

THE REACTIONS OF PURE HYDROCARBONS IN THE PRESENCE OF ALUMINUM CHLORIDE¹

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I. INTRODUCTION

Reactions of pure hydrocarbons of the paraffin, olefin, acetylene, cycloparaffin, cycloolefin, terpene, and aromatic series which occur in the presence of aluminum chloride are finding application for the production of isomers and lower and higher hydrocarbons. Many studies have been made, and it is believed that more information as to the reactions and mechanisms could be developed by a digest of all the recorded work. In the seven groups of hydrocarbons studied in the presence of aluminum chloride, the reactions of dissociation, dehydrogenation, hydrogenation, isomerization, cyclization, polymerization, alkylation, and aromatization play principal rôles, with some exceptions. A striking fact stands out, namely, that the butanes, particularly isobutane, are key hydrocarbons resulting from many of these reactions.

Owing to a lack of definite knowledge of the exact rôle of aluminum chloride in hydrocarbon reactions, in the broadest sense it is looked upon as a catalyst. From the standpoint of the mechanism of the reaction, it becomes of interest to know if the aluminum chloride functions as a catalyst, as a component part of the reaction, or as both. The changes taking place with pure hydrocarbons, with some exceptions, in the presence of aluminum chloride seem to be a variation of the Friedel-Crafts reaction. In some cases, aluminum chloride reacts with the hydrocarbon to give hydrogen chloride (44, 100), which in turn reacts with another hydrocarbon molecule. In other cases, a complex compound containing hydrogen chloride, aluminum chloride, and hydrocarbon is produced. There are a number of hydrocarbons which do not react readily in the presence of aluminum chloride, but do when hydrogen chloride is added. The formation of alkyl chlorides has not been shown in all reactions,

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which is explained by the fact that at certain temperatures alkyl chlorides are unstable compounds in the presence of aluminum chloride and form olefins or other reaction products; however, in the case of the methylated benzenes, methyl chloride results under vigorous experimental conditions.

All forms of aluminum chloride are not adapted to use as a catalyst, as the method of preparation has an effect on the nature of its action. It was found (21) that with aluminum chloride prepared from hydrogen chloride and aluminum, the reaction of benzene and acetylene proceeded slowly, but with that prepared from aluminum and chlorine the action was rapid. Freshly prepared aluminum chloride (27) was found to be too active for the same reaction, and any degree of activity could be obtained by aging for various periods of time. More liquid products were formed when freshly prepared aluminum chloride was used in the polymerization of ethylene (86), and its activity may be due to the physical state rather than to the agents used in preparation and the time elapsing before use.

The reactions of pure hydrocarbons in the presence of aluminum chloride are usually characterized by the formation of colored reaction mixtures. The color usually appears when aluminum chloride comes in contact with the hydrocarbon. This would seem to indicate that the color was caused by some change in the nature of the aluminum atom. Color is a characteristic property of certain complex compounds, and since aluminum chloride forms complexes with hydrocarbons, there is a probable relationship. The cause of these colors is unknown, and they cannot be considered necessary for the occurrence of a reaction since colorless reaction mixtures are known.

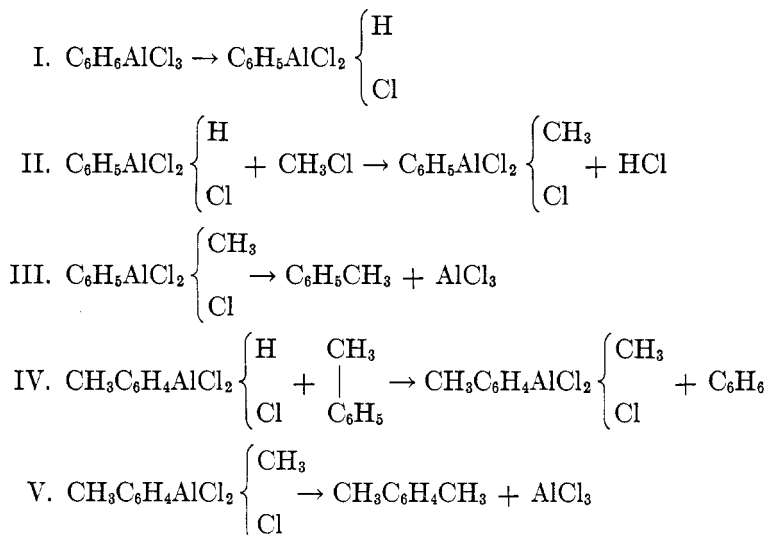
Hydrocarbon reactions are not induced by aluminum chloride hexahydrate. Its water of crystallization is held strongly enough to shield the forces of attraction in the aluminum chloride hydrate molecule, thereby preventing formation of complexes with hydrocarbons.

Numerous addition compounds of hydrocarbons are formed with aluminum chloride, as shown in table 18. Two types (60, 61, 62, 63) of complexes are recognized: (1) addition compounds of aluminum chloride with unit amounts of an aromatic or unsaturated hydrocarbon; (2) addition compounds with greater than unit amounts of hydrocarbon. The complexes of the first type are very reactive (60) towards ether, acetone, and aromatic hydrocarbons. With the aromatic hydrocarbons, complexes of the second type are formed, having high dissociation pressures. Hence, the first-type complexes are considered as "hydrocarbon of constitution," analogous to water of constitution. It is of interest to recall that $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ upon heating retains one molecule of water of crystallization with greater strength than the other four. The simpler aluminum chloride hydrocarbon complexes act similarly.

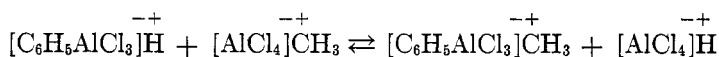
In many of these reactions hydrogen chloride is a highly important

component of the system; it may be added to the reaction, or may be present as a result of hydrolysis of the aluminum chloride by water, or may arise as a product of the hydrocarbon reaction.

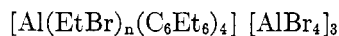
Aluminum chloride has been thought of as a hydrohalogenating-dehydrohalogenating agent. This involves the formation and decomposition of complex compounds in which hydrogen chloride acts as part of the reaction system. The series of reactions (126) for benzene, toluene, and aluminum chloride which will serve as an example are shown as follows:



An ionic equilibrium as the mechanism of reaction, whereby active hydrogen and methyl ions are interchangeable, is given (112):

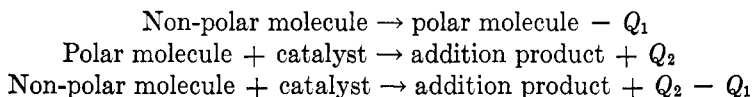


Conductance measurements (149) show that there is but little ionization in a benzene solution of aluminum bromide. A small amount of ethyl bromide slightly increases the conductance of a solution of aluminum bromide in benzene, and a small amount of benzene increases the conductance of aluminum bromide in ethyl bromide, whereupon reaction follows. Evidence was obtained for the formation of an aluminum bromide and hexaethylbenzene complex, to which is ascribed the formula,



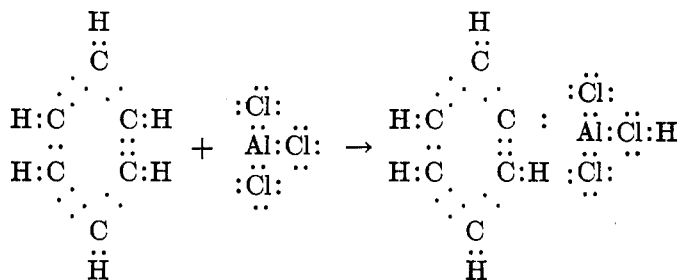
The corresponding crystalline substance, $2\text{AlBr}_3 \cdot \text{C}_6(\text{C}_2\text{H}_5)_6$, was also obtained (83).

The rôle of polarity and energy change in aluminum chloride reactions is shown (112) as:

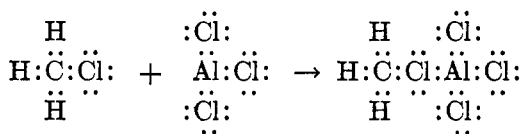


The octet theory of valence offers another viewpoint in these mechanisms. The aluminum atom of the chloride requires two electrons to complete its shell (36), and therefore unites readily with the chloride of an alkyl chloride, which is able to share two of its electrons with aluminum.

The aluminum chloride reaction can be interpreted in the light of the octet theory. Addition compounds are formed according to two equations:



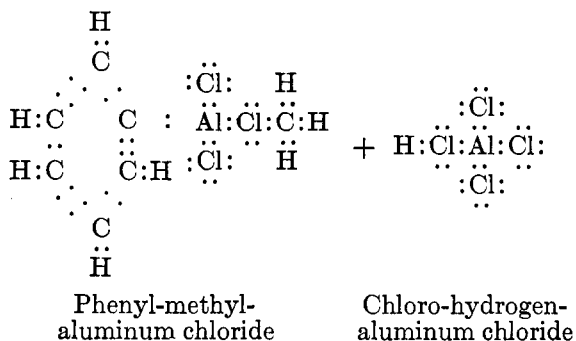
Benzene

A
Phenyl-hydrogen-
aluminum chloride

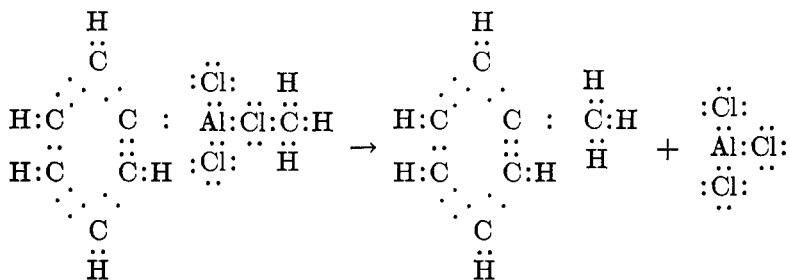
Methyl chloride

B
Chloro-methyl-
aluminum chloride

Then double decomposition occurs between the complexes A and B to form:

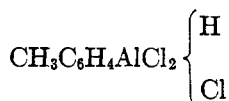
Phenyl-methyl-
aluminum chlorideChloro-hydrogen-
aluminum chloride

The compound $[C_6H_5AlCl_3]CH_3$ is identical with $C_6H_5AlCl_2 \begin{cases} CH_3 \\ Cl \end{cases}$, and further decomposition is represented by the following equation:

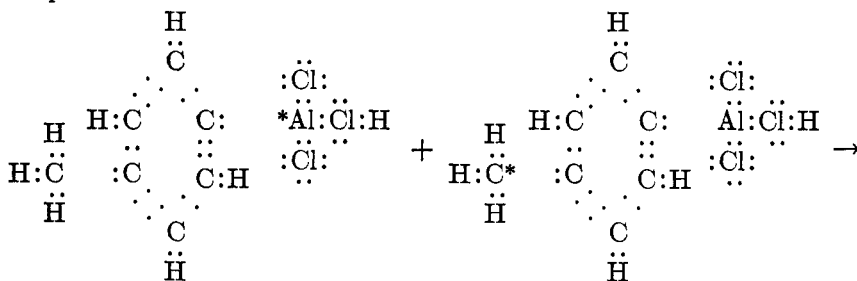


Phenyl-methyl-aluminum chloride Toluene

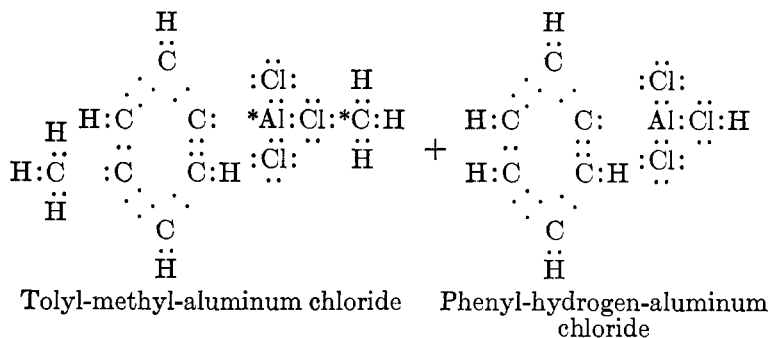
The action of aluminum chloride on toluene (126) with the formation of benzene and xylenes may be reinterpreted by the octet theory. First, a toluene-aluminum chloride complex is formed, corresponding to



Then, double decomposition occurs between electromeric forms of the complex so formed:

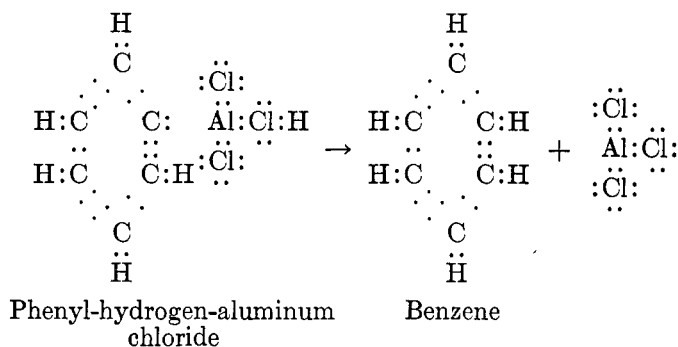
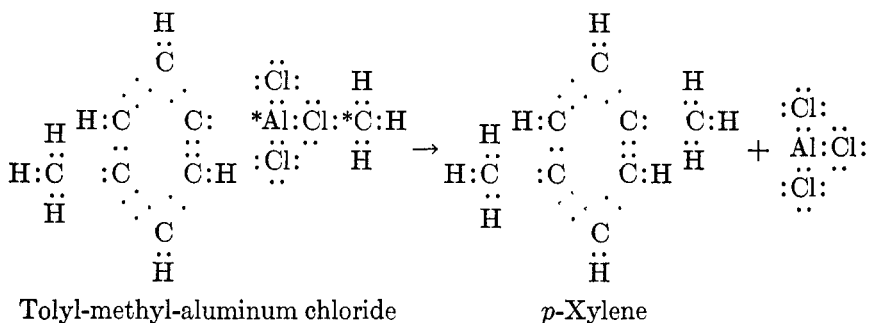


Tolyl-hydrogen-aluminum chloride Tolyl-hydrogen-aluminum chloride



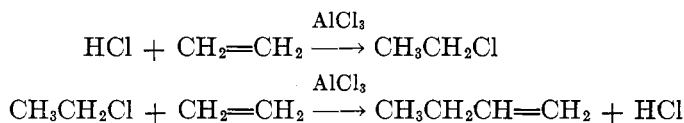
Tolyl-methyl-aluminum chloride Phenyl-hydrogen-aluminum chloride

Asterisks have been introduced in these equations corresponding to a shift of the electron doublet which makes the methyl group positive relative (90) to the aromatic nucleus. The final decompositions are shown in the equations:



The sharing of electrons will be affected by the difference in bond strength in the various hydrocarbons. At present, it is impossible to say just where all hydrocarbons share electrons with the aluminum atom.

