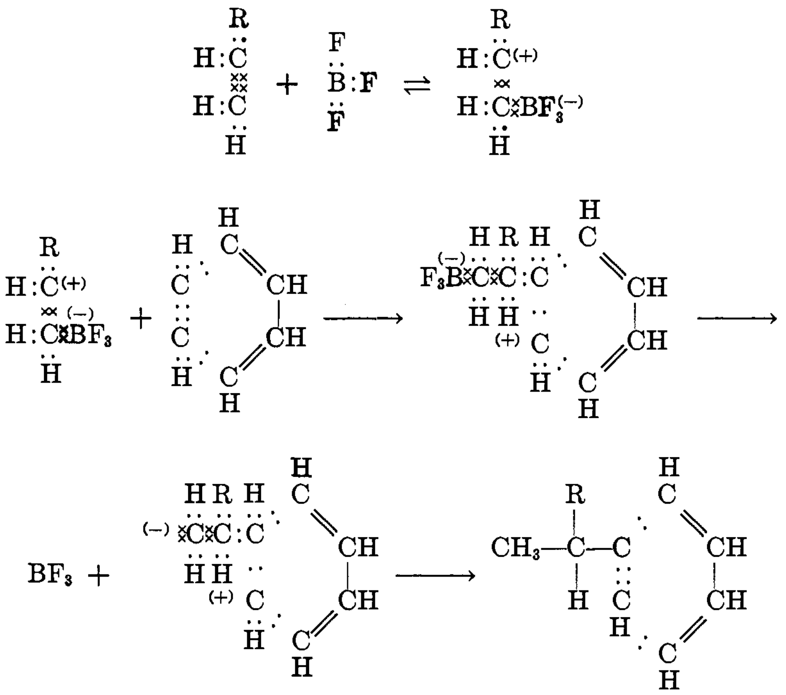
$$R\!:\!\underset{\cdot\cdot}{\ddot{O}}\!:\!\overset{F}{\underset{\underset{F}{\cdot\cdot}}{\ddot{B}}}\!:\!F + R'^{+}$$

R represents an alkyl group and R′ may be hydrogen, an alkyl group, or an acyl group. In support of this view there is the fact that boron fluoride–alcohol complexes are strong acids.

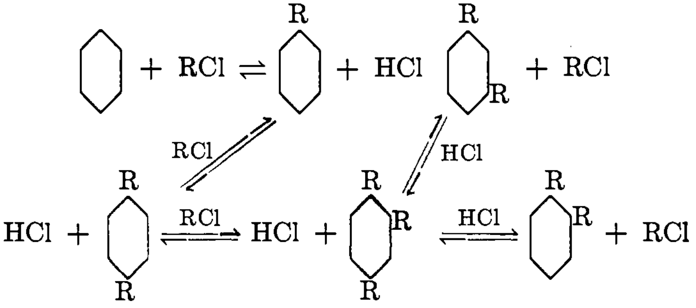
In any case, the positive carbonium ion is considered as the active alkylating agent. It may exist only momentarily in the mixture, and subsequently coördinates with an electron pair from the benzene nucleus.



Olefins may coördinate with the boron fluoride or aluminum chloride, and the positive ion so formed may be in turn coördinate with an electron pair from the benzene ring, followed by dissociation of the boron fluoride and an α,γ-shift of a proton.



The formation of predominantly meta- as well as para- and ortho-dialkylbenzenes is explained by the following reaction scheme:



The dealkylation of the 1,2,4-hydrocarbon is considered as a substitution of hydrogen in place of an alkyl group, the two radicals in the 1- and 3-positions directing the incoming hydrogen to the 4-position.

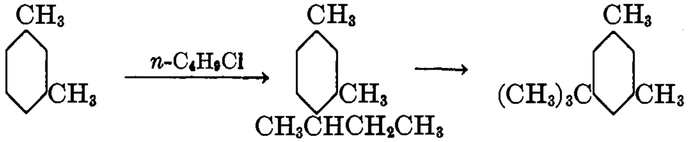
Anschütz and Immendorf (2) had explained the formation of *m*-xylene from pseudocumene in this manner, and Baddeley and Kenner (3) agreed that such an explanation was entirely plausible to account for the formation of *m*-xylene from *p*-xylene, but they discarded the theory.

In support of the view that a 1,2,4-trialkylbenzene is first formed during alkylation and subsequently rearranged to yield finally the 1,3,5-isomer (72, 81a, 61), there is the fact that a 4:1 mixture of pseudocumene and mesitylene results from the methylation of pure *m*-xylene with methyl chloride at 75–80°C. (42). Technical triethylbenzene, presumably prepared from ethyl chloride and benzene, is a mixture of similar composition under some conditions (49). The trimethylbenzenes, and probably the triethylbenzenes, appear to be more stable in the presence of aluminum chloride than are the other alkylbenzenes, and therefore much more of the 1,2,4-hydrocarbon could survive the action of the metal halide, even at temperatures up to 140°C.

The product of the reaction of *n*-propyl formate, benzene, and aluminum chloride is reported as *n*-propylbenzene (13). When *m*-xylene reacts with *n*-propyl formate under the same conditions, the product is 1,3-dimethyl-5-isopropylbenzene (65). Oxidation of the hydrocarbon produces trimesic acid and derivatives of the hydrocarbon do not depress the melting point of derivatives of the hydrocarbon formed from *m*-xylene and isopropyl chloride. These results are explainable on the basis of rearrangement during alkylation, although pure 1,3-dimethyl-4-*n*-propylbenzene is not completely rearranged to 1,3-dimethyl-5-isopropylbenzene even after heating with aluminum chloride at 100°C. for 4 hr. (65).