Ethylene is reported to react in the presence of aluminum chloride only when hydrogen chloride is present. The addition of hydrogen chloride to the ethylene molecule under the influence of aluminum chloride is thought to be the primary step in the mechanism (77), which is followed by a coupling of the ethyl chloride with another ethylene molecule and the separation of hydrogen chloride.



Propene acts similarly in the presence of floridin, and it is probable that the formation of an alkyl chloride may be a general reaction for olefins and

hydrogen chloride. This mechanism does not necessarily involve the formation of complexes of aluminum chloride with olefins, although it is known that these do form. In the alkylation of benzene by ethylene in the presence of aluminum chloride, hydrogen chloride is necessary (16).

Hydrogen bromide is exceptionally effective (51) in activating aluminum chloride, and that activation is possible prior to hydrocarbon introduction. This indicates that the catalyst in its active form is a hydrogen-halide-aluminum chloride, which gives support to the octet interpretation but does not necessarily conflict with an alkyl halide mechanism.

The above theories stress the effect of aluminum chloride and hydrogen chloride, but they do not consider the difference due to the hydrocarbon structure. Reactions are induced by fundamental differences in structure (90, 131); therefore, the aluminum chloride reaction analogously must involve primary, secondary, tertiary, and quaternary carbon atoms and the structure of the hydrocarbon groups attached thereto, and also their initial activity and final stability. Complexes with olefins, acetylene, and aromatics are known. Although no complex compounds of aluminum chloride and paraffins have been reported as yet, it is an excellent catalyst in most paraffin reactions. In particular, the activity of the tertiary hydrocarbon group and, to a lesser extent, that of the secondary is greatly enhanced by the presence of aluminum chloride and hydrogen chloride (53).

Although reactions between either aluminum chloride or hydrogen chloride and the hydrocarbon do occur, these intermediate reactions have not been shown to be a necessary factor for the formation of the end products. Formation of hydrogen chloride or methyl chloride may be a secondary reaction where part of the aluminum chloride acts in a metathetical way. The effect of aluminum chloride on the weakening of the bonds in the hydrocarbon leads one to expect a difference in the nature of the products, depending on the concentration of the aluminum chloride. The products produced will also depend on factors such as temperature, pressure, the presence of a solvent (137), or water.

The activity of aluminum chloride with hydrocarbons may be modified by organic liquids (39), such as acetone, acetophenone, nitrobenzene, and nitromethane. The shielding effect of water of crystallization in aluminum chloride hexahydrate suggests that these liquids, owing to their high dielectric properties and solubility, act to shield the effective centers of anhydrous aluminum chloride by reducing the fields of force. Such compounds (106) are associated liquids possessing high dielectric properties which favor ionization. Furthermore, aluminum chloride in solution has dielectric properties consistent with an increase in activity of dissolved hydrocarbons. Paraffins show an absence (25, 128) of dipole moment or polarity in their molecules, but there must still be sufficient differences in the

TABLE I
Reactions of paraffins

COMPOUNDS	TEMPERATURE °C.	TIME hours	CONCENTRATION OF AlCl_3 per cent	PRESSURE atmospheres	PRODUCTS		REFERENCES
					Gases	Liquids and solids	
CH_4	200 370-500	8-120 40		Sealed tube	Above 370°C. H_2 formed; HCl (due to presence of H_2O)	At 500°C. carbon formed; no liquid formed	(89)
C_2H_6	320-500	72-40		Sealed tube	Above 370°C. H_2 formed; HCl	At 410°C. carbon formed and an oil	(89)
C_3H_8	300-500	40		Sealed tube	Above 320°C. H_2 formed; HCl	At 320°C. oil formed; carbon at 420°C.	(89)
C_4H_{10}	200	10	33.3	70	Ethane, 5 per cent; meth- ane, 2 per cent	Heavy oil	(79)
$n\text{-C}_4\text{H}_{10}$	345-500	40-24		Sealed tube	Above 245°C. H_2 formed	At 350°C. liquid formed	(89)
$iso\text{-C}_4\text{H}_{10}$	245-500	200-40		Sealed tube	Isobutane, 17 per cent; propane, 54 per cent; ethane, 10 per cent; methane, 5.8 per cent;	At 245°C. liquid formed	(89)
$n\text{-C}_4\text{H}_{10} + \text{HCl}$	175	3-4	31	35	hydrogen, 0.1 per cent	Heavy brown oil	(78)
$n\text{-C}_6\text{H}_{12}$	36	5-10 days	23-28 ⁽ⁱ⁾	1	Butanes; isopentane	Tar	(51)
$n\text{-C}_6\text{H}_{12} + \text{nitrogen}$	40-133		100 (at start)	1	Butanes; isopentane; hy- drogen, trace	Liquids, 85-90 per cent; tar	(51)
C_6H_{14} ^(d)	20-110	72-10	37-73 ^(e)	Sealed tube	Saturated hydrocarbons	C_4H_8 , AlBr_3	(57)
C_6H_{14}	100		83-40 ^(b)	1	Butane (large); propane	Pentane; higher hydrocarbons	(48)
C_6H_{14}	15-55	350				No reaction except when cat- alyzed by $\text{C}_3\text{H}_7\text{Br}$	(120)

C_6H_{14}	100	7½	27	1	No gases	2- or 3-methylpentane; cyclohexane	(104)
$C_6H_{14} + HCl$	69-72	3	9	35	Isobutane, 90 per cent; pentane, 9 per cent; hexane, 1 per cent	Isomeric hexanes; saturated hydrocarbons (b.p. -10° to 200°C.); unsaturated hydrocarbons	(78)
$n-C_6H_{14}$	80	1.5	5	Sealed tube		Isomeric hexanes, 2 per cent	(100)
$n-C_6H_{14}$	90	1	5	Sealed tube		Isomeric hexanes, 4 per cent	(100)
$n-C_6H_{14}$	90	2	4	Sealed tube		Isomeric hexanes, 20 per cent	(100)
$n-C_6H_{14}$	90	3	4	Sealed tube		Isomeric hexanes, 23 per cent	(100)
$n-C_6H_{14}$	90	1	5(e)	Sealed tube		Isomeric hexanes, 25 per cent	(100)
$n-C_6H_{14}$	90	2	5(e)	Sealed tube		Isomeric hexanes, 28 per cent	(100)
$n-C_6H_{14}$	45	1	5(e)	Sealed tube		Isomeric hexanes, 23 per cent	(100)
$n-C_6H_{14}$	45	3	5(e)	Sealed tube		Isomeric hexanes, 25 per cent	(100)
C_7H_{16}	100	10	25	1	Propane; isobutane (small amounts)		(104)
C_7H_{16}	100	10	30(e)	1	Propane; isobutane (larger amount than with the anhydrous)	2- or 3-methylpentane; heptane; 1,3-dimethylcyclohexane; methylcyclohexane; bicyclic paraffins	(104)
C_7H_{16}	220	3	1	50		Isomers, 8 per cent	(111)
C_7H_{16}	100			1		2-Methylhexane, hexane	(24)

(i) 0.6 to 0.8 per cent of water added.

(e) 3 per cent of 1-chloropropane added.

(f) 4 per cent of 1-chloropropane added.

(g) 10 per cent of $PbSO_4 \cdot 2HCl$ added.

(h) 10 per cent of $CuSO_4 \cdot 2HCl$ added.

(a) $AlBr_3$.

(b) Added in four parts.

(c) 1 per cent of water added.

(d) C_2H_5Br added.

TABLE 1—Concluded

COMPOUNDS	TEMPERATURE °C.	TIME hours	CONCENTRATION OF AlCl_3 per cent	PRESSURE atmospheres	PRODUCTS		REFERENCES
					Gases	Liquids and solids	
C_7H_{16}	96		63.1	1		Basis: 100 parts of <i>n</i> -heptane reacted— Pentanes and below 64.6 2-Methylpentane 3.4 3-Methylpentane 2.0 <i>n</i> -Hexane 0.4 2,4-Dimethylpentane 1.5 2,2,3-Trimethylbutane 0.5 3,3-Dimethylpentane 0.4 2-Methylhexane 1.2 3-Methylhexane 1.6 Polymerization products 24.4	(23)
$\text{C}_7\text{H}_{16} + \text{H}_2\text{O}$	97-99	3	9	35	Propane, 2 per cent; isobutane, 81 per cent; heptane, 13 per cent; butane + hexane, 4 per cent	Paraffins boiling below and above heptane; unsaturated hydrocarbons (small)	(78)
$n\text{-C}_8\text{H}_{18}$	20	1	8 ^(a)	Sealed tube		Isomeric octanes, 13 per cent	(100)
$n\text{-C}_8\text{H}_{18} + \text{HCl}$	20	22	5			Isomeric octanes, 24.0 per cent	(100)
$n\text{-C}_8\text{H}_{18}$	20	22	10 ^(a)			Isomeric octanes, 17.5 per cent	(100)
$n\text{-C}_8\text{H}_{18}$	20	22	10 ^(b)			Isomeric octanes, 24.3 per cent	(100)
$n\text{-C}_8\text{H}_{18} + \text{HCl}$	20	1.5	10			Isomeric octanes, 5 per cent	(100)
$n\text{-C}_8\text{H}_{18} + \text{HCl}$	20	4	10			Isomeric octanes, 15 per cent	(100)

$n\text{-C}_8\text{H}_{18} + \text{HCl}$	20						Isomeric octanes, 19 per cent	(100)
$n\text{-C}_8\text{H}_{18} + \text{HCl}$	20	8	10				Isomeric octanes, 24 per cent	(100)
$n\text{-C}_8\text{H}_{18} + \text{HCl}$	20	24	10				Isomeric octanes, 38 per cent	(100)
$n\text{-C}_8\text{H}_{18} + \text{HCl}$	20	96	10				Isomeric octanes, 61 per cent	(100)
$n\text{-C}_8\text{H}_{18}$	115-125	8	23	1			Liquid (b.p. 70-120°C.)	(52)
C_8H_{18}	405-410	3	5	70			Isomers, 23 per cent	(111)
2,5-Dimethylhexane.....	100-110	6	22	1			Unsaturated hydrocarbons	(52)
2,2,4-Trimethylpentane + HCl....	20-50	4	9	1			Paraffinic hydrocarbons corresponding to heptanes, nonanes, heptadecane; unsaturated oil	(53)
C_9H_{20}	110-120	8	30	1			Believed amylene-cyclopentane; amylene polymers	(34)
$n\text{-C}_{10}\text{H}_{22}$	140-150	8	26.3	1			Liquid (b.p. 69-73°C.)	(52)
2,7-Dimethyloctane.....	135-145	4	37.5	1			Cyclopentane; liquid (b.p. 50-170°C.)	(52)
2,7-Dimethyloctane.....	135-145	4	28.5	1			Aliphatic hydrocarbons; liquid (b.p. 50-180°C.)	(52)
2,7-Dimethyloctane.....	110-120	7	16	1			Believed dodecane; tridecane; liquid (b.p. 90-285°C.)	(52)
$\text{C}_{16}\text{H}_{34}$	150-200		33.3	1			Higher hydrocarbons	(50)
$\text{C}_{17}\text{H}_{36}$	150-160	4	14	1			Saturated hydrocarbons	(52)
$\text{C}_{18}\text{H}_{38}$	110		20	1			Liquids, 60 per cent; heavy oil, 3.3 per cent; carbon, 23 per cent	(13)
$\text{C}_{38}\text{H}_{74}$	150		20	1			Liquids, 33 per cent; heavy oil, 30 per cent; carbon, 24 per cent	(13)

rigidity of hydrocarbon groups and of hydrogen to account for activity in the manner of free radicals, unsaturated groups (38), and labile hydrogen (72). A more general concept of the effect of structure of the hydrocarbon undergoing changes due to aluminum chloride or hydrogen chloride is in the weakening of the bond strengths in the hydrocarbon. This is supported by the fact that catalytic reactions are known in which hydrocarbons react in the presence of aluminum chloride alone or with added hydrogen chloride.

While the theories given explain certain reactions, no one theory or mechanism is entirely adequate.

II. PARAFFINS

The paraffins in the presence of aluminum chloride form isomers, lower and higher paraffins, olefins, cycloparaffins, liquids of unknown constitution, carbon, and hydrogen, depending upon the original paraffin and the experimental conditions. In general, a key hydrocarbon in the form of butane results from treatment of higher paraffins.

Little work has been done on the first five members of this series, as shown in table 1. In some experiments, methane and ethane appeared to be inert (89), dissociating largely to carbon and hydrogen at high temperatures. Ethane, propane, *n*-butane, and isobutane yielded liquids. Propane reacted to give methane, ethane, and a heavy oil, whereas *n*-butane in the presence of hydrogen chloride and aluminum chloride formed lower paraffin and unsaturated hydrocarbons, besides some isobutane (79). *n*-Pentane reacted with aluminum chloride to give *n*-butane, isobutane, and isopentane, and the aluminum chloride surface was coated with a tarry (51) layer.

Hexane and higher paraffins dissociate principally to butanes, small amounts of propane and pentanes, and some higher paraffins. Although butane was the hydrocarbon given off in largest amounts, some workers reported *n*-butane and others isobutane. This may be due to an error in identification, but, as the data stand now, it appears that *n*-butane in some cases and isobutane in others, or both, are actually formed.

An examination of the quantities and kind of aluminum chloride reported indicates that when a low concentration (1 to 10 per cent) is used or water is added, isobutane predominates; when concentrations of 20 to 50 per cent are used, *n*-butane is obtained. These results should be carefully checked under comparable conditions. Besides gaseous hydrocarbons, the higher paraffins yield isomers, still higher paraffins, and unsaturated hydrocarbons. Again the appearance of isomers of the paraffins is linked with relatively low concentrations of aluminum chloride.

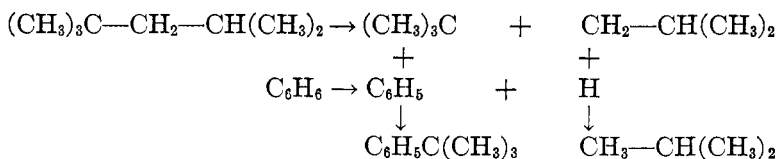
The following conclusions as a result of a study (100) of the action of

low concentrations of aluminum chloride upon *n*-hexane and *n*-octane have been made: (1) isomerization occurs; (2) isomerization by aluminum chloride is activated strongly by hydrogen chloride or substances readily giving off hydrogen chloride, such as alkyl chlorides and compounds of hydrogen chloride with anhydrous sulfates of heavy metals; (3) in the absence of hydrogen chloride, isomerization by aluminum chloride proceeds with considerable velocity only at increased temperature and with an induction period which corresponded to hydrogen chloride formation; and (4) an increase in exposed surface of aluminum chloride and stirring strongly accelerate the reaction of isomerization.

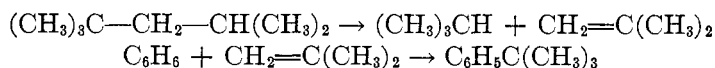
Paraffins react not only alone in the presence of aluminum chloride but also with a second hydrocarbon forming a higher one (50, 53, 80, 81).

Paraffins are alkylated by olefins and by cyclopropane, giving mainly higher paraffins. This work is shown in table 2. This reaction is similar to the alkylation of benzene, toluene, and xylenes by olefins.

A particularly interesting paraffin studied (53) is 2,2,4-trimethylpentane. When the reaction of this paraffin and benzene is catalyzed by aluminum chloride and hydrogen chloride, mono- and di-tertiary-butyl benzenes are obtained. Apparently the chain breaks into four-carbon atom radicals with a tertiary carbon atom. The tertiary carbon radical unites with a phenyl group, while the other unites with a hydrogen atom to give isobutane, as shown:



An alternate mechanism for the reaction involves the formation of an olefin and a paraffin from the starting paraffin. The olefin in turn reacts with the aromatic hydrocarbon, as illustrated.



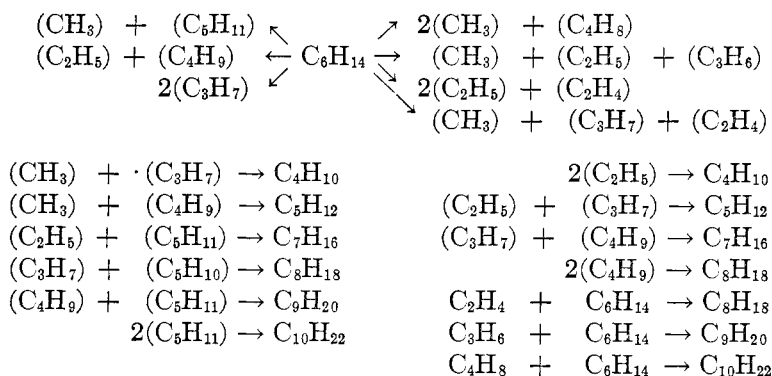
Unsaturated hydrocarbons have been found in the lower layer of the reaction mixture, and in certain cases aluminum chloride addition compounds with the unsaturates have been identified. The thermal reactions of gaseous paraffins are characterized by the formation of unsaturated hydrocarbons, while in the presence of aluminum chloride the reactions yield a layer of paraffins and a layer of unsaturates. This points to a preferential reaction of aluminum chloride for the weakening of the carbon-carbon bond, causing cleavage into two-carbon atom radicals and un-

TABLE 2
Reactions of paraffins with other hydrocarbons

COMPOUNDS	TEMPERATURE °C.	TIME hours	CONCENTRATION OF $AlCl_3$ per cent	PRESSURE atm.	PRODUCTS		REFER- ENCES
					Gases	Liquids and solids	
iso-C ₄ H ₁₀ + C ₂ H ₄ + HCl	20-30	32-40	12	1	No	Higher paraffins; unsaturated hydrocarbons	(80)
iso-C ₄ H ₁₀ + C ₂ H ₄ + HCl	25	10	12	15		Paraffins (hexanes, octanes, decanes)	(81)
n-C ₆ H ₁₄ + C ₂ H ₄ + HCl	29-33	15	10	1		Higher paraffins; cycloparaffins; unsaturated hydrocarbons	(81)
n-C ₆ H ₁₄ + C ₂ H ₄ + HCl	25	36	10	15		Paraffinic hydrocarbons	(81)
iso-C ₆ H ₁₂ + C ₆ H ₆ + HCl	125	23	10	1	Propane	Alkylated benzenes	(80)
n-C ₆ H ₁₄ + C ₆ H ₆ + HCl	100	17	10	1	Butane	Paraffins below hexane; alkylated benzenes (b.p. 90-200°C.)	(80)
2,2,4-(CH ₃) ₃ C ₃ H ₉ + C ₆ H ₆ + HCl	20-50	4	9	1	Isobutane; propane (trace); pentane	Tertiary-butylbenzene; disubstituted hydrocarbons	(53)
iso-C ₄ H ₁₀ + cyclopropane + HCl	-30 to +30					Heptanes and higher paraffins	(54)

saturated carbon chains. The unsaturated chain or radical polymerizes, unites with a paraffin, or forms addition compounds with the aluminum chloride. The polymerization products of ethylene, such as hexene and octene, may rearrange to give cycloparaffins as they do in the thermal reactions of ethylene.

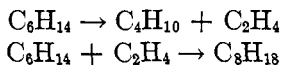
In the thermal reactions of gaseous paraffinic hydrocarbons, the weakest bond appears to be the carbon-carbon linkage. The work on the heats of combustion (116) of isomeric octanes gives a constant value for the carbon-carbon bond. It has been indicated (117) that for hexane and lower members of the series, the strength of the carbon-carbon bond and of the carbon-hydrogen bond is dependent on the position of the bond. It appears that these variations in bond strengths are small, and therefore do not seriously affect the assumption of constancy in the carbon-carbon bond. However, there are other indications that these variations may not be a negligible factor. In the thermal reactions of hydrocarbons there is a tendency for scissions in the carbon-carbon bonds with the formation of an unsaturated molecule with two carbon atoms (38). When most hydrocarbons react in the presence of aluminum chloride, butane is the principal gaseous product. This points to a scission of the chain into a unit with four carbon atoms or into units with two carbon atoms which combine to give butane. Less probable scissions along the chain do occur, as is evident from the appearance of propane and pentane. If hexane is taken as an example of a higher paraffin, the formation of paraffins may be represented in the following equations:



This explanation arises from the consideration that the energy necessary to cause the hydrocarbon to react is supplied in the case of thermal reactions by heat alone and in the case of catalytic reactions by the energy induced by aluminum chloride.

If the reaction is described in terms of the products, it would be stated

that the original paraffin forms a lower member and an olefin, while the olefin adds to another molecule of the original paraffin to give a higher member, as indicated by the reaction of hexane.



The mechanism is supported by the fact that olefins have been shown to alkylate paraffins, forming higher ones (see table 2).

Ethylene polymerizes to butene or higher olefins in the *absence* (37a, 38) of aluminum chloride. If ethylene is a reaction product of dissociation of the paraffin, it might polymerize to higher olefins before it alkylates part of the original paraffin. The greater tendency for the formation of paraffins rather than olefins in the presence of aluminum chloride indicates that higher paraffins form through the union of alkyl radicals rather than through a primary decomposition into olefins and subsequent addition to a paraffin. This is supported by the predominant appearance of the butanes in the gaseous products, even with a large variation in the nature of the original paraffin. The aluminum chloride increases the tendency for the scission of the carbon-carbon bonds into smaller units, and when present in small amounts or in the partially hydrated or hydroxy form, causes a shifting of carbon atoms within the molecule. Thus *n*-hexane gives some isobutane, methylcyclopentane, and hexane isomers; heptane yields isomeric heptanes. The variance in the form of butane obtained probably arises from isomerization of the *n*-butane into isobutane.

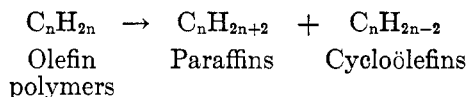
III. OLEFINS

Olefins in the presence of aluminum chloride polymerize, isomerize, cyclicize, and form paraffins and more highly unsaturated compounds. Polymerization yields unsaturated liquid and solid products. Isomerization of olefins gives cycloparaffins, while polymerization followed by isomerization also yields cycloparaffins. Dehydrogenation may produce diolefins, which cyclicize to cycloolefins; or the cycloparaffins may dehydrogenate to the corresponding cycloolefins. Hydrogen from the latter reaction hydrogenates an olefin to a paraffin. Isomerization, polymerization, and dehydrogenation yield aromatic compounds. The gases formed are hydrogen, propane, and butane, the latter not so consistently as in the case of the paraffins. These products and reactions are similar to those observed in thermal reactions, except that a lower temperature is used, which gives a wider range to the type and size of molecules formed without decomposition taking place.

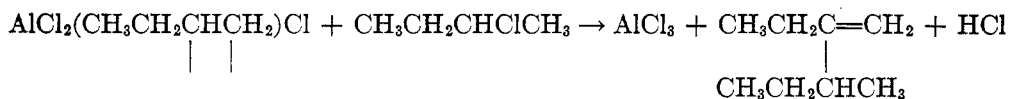
Subjecting ethylene (37a, 38) to temperatures of 350–400°C. causes a thermal polymerization to butene, hexene, and higher olefins. At slightly

higher temperatures scissions of carbon-carbon bonds occur along the chain of the olefins, giving two types of radicals which on hydrogenation form olefins and paraffins. Since the catalytic action of aluminum chloride appears to consist of the weakening of the bonds, these reactions should occur at lower temperature in its presence. It follows that in the catalytic reaction of ethylene, polymerization probably takes place first. This will be followed by scissions of the carbon-carbon bond in higher olefins, resulting in the formation of paraffins, owing to coupling of the alkyl radicals, and the formation of cycloolefins, owing to the combination of the unsaturated radicals. Ethylene is known to yield some cyclohexane when polymerized by heat; apparently ethylene polymerizes to hexene, which in turn cyclizes.

The nature of the products from the polymerization of ethylene has been investigated by a number of experimenters (77, 119, 129). They found an upper layer of "free oil", paraffinic in character, and a lower layer of "combined oil", consisting of cycloolefins in combination with aluminum chloride. The polymerization of ethylene with aluminum chloride is accompanied therefore by dehydrogenation-hydrogenation reactions, so that the final products are not true polymers of ethylene. The term "conjunct polymerization" (77) has been suggested for such reactions, which can be represented as follows:



The polymerization of butene in the presence of aluminum chloride and hydrogen chloride has been reported to take place as follows (76a):

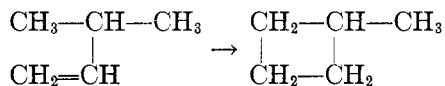


The octene decomposes into a paraffin and into a diolefin which cyclicizes readily.

It was found that the course of the polymerization of isobutene depends upon the temperature gradient (143). At room temperature the reaction with aluminum chloride is moderate, whereas a violent reaction takes place at -78°C ., sometimes explosively. When 2-butene is treated with aluminum chloride at -10°C ., a high yield of cycloparaffins (146) results.

Rapid polymerization of certain pentenes occurs even at -80°C . in the presence of aluminum chloride (95). Amylene produced a resinous mass which, upon treatment with hydrochloric acid, resulted in the elimination of aluminum and the formation of a thick oil which yielded a

yellow oil and an asphaltic residue (41). Other experiments showed that cycloparaffins resembling lubricating oil, methylcyclobutane, and hexane were formed (5). The formation of methylcyclobutane indicates an isomerization by ring closure as indicated by the equation:



The polymers produced from 2-pentene and from 3-methyl-1-butene having a partly cyclic structure have been reported (140).

The effect of high aluminum chloride concentration was shown (40) by treating trimethylethylene at room temperatures for five weeks with an equal weight of aluminum chloride, producing *n*-pentane, isopentane, hexane, heptane, octane, and decane rather than heavy oils.

Ethylene, propene, isobutene, octene, and pentene form paraffins and cycloparaffin liquids when treated with aluminum chloride at 100° to 150°C. (134). Liquids with five to eight carbon atoms per molecule were formed from ethylene, propene, and butene when subjected for 0.5 to 100 seconds to temperatures up to 300°C. in the presence of aluminum chloride (76). These observations indicate that higher temperatures, approaching the point of thermal reactivity of the hydrocarbons themselves, are suitable conditions for the formation of products from olefins and aluminum chloride.

The lower olefins have been polymerized both in the absence (28, 52, 71, 108) and in the presence of a hydrocarbon which was considered an inert solvent (140, 142, 143, 144).

When olefins are heated from 100° to 200°C. in the presence of aluminum chloride at atmospheric pressure or at 20° to 100°C. with increased pressure (86) and in the absence of added solvents, two oily layers are formed. The oil in the upper layer has been called "free oil", and that in the lower layer "fixed" or "combined" oil. The latter may be freed from the aluminum chloride if the reaction mixture is poured over ice. The "free oil" may be decanted from the aluminum chloride sludge, which after refining is a "good lubricant." The "combined oil" after hydrolysis yields an inferior lubricant. Since these oils are better than the natural oils in quality, the reaction has been considered an important one. Patents have been issued for the production of oils and resins from olefins or cracked distillates (8, 22, 68, 71, 96, 97, 107, 113, 119, 136, 145).

Aluminum chloride suspended in petroleum ether or gasoline is capable of polymerizing ethylene, propene, butenes, and pentenes, forming a hydrocarbon mixture still containing olefin bonds (115). Such investigators as have considered petroleum ether or gasoline or certain paraffins as inert

solvents are in error, because paraffins have been shown to undergo (1) autodestructive alkylation and isomerization in the presence of aluminum chloride and hydrogen chloride (see table 1), and (2) alkylation by olefins in the presence of this catalyst (see table 2).

The aluminum chloride and the thermal (38) mechanisms indicate a directing force in the aluminum chloride reaction with olefins to form paraffins, cycloparaffins, or cycloölefins preferentially. With lower olefins the primary reaction is the polymerization to higher ones. Lubricating oils were produced by thermal polymerization of ethylene (8), completing the polymerization reaction by treatment with aluminum chloride at room temperature. The extent of polymerization depends on the size and structure of the olefin. From the thermal reactions of the gaseous olefins it appears that the more straight chain the molecule is, the less readily it will polymerize. It would be expected that these relationships hold even when aluminum chloride is present, and this appears to be borne out by the report that aluminum chloride polymerizes ethylene, propene, 1-butene, 2-butene, isobutene, 1-pentene, 2-pentene, 2-methyl-1-butene, 3-methyl-1-butene, trimethylethylene, 1-hexene, 1-octene, and cetene primarily into high-boiling liquids (133). The results of the experiments show that the more branched the olefin structure, the poorer the lubricating quality of the oil becomes, owing to the high change in viscosity as a function of temperature rise. The long-chain paraffin hydrocarbons are superior lubricants compared to the cycloparaffins, olefins, and aromatics. Since the viscosity factor of the oil is important, the paraffins produced should have large molecules. Starting with the lower olefins, polymerization should proceed slowly in order that long-chain molecules be built up; and it was found that the amount of paraffinic oil depended on the contact time (129).