When the *m*-xylene reacts with *tert*-butyl chloride, the 1,3-dimethyl-5-*tert*-butylbenzene is the principal product. If the assumption is correct that the larger alkyl radicals are more readily detatched from the benzene ring than are the smaller radicals, then it would follow that any 1,3-dimethyl-4-*tert*-butylbenzene initially formed would be very largely rearranged to the 1,3,5-hydrocarbon during alkylation.

On the other hand, if this view is correct, the reaction between *m*-xylene and *n*-butyl chloride should lead finally to the 1,3-dimethyl-5-*tert*-butylbenzene:



The 1,3-dimethyl-4-*sec*-butylbenzene would be formed in the first stage of the reaction. The *sec*-butyl radical would dissociate and undergo further isomerization during migration, as is the case when 1,3-dimethyl-4-*sec*-butylbenzene is warmed with aluminum chloride, and the final product of the reaction should be the 5-*tert*-butyl hydrocarbon. Actually the product of this reaction is the 5-*sec*-butyl hydrocarbon.

A summary of some of the data relative to the proportions of the two trialkylbenzenes formed during the alkylation of benzene or *m*-xylene with olefins or alkyl chlorides by means of the Friedel–Crafts reaction is given in table 11.

From this qualitative evidence and other data already cited (12, 39a), the inference is that the 1,2,4-trimethyl- and triethyl-benzenes would not be as readily rearranged as are the higher homologs, since the methyl and ethyl radicals are more firmly bound to the benzene ring than are the larger radicals. The data relative to the proportions of the triethylbenzenes are conflicting, however. The isopropyl group appears to be more easily dissociated, and radicals larger than propyl probably are nearly completely dissociated in the 4-position.

The yields of paraffin hydrocarbons from the reaction between an alkylbenzene and the naphthenes (table 8) lend support to this view.

TABLE 11

Proportions of trialkylbenzenes

TRIALKYLBENZENES	1, 2, 4-ISOMER	1, 3, 5-ISOMER
	per cent	*per cent*
Trimethylbenzenes (benzene and methyl chloride).......	75	25
Triethylbenzenes (benzene and ethyl chloride)..........	70	30
Triisopropylbenzenes (benzene and propylene)..........	25	75
Triisopropylbenzene (benzene and isopropyl chloride)...	No evidence	100
1,3-Dimethyl-R benzenes, where R is larger than propyl (from olefin or RCl)..................................	No evidence	100

The isomerization of alkyl radicals during any of these reactions can be readily explained on the basis of Whitmore's theory of intramolecular rearrangements (91). In the case of the *n*-propyl radical, the changes involved would be

$$CH_3CH_2\overset{+}{C}H_2 \xrightarrow{\text{H: shift}} CH_3\overset{+}{C}HCH_3$$

The isomerization of the butyl radicals has already been discussed.

VIII. SUMMARY

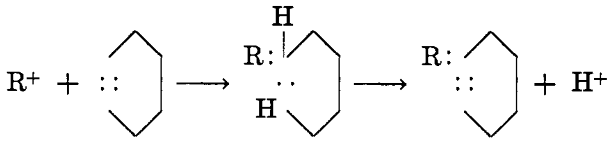
From the experimental evidence available at the present time, the following generalizations may be made relative to the mechanism of alkylations by means of aluminum chloride.

1. The metal halide probably forms a non-conducting, unstable complex with the reacting aromatic hydrocarbon.
2. The aluminum chloride forms a complex, not isolated, with the alkyl

halide of the type $R{:}X{:}AlCl_3$. This complex can ionize, yielding a positive carbonium ion and the negative ion $XAlCl_3$.

$$R{:}X{:}AlCl_3 \rightarrow R^+ + (X{:}AlCl_3)^-$$

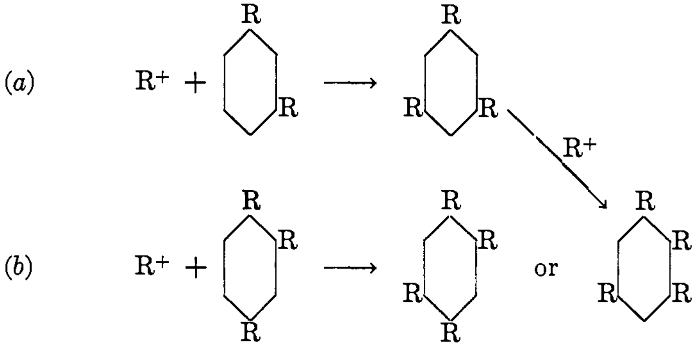
3. Alkylation may then proceed in two ways: (*a*) The R^+ may coordinate with a pair of electrons from a double bond in the benzene ring, followed by the loss of a proton (Price):



$$H^+ + (X{:}AlCl_3)^- \longrightarrow HX + AlCl_3$$

(*b*) The compound $R{:}X{:}AlCl_3$ may form a ternary complex with the reacting aromatic hydrocarbon, in which alkylation takes place with the loss of halogen acid (Wertyporoch).

4. The formation of a 1,3,5-hydrocarbon from a 1,2,4-hydrocarbon is explainable on the basis of Price's theory. According to this view, the alkyl radicals in the 2- and 4-positions direct the entering hydrogen to the 1-position, replacing the dissociated alkyl radical. The carbonium ion may then either (*a*) re-alkylate the benzene ring from which it came to form a 1,3,5-hydrocarbon, or (*b*) alkylate another molecule of the 1,2,4- or a 1,3,5-hydrocarbon, or (*c*) be hydrogenated to form an aliphatic hydrocarbon. Reaction (*a*) is also in accordance with the theory of Smith and Perry.



(*c*) $R^+ \longrightarrow RH$

Again, it must be emphasized that there are much conflicting data in the literature and that no one theory seems adequate to explain these data.

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