Aluminum chloride weakens the bonds in the olefins, and if the hydrocarbons are treated to build higher paraffins, the action of the catalyst should not be so vigorous that the hydrocarbon molecule will split into small radicals. Therefore a low concentration is desirable, as shown by the use of 3 to 5 per cent aluminum chloride in the polymerization of olefins to lubricating oils. On the other hand, for the production of lower paraffins out of high-boiling fractions, a higher concentration of aluminum chloride is desirable. An inspection of table 3 indicates the nature of the reaction of olefins with aluminum chloride. Predominantly, there is a direct polymerization to higher olefins. Secondarily, higher olefins by cyclization produce cycloparaffins. Finally, dehydrogenation-hydrogenation reactions change these cycloparaffins into cycloölefins, aromatics, or carbon (as products of dehydrogenation) and paraffins.

TABLE 3
Reactions of olefins

COMPOUNDS	TEMPERATURE °C.	TIME <i>hours</i>	CONCENTRATION OF AlCl_3 <i>per cent</i>	PRODUCTS		REFERENCES
				Gases	Liquids and solids	
Ethylene + HCl	100	1 week		C_2H_4 + HCl from crystal- line product	Complex compound, $\text{AlCl}_3 \cdot \text{C}_4\text{H}_8$ Crystalline product, $\text{AlCl}_3 \cdot 3\text{C}_2\text{H}_4 \cdot$ H_2O	(58) (67)
Ethylene + ethyl alcohol	Room					
Ethylene	40-300	0.5-100 sec- onds	100 (at start)		Liquid hydrocarbons with five and more carbon atoms per molecule	(76)
Ethylene	20-30		34.1		Paraffins, 52.8 per cent; unsatu- rated cyclic hydrocarbons, 47.2 per cent	(77)
Ethylene	Room				Low-boiling paraffins; high-boil- ing cycloparaffins	(86)
Ethylene	200-280				Carbon	(86)
Ethylene + petroleum ether	Room-100	4-12 days			Paraffins; olefins; aromatics	(110)
Ethylene + gasoline	Room	Short	16.7 (at start)		Unsaturated liquid hydrocarbons	(115)
Ethylene + petroleum ether	Room	Few hours			Unsaturated liquid hydrocarbons	(115)
Ethylene	Room-180				Paraffins; cycloparaffins; olefins	(115)
Ethylene + naphtha	100-150				Polymerization product	(133)
Ethylene					Low-boiling paraffins and higher boiling cycloparaffins	(134)
Propene + nitrobenzene	Room	3-65	17.2 (at start)		Product of b.p. 80-200°C.	(39)

Propene + nitrobenzene.....	50				Viscous oils	(39)
Propene + ethyl alcohol.....	40-300	0.5-100 seconds	100 (at start)		Crystalline product	(67)
Propene.....		Short			Liquid hydrocarbons with five and more carbon atoms per molecule	(76)
Propene + petroleum ether.....	Room				Unsaturated liquid hydrocarbons	(115)
Propene + naphtha.....	150				Polymerization product, 33.3 per cent	(133)
Propene.....	10-30				Low-boiling paraffins and higher boiling cycloparaffins	(134)
Allene.....	40-300	0.5-100 seconds	100 (at start)		High-boiling polymerization products	(75)
Butene + ethyl alcohol.....	Room	Few hours	16.7 (at start)		Crystalline product	(67)
Butene.....					Liquid hydrocarbons with five and more carbon atoms per molecule	(76)
Butenes + petroleum ether.....					Unsaturated liquid hydrocarbons, low-boiling paraffins and higher boiling cycloparaffins	(115)
1-Butene + naphtha.....					Polymerization product, 46.4 per cent	(133)
2-Butene + naphtha.....					Polymerization product, 33.3 per cent	(133)
2-Butene.....	-10	2	1.75		Cycloparaffins, 92.9 per cent	(146)
Isobutene + nitrobenzene.....			17.2 (at start)		Product of b.p. 60-190°C.	(39)
Isobutene + benzene + diphenylsulfone.....	Room	4.1	8.33 (at start)		Diisobutene; triisobutene; higher polymerization products	(39)
Isobutene + nitromethane.....	0				Very viscous oil	(39)
Isobutene + naphtha.....					Polymerization product, 42.0 per cent	(133)

TABLE 3—Continued

COMPOUNDS	TEMPERATURE °C.	TIME hours	CONCENTRATION OF $AlCl_3$ per cent	PRODUCTS		REFERENCES
				Gases	Liquids and solids	
Isobutene.....	100-150				Low-boiling paraffins; higher boiling cycloparaffins	(134)
Isobutene + pentane.....	-78	2	5.26		Very viscous polymer of high molecular weight	(143)
Isobutene + pentane.....	-35 to -40	2	5.26		Polymerization product	(143)
Isobutene + pentane.....	+7 to +16	2	3.23		Polymerization product	(143)
Butadiene.....		Slow			Polymerization product	(151)
Amylene + ethyl alcohol..					Crystalline product	(67)
Amylene.....	Room				Viscous yellow oil and asphaltic residue	(41)
Amylene + petroleum ether.....	Room	Short			Unsaturated liquid hydrocarbons	(115)
Amylene.....	0-20	5 weeks	50	Unidentified gas	Cycloparaffins resembling lubricating oil; unidentified hexane; methylcyclobutane	(5)
1-Pentene + naphtha.....					Polymerization product, 59.8 per cent	(133)
1-Pentene.....	-80	5½			Polymerization product, small yield	(95)
2-Pentene.....	-80	5½			Polymerization product, small yield	(95)
2-Pentene.....	Room	Short			Polymers	(95)
2-Pentene + HCl.....	-80				2- and 3-chloropentanes, 40 per cent; hydrochlorides of alkenes of polymerization, 60 per cent	(95)
2-Pentene + naphtha.....					Polymerization product, 38.5-53.0 per cent	(133)

2-Pentene.....	0				Polymers with a partly cyclic structure	(140)
2-Methyl-1-butene + naphtha.....					Polymerization product, 34.5 per cent	(133)
2-Methyl-1-butene + HCl.	-80				2-Chloro-2-methylbutane; hydrochlorides of alkenes of polymerization	(95)
2-Methyl-1-butene.....	-80	5½			Polymers, 49 per cent	(95)
2-Methyl-2-butene + naphtha.....					Polymerization product, 29.3 per cent	(133)
2-Methyl-2-butene.....	Room	5 weeks		50	Pentane; isopentane; hexane; heptane; octane; decane	(40)
2-Methyl-2-butene.....	-80	5½			Polymers, 82 per cent	(95)
2-Methyl-2-butene + HCl.	-80				2-Chloro-2-methylbutane; hydrochlorides of alkenes of polymerization	(95)
3-Methyl-1-butene + naphtha.....					Polymerization product, 50.8 per cent	(133)
3-Methyl-1-butene.....	-80				Alkenes of polymerization	(94)
3-Methyl-1-butene.....	-80	Very slow			Polymers, 60 per cent	(95)
3-Methyl-1-butene + HCl.	-80	44			Hydrochlorides of alkenes of polymerization, 60 per cent; 2-chloro-3-methylbutane, 20 per cent	(94)
3-Methyl-1-butene + benzene.....	85				Polymers with a partly cyclic structure	(140)
3-Methyl-1-butene + benzene.....	200				Polymers with a partly cyclic structure	(140)

TABLE 3—Concluded

COMPOUNDS	TEMPERATURE °C.	TIME <i>hours</i>	CONCENTRATION OF $AlCl_3$ <i>per cent</i>	PRODUCTS		REFERENCES
				Gases	Liquids and solids	
Isoprene.....	151	24			White, soft polymer	(151)
Isoprene + nitrobenzene..					Soluble polymer of isoprene	(137)
Isoprene + ethyl acetate..					Soluble and insoluble polymers	(137)
Isoprene + HCl					Soluble and insoluble polymers	(137)
Isoprene.....	Room	Slow			Insoluble polymer	(137)
Isoprene + 2-pentene.....					Insoluble polymer and one soluble polymer of isoprene	(137)
Isoprene.....	Room	Few min- utes			Polymer of high molecular weight	(6)
"Commercial" isoprene....		24			Insoluble and soluble solids of unsaturated character	(7)
Isoprene.....					Yellow flaky polymer	(148)
Isoprene + benzene.....					Polymers of isoprene	(21)
Isoprene + pentene.....					Amorphous condensation product	(6)
Isoprene + 2-methyl- 2-butene.....					Amorphous condensation product	(6)
1-Hexene + naphtha.....					Polymerization product	(133)
2,3-Dimethylbutadiene....		24			White, soft polymer	(151)
1-Octene + naphtha.....					Polymerization product	(133)
Octene.....	100-150				Low-boiling paraffins and higher boiling cycloparaffins	(134)
Diamylene.....	150			Butane + propane	Low-boiling paraffins and higher boiling cycloparaffins	(134)
Cetene.....	57.2				Polymerization product, 85.0 per cent	(133)

III. DIOLEFINS

Diolefins are polymerized in the presence of aluminum chloride. It is reported that allene (75) yields products of polymerization by contact with aluminum chloride at room temperature and below. Various polymerization products have been obtained from the action of aluminum chloride on butadiene, isoprene, and 2,3-dimethylbutadiene (151). Isoprene yields a high molecular weight hydrocarbon in the presence of aluminum chloride, and upon standing soft white, flaky yellow, soluble, or insoluble polymers are formed, depending upon the conditions of the reaction (6, 7, 148).

Solvents have an important influence on the degree of polymerization of isoprene (137). Any solvent in which isoprene and aluminum chloride were mutually soluble favored the formation of soluble polymers. Pure isoprene underwent a slow polymerization to insoluble polymers in the presence of aluminum chloride at room temperature. Addition of dry hydrogen chloride to the isoprene led to both soluble and insoluble polymers, probably owing to the presence of the solvent-like hydrochloride of isoprene which was also formed.

IV. ACETYLENES

A complex compound which acetylene forms with aluminum chloride has been isolated and identified and is relatively unstable (67). Acetylene was absorbed by anhydrous aluminum chloride even in the cold (12). At 70°C., the acetylene is absorbed in a few minutes to give a reddish sublimate, which becomes black as more acetylene is absorbed at 120–130°C.

It has been reported (75) that allylene and diacetylene yield products of polymerization by contact with aluminum chloride at room temperature and below.

Vinylacetylene treated at 50–110°C. with less than 2 per cent of aluminum chloride yields unsaturated polymers of non-benzenoid character (25).

The reactions of the acetylenes with aluminum chloride are summarized in table 4. Reactions of acetylene in the presence of aromatics and aluminum chloride are considered in table 14.

V. CYCLOPARAFFINS

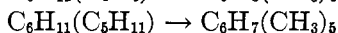
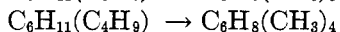
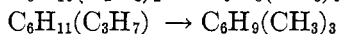
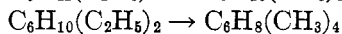
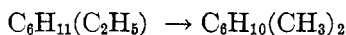
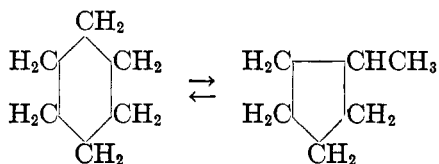
Cycloparaffins isomerize and dehydrogenate readily. Alkyl side chains of two more carbon atoms rearrange to methylate the cycloparaffin. Polycyclization takes place by dehydrogenation or isomerization. In general, butane, with higher and lower paraffins and olefins, is formed from the reaction of cycloparaffins and aluminum chloride.

Cyclopentane and cyclohexane were found to be stable below 60°C. with aluminum chloride. In the presence of water at somewhat higher temperature cyclohexane isomerized into methylcyclopentane. The for-

TABLE 4
Reactions of acetylenes

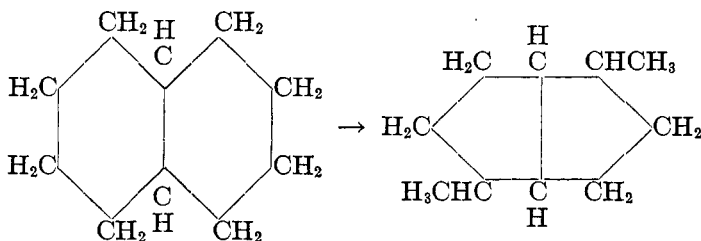
COMPOUNDS	TEMPERATURE °C.	TIME	CONCENTRATION OF $AlCl_3$	PRODUCTS		REFERENCES
				Gases	Liquids and solids	
Acetylene.....	60-62	hours	100	Dense fumes	Reddish-brown sublimate	(67)
Acetylene + ethyl alcohol...	Room	5 days	per cent	C_2H_2 + HCl from the crystalline product	Colorless crystals of $AlCl_3 \cdot 2C_2H_2 \cdot 2H_2O$	(67)
Acetylene.....	70	Few minutes	100		Red sublimate, $(C_{10}H_{16.6})_7 \cdot Al_2Cl_6$	(12)
Acetylene.....	120-130		100		Black substance, $(C_{20}H_{16})_7 \cdot Al_2Cl_6$	(12)
Allylene.....	10-30				High-boiling polymerization products	(75)
Vinylacetylene.....	50-110		<2		Unsaturated polymers of non-benzoid character	(25)
Diacetylene.....	10-30				High-boiling polymerization products	(75)
Pentanes + nitromethane....	20		19.8		Viscous oil	(39)

mation of isobutane (82), as well as dicyclohexyl, *m*-dimethylcyclohexane, and dimethyldicyclopentyl, was observed at 150°C. when cyclohexane was treated with aluminum chloride. In the presence of an acceptor for hydrogen such as arsenic chloride, di- and tri-cyclohexyl were obtained from cyclohexane (105). Working with alkylated cyclohexanes it was found that the *o*- and *p*-dimethylcyclohexanes gave the meta form. This preference for the meta form was observed also with aromatics. Ethylcyclohexane when heated with aluminum chloride gave dimethylcyclohexane; and the diethylcyclohexanes yielded di- or tetra-methyl compounds. This is especially interesting, since the alkyl group as a side chain has been ruptured within the chain. Scission in the side chain and distribution of the methyl group around the cyclohexane ring is a function of the size of the original alkyl group. Thus, propylcyclohexane yielded trimethylcyclohexane, butylcyclohexane produced tetramethylcyclohexane, and amylcyclohexane was converted into pentamethylcyclohexane; in addition to the methylcyclohexanes, *n*-butane was reported in all cases except from isoamylcyclohexane, when some isobutane was formed. If a fairly high concentration of aluminum chloride was used, the resulting vigorous exothermic reaction probably removed *n*-butane before any isomerization to isobutane occurred. Some reactions of the cycloparaffins are shown in the following equations:

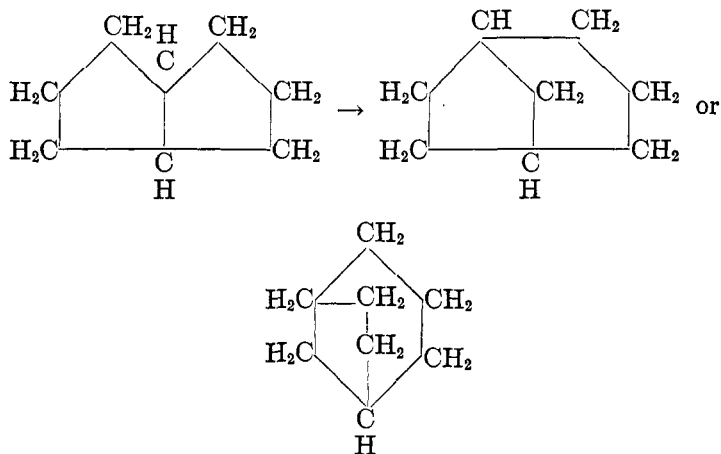


Decalin and aluminum chloride at 130°C. gave cyclohexane, methylcyclohexane, and 1,3,5-trimethylcyclohexane (88) in small amounts; however at 150°C. charring occurred.

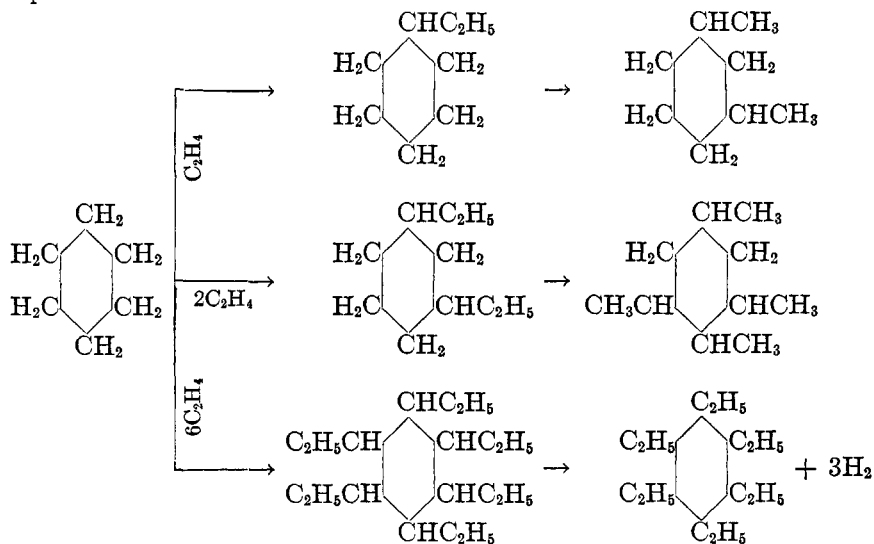
trans-1,4-Dimethylbicyclo(0,3,3)octane was also isolated, indicating a transformation of cyclohexane rings into methylcyclopentane rings, as follows:



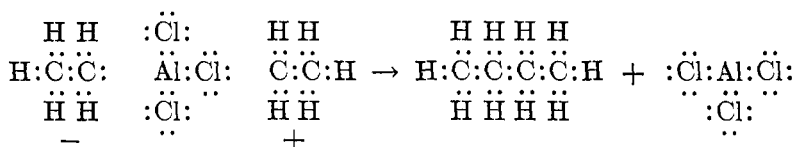
Cyclopentane rings can also be converted into cyclohexane rings, as shown (11) by the conversion of *cis*-bicyclo(0,3,3)octane into bicyclo(1,2,3)octane:



In the reaction of cyclohexane and ethylene in the presence of aluminum chloride, which has been studied (83), the action of the alkylated cyclohexanes and the relation of these to hexaethylbenzene is shown in table 6. Instead of ethyl- or diethyl-cyclohexane forming, as would be expected from other ethylating reactions, *m*-dimethyl- and 1,3,4,5-tetramethyl-cyclohexane were formed; instead of hexaethylcyclohexane, hexaethylbenzene resulted. These reactions may be represented by the following equations:



Butane is usually the gaseous hydrocarbon formed, except in the case of propylcyclohexanes, where propane results. Butane formed by the ethylated cyclo compounds probably results from the union of two ethyl radicals. From the amylcyclohexane, butane formation appears from a scission of the carbon-carbon bond within the side chain. The preference for the formation of a four-carbon atom paraffin in the reaction of pure hydrocarbons with aluminum chloride and the formation of the two-carbon atom olefin which occurs on thermal treatment find an explanation in the mechanism of the two reactions. Aluminum chloride weakens the bonds, making the simple scission into alkyl groups possible at low temperatures at which butane is stable, while in the thermal case butane is not readily formed. The preferential formation of butane can be ascribed to the building-up tendency of complexes of aluminum chloride with two-carbon atom molecules, as shown:



In contrast to the splitting-off of the whole alkyl group from the benzene ring, is the splitting within the side chain of the alkylated cyclohexanes, giving the methylated cyclohexanes. It will be shown that for aromatic compounds the weakest carbon-carbon bond is the one between the ring and side chain and not within the side chain as might be expected. The benzene ring appears to exert a repulsive force on the side chain, indicating that the unsubstituted benzene ring is the most stable form. This repulsive force must result from the nature of the benzene ring, since it is not observed, at least to the same degree, with the cycloparaffin rings. In the cycloparaffin compounds the difference in the strengths of these bonds had decreased so that both scissions occur.

The detailed data of cycloparaffin reactions are given in tables 5 and 6.

VI. CYCLOÖLEFINS

Relatively few experiments have been conducted with cycloölefins and aluminum chloride. Cycloölefins isomerize, polymerize, hydrogenate, and dehydrogenate and react readily with other hydrocarbons such as aromatics and aluminum chloride.

When cyclohexene was treated at 70°C., high molecular weight polymers (133, 142) were produced; another experimenter (142), operating at a temperature of -78°C. in the presence of hydrogen chloride, aluminum chloride, and pentane, found chlorinated cyclohexane and polycyclohexyl.

TABLE 5
Reactions of cycloparaffins

COMPOUNDS	TEMPERATURE °C.	TIME hours	CON- CEN- TRA- TION OF AlCl ₃ per cent	PRODUCTS		REFER- ENCES
				Gases	Liquids and solids	
Cyclopentane.....	60	8	23		No change	(34)
Methylcyclopentane.....	65-70	30	25		Cyclohexane (equilibrium mixture)	(103)
Cyclohexane.....	65-70	16	25*		Methylcyclopentane	(103)
Cyclohexane.....	100	72	25	HCl	Methylcyclopentane	(5)
Cyclohexane.....	100	24	50		Methylcyclopentane; dimethylcyclo- butane	(153)
Cyclohexane.....	135-145	6-8	14†		No change	(52)
Cyclohexane + HCl.....	150	24	10	Isobutane	Methylcyclopentane; dicyclohexyl; dimethyldicyclopentyl; <i>m</i> -dimeth- ylcyclohexane	(82)
Cyclohexane + AsCl ₃	65-70	16	16†	HCl	Dicyclohexane; tricyclohexane	(105)
Methylcyclohexane.....	140-150	3	9†		No change	(52)
Methylcyclohexane.....	120-130		10		Hexamethylene; pentamethylene; paraffins	(138)
<i>o</i> - or <i>p</i> -Dimethylcyclohexane.....	115-120	7	23	Trace of gas	<i>m</i> -Dimethylcyclohexane	(52)
<i>m</i> -Dimethylcyclohexane.....	115-120	7	23	Trace of gas	Traces of unsaturated hydrocarbons	(52)
Dimethylcyclohexane.....	120-130		10		Hexamethylene; pentamethylene; paraffins	(138)
Ethylcyclohexane.....	115-120	8	21	Gas (small); ethane	<i>m</i> -Dimethylcyclohexane	(52)
Ethylcyclohexane.....	135-140				<i>m</i> -Dimethylcyclohexane	(138)
<i>m</i> -Diethylcyclohexane.....	120-130	4	23	Butane (small)	Tetramethylcyclohexane; polymer- ized cyclohexene	(52)
<i>m</i> -Diethylcyclohexane.....	100-130	1-2	20	No gas	Dimethylcyclohexane	(52)
<i>m</i> -Diethylcyclohexane.....	115-120	4	20	Butane	Dimethylcyclohexane	(52)

<i>m</i> -Diethylcyclohexane.....	115-120	5	50	Butane (largest)	Dimethylcyclohexane	(52)
<i>n</i> -Propylcyclohexane.....	135-145	7.5	30	Propane	Trimethylcyclohexane	(52)
Isopropylcyclohexane.....	130-145	7	23	Propane	Trimethylcyclohexane	(52)
<i>n</i> -, <i>sec</i> -, or <i>tert</i> -Butylcyclohexane.....	150-160	8	20-23	Butane (secondary, large; tertiary, small)	Tetramethylcyclohexane; liquid (b.p. 155-165°C.)	(52)
Amylcyclohexane.....	130-155	7	25	Butane	Isoamylcyclohexane; methyl- and tetramethyl-cyclohexanes	(52)
Isoamylcyclohexane.....	130-140	5	17	<i>n</i> -Butane and isobutane	Pentamethylcyclohexane; methyl- and tetramethyl-cyclohexanes	(52)
Cycloheptane.....	100-300	3 days	55	Isobutane; <i>n</i> -butane		(152)
<i>cis</i> -Bicyclo-(0,3,3)-octane.....	Room	48	28.6		Bicyclo-(1,2,3)-octane	(11)
Decalin, 75 per cent <i>trans</i>	130		24.2		Cyclohexane; methylcyclohexane; 1,3,5-trimethylcyclohexane; 1,4-dimethylbicyclo-(0,3,3)-octane	(88)
<i>cis</i> -Decalin.....	100	12	24.3		<i>trans</i> -Decalin	(153)
<i>cis</i> -Decalin.....	Room	22	28.6		<i>trans</i> -Decalin	(153)

* Added water (0.6 per cent).

† Under pressure.

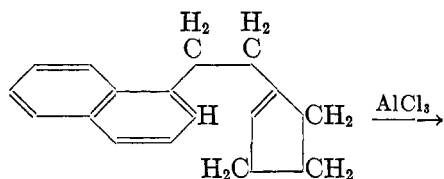
‡ 22 per cent of AsCl₃ present.

TABLE 6
Reactions of cycloparaffins with ethylene

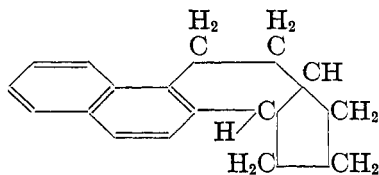
COMPOUNDS	TEMPERATURE °C.	TIME hours	CONCENTRATION OF AlCl_3 per cent	PRODUCTS		REFERENCES
				Gases	Liquids and solids	
Cyclohexane + ethylene + HCl.....	50-60	13	11.1	Ethane	<i>n</i> -Dimethylcyclohexane; tetramethylcyclohexane; hexaethylbenzene	(83)
Methylcyclohexane + ethylene.....	70	10			Cycloparaffins (b.p. 110°C. and up)	(83)
Methylisopropylcyclo- hexane + ethylene....	80	2.5			Cycloparaffins (b.p. 175°C. and up)	(83)

The reactions of cyclohexene in the presence of aromatic hydrocarbons (table 16) give cyclohexyl derivatives (16, 18).

The treatment of 1-(β -1'-naphthylethyl)cyclo-1-pentene in carbon disulfide solution with aluminum chloride produced 1,2-cyclopentano-1,2,3,4-tetrahydrophenanthrene (31). In this reaction, ring closure upon an active double bond occurs, and the cyclization is represented as follows:

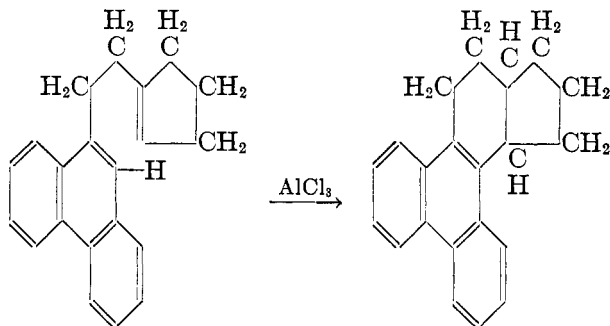


1-(β -1'-Naphthylethyl)cyclo-1-pentene

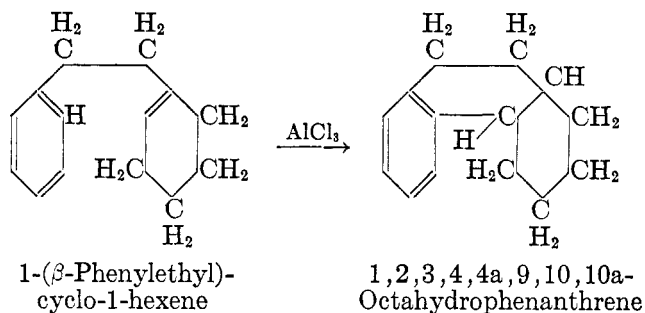


1,2-Cyclopentano-1,2,3,4-tetrahydrophenanthrene

In like manner 1-(β -9-phenanthrylethyl)cyclo-1-pentene was treated in carbon disulfide solution with aluminum chloride at room temperature, giving tetrahydrocyclopentenotriphenylene (14) as indicated in the following equation:

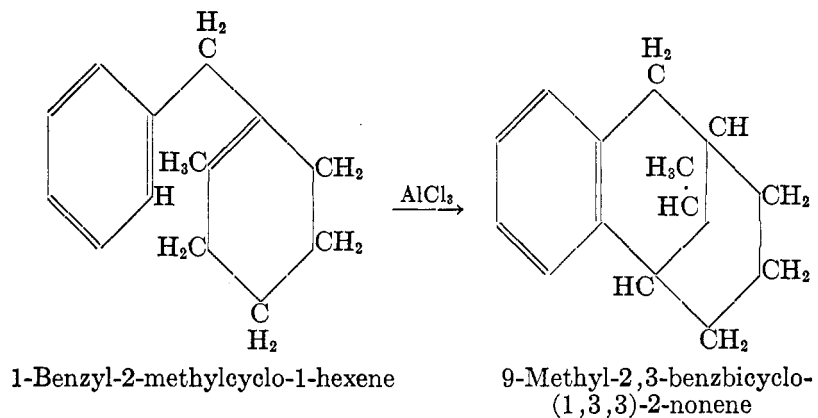


The compound 1-(β -phenylethyl)cyclo-1-hexene was treated in carbon disulfide solution with aluminum chloride; this yielded 1,2,3,4,4a,9,-10,10a-octahydrophenanthrene (29, 31) according to the equation shown:

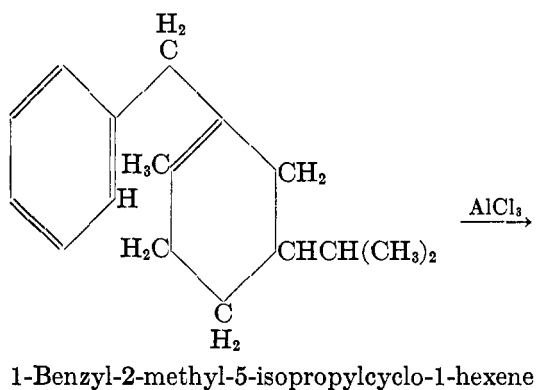
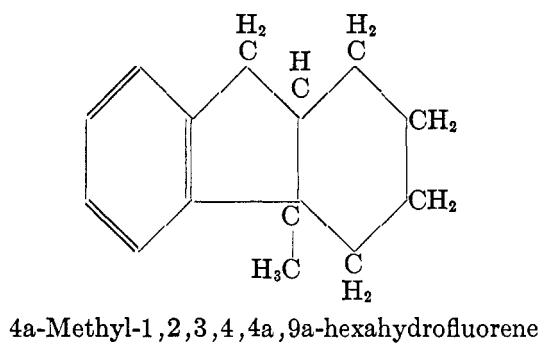


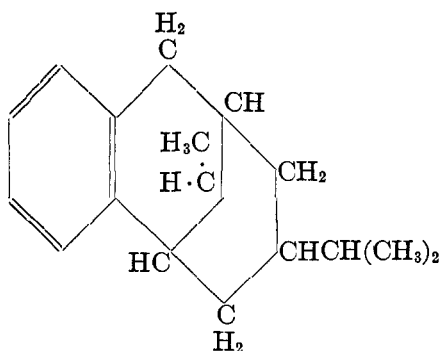
In these syntheses an isomerization of the unsaturated chain to a six-carbon atom ring structure occurs as a result of the action of aluminum chloride upon the double bond of a cycloolefin. The analogous alkylation of aromatics with olefins is discussed in section XI.

The compounds 1-benzyl-2-methylcyclo-1-hexene and 1-benzyl-2-methyl-5-isopropylcyclo-1-hexene, when treated with aluminum chloride at 0°C., gave hydrocarbons of the same empirical formulas but without an active olefin bond (32). It was shown that the cyclization products cannot be hexahydrofluorenes, although it was not demonstrated that benzobicyclononenes are formed. Apparently, in this synthesis, closure to a six-carbon atom ring structure rather than to a five-carbon atom ring is favored by aluminum chloride, as indicated in the equations:



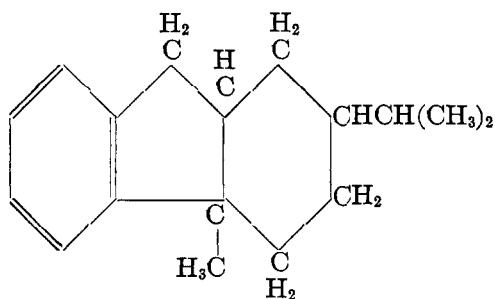
rather than





7-Isopropyl-9-methyl-2,3-benzbicyclo(1,3,3)-2-nonene

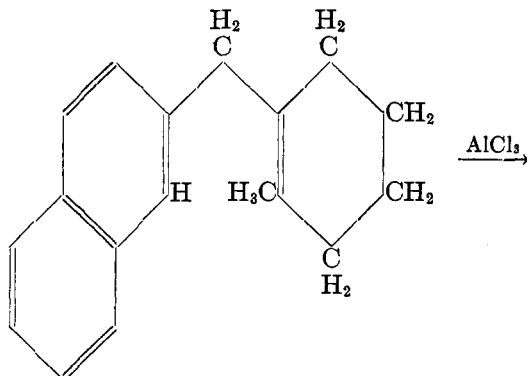
rather than



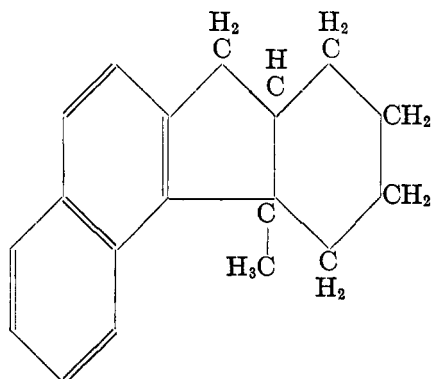
2-Isopropyl-4a-methyl-1,2,3,4,4a,9a-hexahydrofluorene

Apparently the strainless benzbicyclononene system is formed in preference to the hexahydrofluorenes after an initial isomerization of cyclo-1-hexenes to cyclo-2-hexenes.

The compound 1-methyl-2-(2'-naphthylmethyl)cyclo-1-hexene was treated in carbon disulfide solution with aluminum chloride, giving 7a,8,9,10,11,11a-hexahydro-11a-methyl-3,4-benzofluorene (28), as follows:

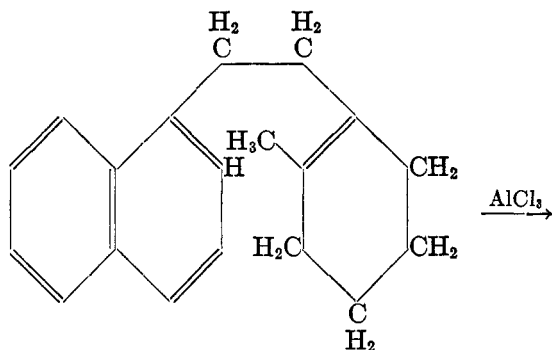
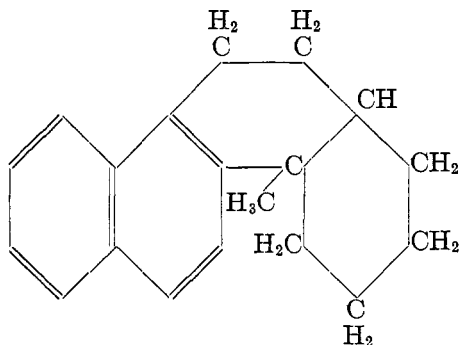


1-Methyl-2-(2'-naphthylmethyl)cyclo-1-hexene



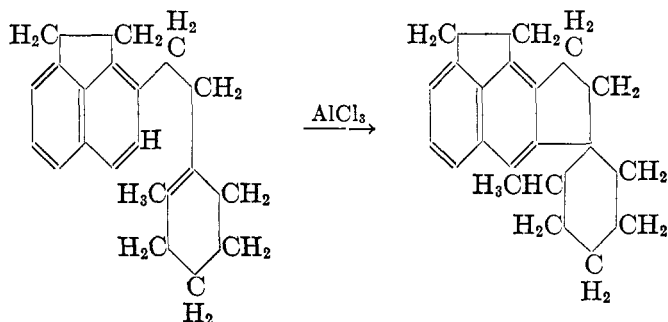
7a,8,9,10,11,11a-Hexahydro-11a-methyl-3,4-benzofluorene

The substance 1-(β -2-methyl- Δ^1 -cyclohexenylethyl)naphthalene was subjected to treatment in carbon disulfide solution with aluminum chloride, giving 1,2,2a,3,4,5,6,6a-octahydro-6a-methylchrysene (30):

1-(β -2-Methyl- Δ^1 -cyclohexenylethyl)naphthalene
(i.e., 2-methyl-(β -1'-naphthylethyl)cyclo-1-hexene)

1,2,2a,3,4,5,6,6a-Octahydro-6a-methylchrysene

The investigations showed that substitution of acenaphthyl for naphthyl in the previous cyclohexene derivative leads to formation of a spiran, as follows:



1-(β -2-Methyl- Δ^1 -cyclohexenylethyl)-
acenaphthene (i.e., 2-methyl-
(β -1'-acenaphthylethyl)-
cyclo-1-hexene)

8,9-Dihydro-2'-methylspiro-
(β -acenaphthindan-3,1'-
cyclohexane)

The general principle of cyclization for the naphthalenes and related hydrocarbons with cyclopentenylethyl, cyclohexenylethyl, or cyclohexenylmethyl groups in the alpha and beta positions, as considered in this section, is stated thus:—the cyclization of the alpha-substituted naphthalenes and related compounds and of the analogous monosubstituted benzene produces six-carbon atom rings. Cyclization of beta-substituted naphthalenes and related hydrocarbons produces five-carbon atom rings (72).

The details of the reactions in this section and those involving cyclohexadienes are given in tables 7 and 16.

VII. TERPENES

The reactions of terpenes catalyzed by aluminum chloride result in the formation of polymers and of hydrogenated and chlorinated compounds. Paraffins, cycloparaffins, olefins, polyolefins, polynaphthenes, dihydropinene, and benzene are types of the products formed. The reactions are summarized in table 8.

The simultaneous action of aluminum chloride and iodine, which acted as an activator of the aluminum chloride upon pinene (44), produced pinene hydrochloride and iodides of pinene. The presence of pinene hydrochloride indicates that hydrogen chloride is produced by the action of aluminum chloride on the terpenes, and probably has an important function in the polymerizations of the terpenes.

When pinene, dipentene, sylvestrene, camphene, and isopinene reacted

TABLE 7
Reactions of cycloolefins

COMPOUNDS	TEMPERATURE °C.	TIME hours	CONCENTRATION OF $AlCl_3$ per cent	PRODUCTS		REFERENCES
				Gases	Liquids and solids	
1-(β -1'-Naphthylethyl)cyclo-1-pentene + CS_2	0	24	8.13		1,2-Cyclopentano-1,2,3,4-tetrahydro- phenanthrene, 83% (<i>cis</i> + <i>trans</i>)	(31)
1-(β -9-Phenanthrylethyl)cyclo-1- pentene + CS_2	Room	12			Tetrahydrocyclopentotriphenylene	(14)
Cyclohexene					Polymerization product	(133)
Cyclohexene + pentane + HCl	-78	2.5	<10		Chlorocyclohexane, 50%; chloropoly- cyclohexyl compounds	(142)
Cyclohexene	70	7	6-7		High molecular polymers	(142)
1,3-Cyclohexadiene	Warmed				Polymerization product	(151)
1,4-Cyclohexadiene	Warmed				Partly hydrogenated product of poly- merization; benzene	(151)
1-(β -Phenylethyl)cyclo-1-hexene + CS_2		24	37.8		1,2,3,4,4a,9,10,10a-Octahydrophen- anthrene, 85%	(31)
1-(β -Phenylethyl)cyclo-1-hexene + CS_2	Room	6			1,2,3,4,4a,9,10,10a-Octahydrophen- anthrene	(29)
1-Benzyl-2-methylcyclo-1-hexene	0	3	62		Methylbenzobicyclononene, 70%	(32)
1-Benzyl-2-methyl-5-isopropylcyclo-1- hexene	0	5			Methylisopropylbenzobicyclononene, 75%	(32)
1-Methyl-2-(2'-naphthylmethyl)cyclo- 1-hexene + CS_2	0	6	6.8		7a,8,9,10,11,11a-Hexahydro-11a- methyl-3,4-benzofluorene, 47%	(28)
1-(β -2-Methyl- Δ' -cyclohexenylethyl)- naphthalene + CS_2	0	7	8.7		1,2,2a,3,4,5,6,6a-Octahydro-6a- methylchrycene, 60%	(30)
1-(β -2-Methyl- Δ' -cyclohexenylethyl)- acenaphthene + CS_2	0	21	7.3		8,9-Dihydro-2'-methyl-spiro-(β -ace- naphthindan-3,1'-cyclohexane)	(30)

TABLE 8
Reactions of terpenes

COMPOUND	TEMPERATURE °C.	TIME hours	CONCENTRATION OF $AlCl_3$ per cent	PRODUCTS		REFERENCES
				Classes	Liquids and solids	
L-Pinene.....	0 to room	1	33.33		Brittle solid polymer $(C_{10}H_{16})_x$ of m.p. 77-78°C.; liquid	(130)
Pinene.....	Room		*		Pinene hydrochloride; iodides of pinene	(44)
Finnish turpentine oil (b.p. 160-167°C.).....	Room			Methyl and ethyl chlorides	Paraffin, olefin, polyolefin, and cycloparaffin mixture	(118)
Finnish crude turpentine.....	Room	1-25 days	20-33.33		Semisolid pitchy substances	(118)
French turpentine oil.....	Room	16	30.33		Solid or semisolid polymers	(45)
French turpentine oil.....	0 to room				Brittle solid polymer $(C_{10}H_{16})_x$ of m.p. 77-78°C.; liquid	(130)
French turpentine oil.....	Heated	2	25	Paraffins + cycloparaffins	Liquid, 63 per cent, containing pentane, isopentane, trimethylethylmethane, cyclooctane, cyclodecane, polynaphthenes, dihydropinene, benzene, and unsaturates	(130)
Sumatra turpentine oil (b.p. 156.8-157.2°C.) + pentane.....	-15		15-25		Colorless oil of molecular weight 300; resin of molecular weight 500 to 600	(141)
Turpentine.....					Polymerization product	(133)
Pinene + isoprene.....					Amorphous condensation product	(6)
Dipentene + isoprene.....					Amorphous condensation product	(6)
Isopinene + isoprene.....					Amorphous condensation product	(6)
Camphene + isoprene.....					Amorphous condensation product	(6)
Sylvestrene + isoprene.....					Amorphous condensation product	(6)

* Iodine present also.

TABLE 9
Reactions of benzene and methylbenzenes

COMPOUNDS	TEMPERATURE °C.	TIME	CON- CEN- TRA- TION OF AlCl ₃	PRESSURE	PRODUCTS		REFER- ENCES
					Gases	Liquids and solids	
C ₆ H ₆	180-200	hours	per cent	atmospheres			
C ₆ H ₆	100	48 10-14 days	17 20	Sealed tube Sealed tube		Toluene; ethylbenzene; diphenyl Toluene; xylene; mono- and di- ethylbenzenes	(47) (70)
C ₆ H ₆	80	24	10		HCl	Tar; phenol, 1 per cent; benzene, 92 per cent	(101)
C ₆ H ₆ + HCl.....	100	Many		Sealed tube		1-Methyl-3-phenylcyclopentane; diphenylcyclohexane	(64)
C ₆ H ₆ + HCl.....	20	20 weeks	12.5*			Complex compound, AlCl ₃ ·3C ₆ H ₆	(55)
C ₆ H ₆	20					Phenylcyclohexane; diphenyl; <i>o</i> -di- phenylcyclohexane; cyclohexane; phenylmethylcyclopentane	(147)
C ₆ H ₆ + HCl.....	125	24	10	Under pres- sure		Ethylbenzene; diphenyl, 0.84 per cent; unsaturated oil; unsaturated ethylene polymers	(82)
C ₆ H ₅ CH ₃	200	36-48	25	Sealed tube		Xylene; <i>o</i> - and <i>p</i> -ethyltoluenes; di- tolyl	(47)
C ₆ H ₅ CH ₃	111	3	20	Sealed tube		Benzene; <i>m</i> - and <i>p</i> -xylenes	(3, 4)
C ₆ H ₅ CH ₃	111	Several	9			Benzene; <i>m</i> - and <i>p</i> -xylenes; higher methylated benzenes; dimethyl- anthracene	(93)
C ₆ H ₅ CH ₃	111	24	10		HCl	Benzene; xylene; hexahydrofluorene Complex compound, AlCl ₃ ·3C ₇ H ₈	(101) (55)

$m\text{-C}_6\text{H}_4(\text{CH}_3)_2 + \text{HCl}$								Complex compounds, 2AlCl_3 , $\text{C}_6\text{H}_4(\text{CH}_3)_2$ and 2AlCl_3 .	(60)
$m\text{-C}_6\text{H}_4(\text{CH}_3)_2$	110-119	Few	20					Benzene; toluene; mesitylene; pseudocumene; durene; isodurene	(3, 4)
$m\text{-C}_6\text{H}_4(\text{CH}_3)_2$	135	4	16.7				CH_3Cl	Benzene; toluene (large); mesitylene, durene, pseudocumene (small)	(87)
$\text{C}_6\text{H}_4(\text{CH}_3)_2$	135	1.5	4		18			Toluene	(43)
$m\text{-C}_6\text{H}_4(\text{CH}_3)_2$	135	24	10				HCl	Toluene; benzene; hexahydro-toluene	(101)
$m\text{-C}_6\text{H}_4(\text{CH}_3)_2 + \text{CH}_3\text{Cl}$ $o\text{- and } p\text{-C}_6\text{H}_4(\text{CH}_3)_2$ $+ \text{HCl}$	130-140	8-10	20					Mesitylene; pseudocumene; durene	(127)
$m\text{-C}_6\text{H}_4(\text{CH}_3)_2 + \text{HCl}$	100	6	16.7				No	Benzene; <i>m</i> -xylene (large); mesitylene; pseudocumene	(66)
$m\text{-C}_6\text{H}_4(\text{CH}_3)_2 + \text{HCl}$	100	6	16.7				No	Benzene; toluene; mesitylene; pseudocumene	(66)
$1,2,4\text{-C}_6\text{H}_3(\text{CH}_3)_3$	125-130	2	20					Toluene; <i>m</i> -xylene; <i>p</i> -xylene (trace); mesitylene; durene; isodurene	(3, 4)
$1,2,4\text{-C}_6\text{H}_3(\text{CH}_3)_3$	150-160	6	7.4				$\text{HCl} + \text{CH}_3\text{Cl}$	Benzene, 2 per cent; toluene, 8 per cent; <i>m</i> - and <i>p</i> -xylenes, 27 per cent; durene, 8 per cent; isodurene, 3.2 per cent; mesitylene, 3.6 per cent	(87)
$1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3$	150-160	4	9.1				CH_3Cl	Durene, 5 per cent; isodurene, 16 per cent; <i>m</i> -xylene (large); pseudocumene; benzene, toluene (small amounts)	(87)
$\text{C}_6\text{H}_2(\text{CH}_3)_4$	Low							Trimethylbenzene; xylene	(47)
$1,2,4,5\text{-C}_6\text{H}_2(\text{CH}_3)_4$ $+ \text{HCl}$	130-140		10				CH_3Cl	Lower methylated benzenes	(87)

 * AlBr_3 .

TABLE 9—Concluded

COMPOUNDS	TEMPERATURE °C.	TIME hours days	CONCENTRATION OF AlCl ₃ per cent	PRESSURE atmospheres	PRODUCTS		REFERENCES
					Gases	Liquids and solids	
C ₆ H(CH ₃) ₅	50-55	14	33.3	atmospheres		Pentamethylbenzene (large); hexamethylbenzene (small); isodurene; solids	(87)
C ₆ H(CH ₃) ₅ + HCl.....	100-110	4	20	Sealed tube		Hexamethylbenzene; durene; isodurene; solid (m.p. 250°C.)	(87)
C ₆ H(CH ₃) ₅ + HCl.....	130-140		9		Methyl chloride (large)	Lower methylated benzenes	(87)
C ₆ (CH ₃) ₆	Low		9		Gas with more than two carbon atoms	Pentamethylbenzene; tetramethylbenzene; lower methylated benzenes	(47)
C ₆ (CH ₃) ₆	190-200		33.3		Methyl chloride (large)	Pentamethylbenzene (large); durene and isodurene (large); mesitylene; pseudocumene; <i>m</i> -xylene; toluene and benzene (small)	(87)
C ₆ (CH ₃) ₆ + HCl.....	264		9.1			Benzene; toluene; complete decomposition of original	(87)

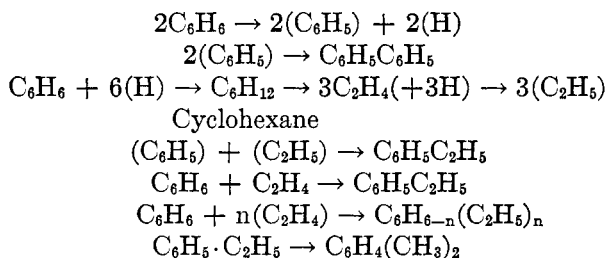
with isoprene in the presence of aluminum chloride, amorphous compounds (6) were formed.

When French turpentine oil and *l*-pinene were treated with aluminum chloride at from 0°C. to room temperature, liquid and solid polymers were produced (130). Reaction at a higher temperature gave a liquid containing paraffins, cycloparaffins, and unsaturated hydrocarbons. French turpentine was also treated for a long period of time with aluminum chloride at room temperature, resulting in the formation of a solid polymer (45). Finnish turpentine oil treated at room temperature yielded a mixture of paraffins, olefins, and cycloparaffins, similar in composition to petroleum. Methyl and ethyl chlorides were also formed (118). Sumatra turpentine, pentane being used as a diluent, polymerized to an oil and resin when subjected to the action of aluminum chloride at -15°C. (141).

VIII. BENZENE AND METHYLBENZENES

The reactions of benzene and individual methylbenzenes in the presence of aluminum chloride led to a variable mixture of benzene, methylbenzenes, ethylbenzenes, cycloparaffins, phenylated cycloparaffins, diphenyls, ethylanthracene, and unsaturated compounds. Hydrogen chloride, methyl chloride, and hydrocarbon gases were formed also in some instances. Benzene reacting alone gave alkylated benzenes. The latter, as initial hydrocarbons, reacted to give benzene, lower and higher alkylated benzenes, or diaryl compounds.

Mono- and di-methylbenzene, ethylbenzene, diphenyl, and unsaturated hydrocarbons resulted when benzene was heated above 100°C. with aluminum chloride, as shown in table 9. The formation of these products may be shown by the following equations:



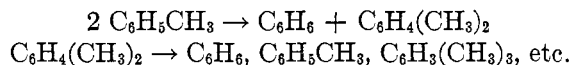
The product, ethylbenzene, arose from the breaking of the benzene ring into two-carbon atom fragments. These two-carbon atom fragments either hydrogenated to an ethyl radical and united with a phenyl radical, or formed an ethylene molecule, which added benzene after scission of a carbon-hydrogen bond in the benzene. Under more strenuous experimental conditions, methyl groups were introduced into the ring. It is probable that the ethyl group splits into methyl and methylene radicals.

The compounds 1-methyl-3-phenylcyclopentane and diphenylcyclohexane were obtained from benzene in the presence of hydrogen chloride and aluminum chloride (65). The two latter hydrocarbons reacted with benzene to give phenylated cycloparaffins. Phenylcyclohexane and *o*-diphenylcyclohexane as well as diphenyl were present when benzene was kept for three weeks in contact with aluminum bromide (147). These experiments give support to the suggestion that benzene is hydrogenated by the hydrogen produced during the formation of diphenyl. From this mechanism one would expect to find diphenyl as one of the principal reaction products, although actually only small quantities have been reported.

When benzene is heated in the absence of aluminum chloride, diphenyl is the principal product. Alkylated benzenes do not form. In the thermal reactions of benzene, therefore, the carbon-carbon bond (135) in the ring shows great strength, and the principal scission occurs at the carbon-hydrogen linkage. In the presence of aluminum chloride, diphenyl is obtained in smaller amounts than the alkylated benzenes; therefore the carbon-hydrogen bond appears stronger than the carbon-carbon bond, unless, as seems to be the case, alkylation occurs as the result of a preliminary hydrogenation of benzene to cyclohexane, which in turn is dissociated into two-carbon atom fragments.

Phenol and anthracene have been reported frequently as end products in the reaction of benzene in the presence of aluminum chloride. Further, the odor of benzaldehyde was noted, and it was believed that the formation of anthracene resulted from the condensation of two molecules of benzaldehyde. Phenol and its alkyl derivatives have been omitted as products throughout this paper, owing to contamination of the reactants with oxygen.

When the reaction of methylbenzenes with aluminum chloride was carried out at a temperature near the boiling point of the particular compound, the products were either benzene or methylated benzenes. The reactions are given as follows:



These products show that there is a striking difference in the behavior of the benzene ring as one or more methyl groups are attached to it. The point of greatest weakness in the methylbenzenes is the carbon-carbon bond between the ring and side chain. This is another instance where the strength of the bond appears to depend on the side chains.

When toluene was subjected to the aluminum chloride reaction, the principal products were benzene and xylene. It has been reported that higher methylated benzenes are formed (93) and that using a sufficiently

high temperature (47) causes a break in the ring and the formation of ethylated products. When aluminum chloride was not present, benzene was the principal product in the thermal reactions of toluene, while lesser amounts of diphenyl and ditolyl were formed. Apparently, the same relationships in the bond strengths hold, since the higher temperature necessary for the thermal reaction causes the methyl group to pass off in the form of methane or ethane rather than to add to another molecule of toluene.

Upon reaction with aluminum chloride *m*-xylene gave toluene, benzene, and small amounts of tri- and tetra-methylbenzenes. The formation of methyl chloride has also been recorded when 16.7 per cent of aluminum chloride was used (87). When methyl chloride is passed into the reaction mixture (127), only tri- and tetra-methylbenzenes are obtained. The small amounts of the higher methylated benzenes obtained by the other investigators are linked with the loss of the methyl group in the form of methyl chloride. Higher methylated benzenes (3, 4, 66) were obtained at lower temperatures. A detailed study (43) of the concentration of aluminum chloride shows that, in general, the effect of time and the temperature of the reaction seems to overbalance the effect of the concentration of the aluminum chloride. When hydrogen chloride was present in the reaction mixture rather than from its production during the reaction, the tendency for the formation of more highly methylated benzenes was increased.

The tri-, tetra- and penta-methylbenzenes show a greater tendency to form lower, rather than higher, methylated benzenes. This is closely related to the temperature of the reaction, the loss of methyl chloride, and the concentration of the aluminum chloride. The data available are not sufficient to distinguish between these effects.

IX. HIGHER ALKYLATED BENZENES

The more highly alkylated benzenes in the presence of aluminum chloride react in the same manner as the methylbenzenes with the difference that propane and isobutane form, depending upon the starting hydrocarbon; that is, the primary scission occurs at the carbon-carbon bond between the ring and the side chain provided that the reaction temperature is not above the boiling point of the alkylated benzene (see table 10). The alkyl group either hydrogenates to give the corresponding paraffin or adds to one of the original alkylated benzenes. The products obtained by experimenters do not show clearly the source of the hydrogen which hydrogenated the alkyl radical; however, formation of the alkylated diaryl compounds would be one source, had they been found when the gaseous paraffin was formed.

TABLE 10
Reactions of higher alkylated benzenes

COMPOUNDS	TEMPERATURE °C.	TIME hours	CONCENTRATION OF AlCl ₃ per cent	PRODUCTS		REFERENCES
				Gases	Liquids and solids	
C ₈ H ₅ C ₂ H ₅	137		23		Benzene; <i>p</i> - and <i>m</i> -diethylbenzenes (large amount)	(34)
C ₈ H ₅ C ₂ H ₅ + HCl.....	136	2			Benzene, 28 per cent; <i>p</i> - and <i>m</i> -diethylbenzenes, 24 per cent; triethylbenzenes, 8 per cent; no xylenes; tar, 5 per cent	(66)
C ₈ H ₅ C ₂ H ₅ + HCl.....	100	10			Benzene, 30 per cent; <i>p</i> - and <i>m</i> -diethylbenzenes, 38 per cent; triethylbenzenes, 3 per cent; tar, 2 per cent	(66)
C ₆ H ₅ (<i>n</i> -C ₃ H ₇) + HCl.....	100	6	16.7		Benzene, 26 per cent; dipropylbenzenes, 36 per cent; no toluene or xylenes; tar, 2 per cent	(45, 66)
C ₆ H ₅ (<i>iso</i> -C ₃ H ₇).....	100	4	16.7	Propane	Benzene, 34 per cent; <i>m</i> - and <i>p</i> -diisopropylbenzenes, 20 per cent; no toluene or xylenes; tar, 10 per cent	(66)
C ₆ H ₅ (<i>iso</i> -C ₃ H ₇).....	50	6	16.7	Propane (less than at 100°C.)	Benzene, 10 per cent; diisopropylbenzenes, 35 per cent; no toluene or xylenes; tar, 1 per cent	(66)
C ₆ H ₅ (<i>iso</i> -C ₃ H ₇).....	154	24	10		Benzene, 15 per cent; toluene, 2.7 per cent; xylene, 26.5 per cent	(101)
C ₆ H ₅ (<i>n</i> -C ₄ H ₉).....	100	5	16.7	No gases	Benzene, 18 per cent; <i>m</i> - and <i>p</i> -dibutylbenzenes, 38 per cent	(66)
C ₆ H ₅ (<i>sec</i> -C ₄ H ₉).....	140-150	7	20	Gas	Liquid (b.p. 120-210°C.)	(132)
C ₆ H ₅ (<i>tert</i> -C ₄ H ₉) + HCl.....	80	3	27	Isobutane (42 per cent of theoretical)	Benzene; higher boiling residue	(84)

$C_6H_4(CH_3)(iso-C_3H_7) + HCl$	175		25	Propane	Complex compound $2AlCl_3 \cdot 3C_{10}H_{14}$	(56)
$p-C_6H_4(CH_2)(iso-C_3H_7)$	175	24	10		Toluene; tar (large amount)	(4)
$p-C_6H_4(CH_2)(iso-C_3H_7)$					Toluene, 14.3 per cent; benzene, 0.8 per cent; xylene, 7 per cent	(101)
$p-C_6H_4(CH_2)(iso-C_3H_7)$	125-150	2.5-3.0	20	Propane	Benzene; toluene (small amount)	(124)
$p-C_6H_4(CH_2)(iso-C_3H_7)$	60-98	32-8	20		Benzene; toluene; <i>m</i> -xylene; 1-methyl-3,5-diisopropylbenzene; 2,3-dimethylbutane	(124)
$p-C_6H_4(CH_2)(iso-C_3H_7)$	20-35	4	50		Benzene; toluene; xylene; 1-methyl-3,5-diisopropylbenzene; high-boiling residue	(92)
$p-C_6H_4(CH_2)(tert-C_4H_9)$	20-35	10	50	Isobutane	Toluene; dibutyltoluene; tributyltoluene	(92)
$C_6H_3(C_2H_5)_2 + HCl$	-10				Yellow crystals of $2AlCl_3 \cdot 2C_6H_3(C_2H_5)_2$	(62, 63)
$p-C_6H_4(n-C_3H_7)_2$	100	2			HCl	(9)
$p-C_6H_4(n-C_3H_7)_2$	100	22	33.3		<i>m</i> -Di- <i>n</i> -propylbenzene, 66.7 per cent; <i>n</i> -propylbenzene; 1,3,5-tripropylbenzene	(9)
$m-C_6H_4(n-C_3H_7)_2$	100	22	33.3		<i>m</i> -Dipropylbenzene, 15.7 per cent; <i>n</i> -propylbenzene, 11.3 per cent	(9)
$1,2,4-C_6H_3(C_3H_7)_3$	100	4			<i>m</i> -Di- <i>n</i> -propylbenzene, largely; <i>p</i> -di- <i>n</i> -propylbenzene, small amount	(9)
					<i>m</i> -Dipropylbenzene, 30 per cent; 1,3,5-tripropylbenzene, 28 per cent; tetrapropylbenzene, 12 per cent	(9)

Ethylbenzene gave benzene and diethylbenzene (3, 4). In the presence of hydrogen chloride, benzene and di- and tri-ethylbenzenes were formed (66), depending on the time and the temperature of the reaction. Xylenes were not formed in these experiments, showing that the ethyl radical was not dissociated. *n*-Propyl- and isopropyl-benzenes gave di-*n*-propylbenzene and diisopropylbenzene, respectively, together with propane and benzene. In the experiments (66) on isopropylbenzene the effect of temperature was shown; at lower temperatures less propane was produced and more diisopropylbenzene formed. At higher temperatures toluene and xylene were obtained, probably resulting from the decomposition of propane or from rupture within the side chain (101).

It was demonstrated that *p*-di-*n*-propylbenzene is rapidly transformed into the meta form at 100°C., while producing some *n*-propylbenzene and ethylbenzenes. The compounds *m*-dipropylbenzene, 1,3,5-tripropylbenzene, and tetrapropylbenzene were formed from 1,2,4-tripropylbenzene.

In the work on butylbenzene (66, 132), butane, benzene, and dibutylbenzene were produced, depending on the temperature of the reaction and the concentration of aluminum chloride.

p-Methylisopropylbenzene and *p*-methyl-tertiary-butylbenzene have two different alkyl groups attached to the same ring, and the end products show that the size of the alkyl group has an effect on the nature of the reaction products. At high temperatures and high concentrations of aluminum chloride, propane, benzene, and toluene were obtained from *p*-methylisopropylbenzene, while a lower temperature and concentration of aluminum chloride did not produce propane, but xylene, diisopropylbenzene, and 1-methyl-3,5-diisopropylbenzene were formed. Experiments show that high concentrations of aluminum chloride strip the alkyl groups from the benzene ring, that high temperatures yield toluene, and that low concentrations of aluminum chloride and low temperatures give alkylated benzenes. Similarly, *p*-methyl-tertiary-butylbenzene gave toluene, methyl-di-tertiary-butylbenzene, and methyltri-tertiary-butylbenzene. The experiments indicate that isopropyl and tertiary-butyl groups are the first to split from the ring, and that the larger the alkyl group the more readily it breaks off.

X. POLYCYCLIC AROMATIC HYDROCARBONS

The data from the experimental work on the reactions of the polycyclic compounds in the presence of aluminum chloride do not lend themselves readily to a study of the mechanism of the reactions. The products formed are more difficult to identify than those from the single ring compounds; consequently accurate, complete, and detailed analyses of the products

have not been obtained in all experiments. Further, these compounds have higher boiling points, which permits a wider range for the reaction temperature and, accordingly, more opportunity for combinations or rearrangements into a larger number of compounds. For polycyclic aromatic compounds, reaction has been effected by either a low temperature and a high concentration of aluminum chloride or the reverse. In general, with these compounds four types of reaction occur: (1) the formation of hydrides of the original compound; (2) the scission of one carbon-hydrogen bond in the original compound and the coupling of the resulting radicals; (3) the breaking-off of one ring giving lower and higher homologues and methylated derivatives; and (4) cyclization by ring closure upon active double bonds. As shown in table 11, naphthalene forms the hydrides of naphthalene, dinaphthyls, tetranaphthyl, methylnaphthalenes, and benzene. Naphthalene and dinaphthyl have been reported to yield perylene. The hydronaphthalenes have lower reaction temperatures than naphthalene, but the same type of reaction products was obtained. This shows that the aromatic ring is more stable than the hydrogenated or partially hydrogenated ring (cycloparaffin or cycloolefin ring).

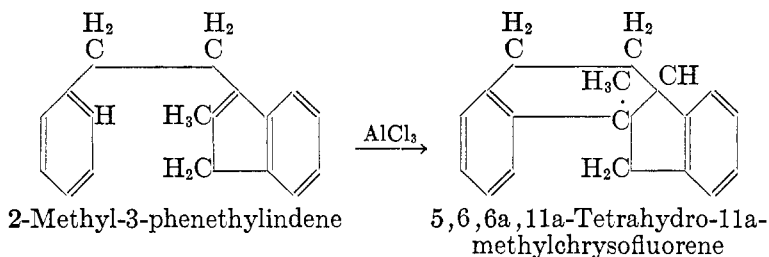
It was reported that benzene, octahydroanthracene, and octahydrophenanthrene resulted from the action of aluminum chloride on tetralin (91) at 100°C. in accordance with the reaction:



Hydroanthracenes, naphthalene, hydronaphthalene, and methylnaphthalenes have been obtained from anthracene and phenanthrene.

The products from phenylated methanes and ethanes were benzene, dibenzylbenzene, anthracene, and dimethylantracene.

The treatment of 2-methyl-3-phenylethylindene in carbon disulfide solution with aluminum chloride yielded 5,6,6a,11a-tetrahydro-11a-methylchrysofluorene (33), as shown in the equation:



It has been found also that under similar conditions 1,2,3,4-tetrahydro-5-(β -(2-methyl-3-indenyl)ethyl)naphthalene forms 1,2,3,4,5,6,6a,11a-

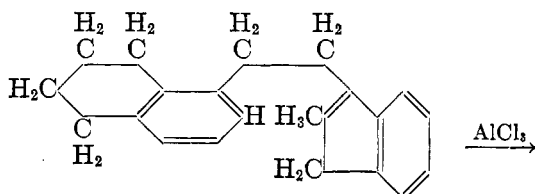
TABLE II
Reactions of polycyclic aromatic compounds

COMPOUNDS	TEMPERATURE °C.	TIME hours	CONCENTRATION OF AlCl ₃ per cent	PRODUCTS		REFER- ENCES
				Gases	Liquids and solids	
Naphthalene.....	100-160	Several	Excess		Benzene; naphthalene hydrides	(46)
Naphthalene.....	100-160	Several	20		Isodinaphthyl; oil	(46)
Naphthalene.....	100-160	Several	25		β, β' -Dinaphthyl; hydrodinaphthyls	(46)
Naphthalene.....	100	0.5-6.0	50		Tetramethylnaphthalene; C ₄₀ H ₂₈ (tetranaphthyl); C ₃₆ H ₂₂ ; tetramethyldinaphthantracene, C ₃₈ H ₂₂	(69)
Naphthalene.....	180	1	80		Perylene	(123)
Tetralin.....	100				Benzene; octracene; octanthrene	(91)
Tetralin.....	30-40		1.0-1.5		Octanthrene; octracene	(125)
Tetralin.....	50-70	10	2		Benzene; octanthrene; octracene; C ₁₄ H ₆ ; 1-phenyl-4(2-tetralyl)butane; 2,2'-naphthyl, 2,6'-ditetralyl	(125)
Tetralin.....	70-80	3	4		Octanthrene; dodecahydrotriphenylene; phenylene-bis- and tetralyloctanthrenylbutane	(125)
Dinaphthyl.....	140	1	80		Perylene	(123)
Hydrodinaphthyl.....					Hydonaphthyls	(46)
Anthracene.....	340		3		Carbon; hydroanthracenes; hydronaphthalenes; methylnaphthalene	(108)
Phenanthrene.....	340		4.7	HCl + hydrocarbon gas	Naphthalene; homologs of naphthalene; brown oil	(108)
Phenanthrene + CS ₂	100				Powder (believed (C ₁₄ H ₁₀) _n)	(121)
Diphenylmethane.....					Anthracene; benzene	(114)
Diphenylmethane.....	Room	17	66		Oil; benzene; <i>o</i> - and <i>p</i> -dibenzylbenzenes; solid	(122)

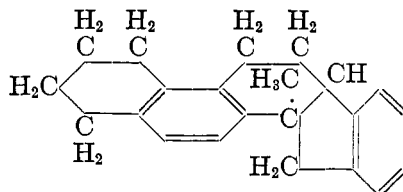
	85	17	66	HCl	Same products as at room temperature meso-Dimethylanthracene Trimer of (C ₁₄ H ₁₂)	(122) (114) (121)
Diphenylmethane.....						
as-Diphenylethane.....	100	8	63.7			
Stilbene + CS ₂						
as-Diphenylethylene + benzene.....	100	24 12	11.9 43*		1, 1, 3-Triphenyl-3-methylindan, 60 per cent <i>trans</i> -Hydrindan	(15) (155)
<i>cis</i> -Hydrindan.....						
2-Methyl-3-phenethylindene + CS ₂	0	3	7.7		5, 6, 6a, 11a-Tetrahydro-11a-methylchryso- fluorene, 82 per cent	(33)
1, 2, 3, 4-Tetrahydro-5-(β-(2- methyl-3-indenyl)ethyl)- naphthalene + CS ₂	0	3	8.33		1, 2, 3, 4, 5, 6, 6a, 11a-Octahydro-11a-methyl- naphtho-(2, 1-a)fluorene, 80 per cent	(33)
7-Isopropyl-4-methyl-3-(β-1- naphthylethyl)naphthalene + CS ₂	0	4			2, 3-Dihydro-4'-isopropyl-7'-methylspiro- (benzophenanthene-1, 1'-indan)	(33)
1, 2, 3, 4-Tetrahydro-5-(β-(7- isopropyl-2, 4-dimethyl-3- indenyl)ethyl)naphthalene + CS ₂	0	3			1, 2, 3, 4, 5, 6, 6a, 11a-Octahydro-10-isopropyl- 7, 11a-dimethylnaphtho(2, 1-a)fluorene, 75 per cent	(33)
2-Methyl-1-phenethyl-3-α- naphthindene + CS ₂	0	4	7		5, 6, 6a, 13a-Tetrahydro-13a-methyldibenzo- (ag)fluorene, 60 per cent	(28)

 * AIBr₃ used.

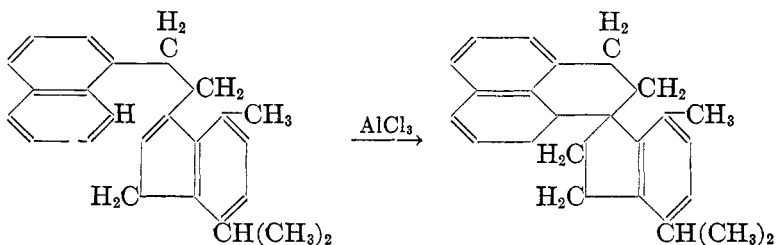
octahydro-11a-methylnaphtho(2,1-a)fluorene, whereas 7-isopropyl-4-methyl-3-(β -1-naphthylethyl)indene forms 2,3-dihydro-4'-isopropyl-7'-methylspiro(benzonaphthene-1,1'-indan), and that 1,2,3,4-tetrahydro-5-(β -(7-isopropyl-2,4-dimethyl-3-indenyl)ethyl)naphthalene forms 1,2,3,4,5,6,6a,11a-octahydro-10-isopropyl-7,11a-dimethylnaphtho(2,1-a)-fluorene, as follows (33):



1,2,3,4-Tetrahydro-5-(β -(2-methyl-3-indenyl)ethyl)naphthalene; i.e., 3-(β -5'-tetrahyloethyl-2-methylindene

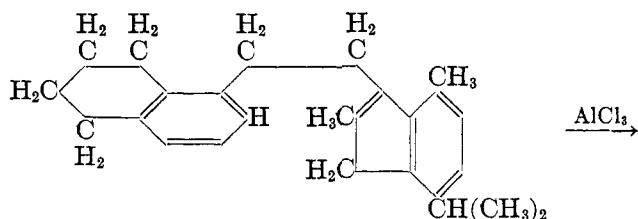


1,2,3,4,5,6a,11a-Octahydro-11a-methylnaphtho(2,1-a)fluorene; i.e., 10-methyl-3,4,10,11,5',6',7',8'-octahydro-2',1'-naphtha-1,2-fluorene

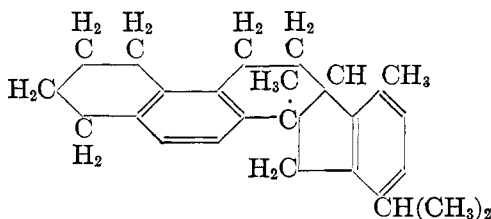


7-Isopropyl-4-methyl-3-(β -1-naphthylethyl)indene

2,3-Dihydro-4'-isopropyl-7'-methylspiro(benzonaphthene-1,1'-indan); i.e., 7-methyl-4-isopropylhydrindene-1,7'-spiro-7',8'-dihydrophenalene

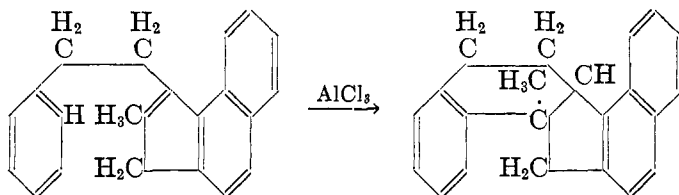


1,2,3,4-Tetrahydro-5-(β -(7-isopropyl-2,4-dimethyl-3-indenyl)ethyl)naphthalene; i.e., 3-(β -5'-tetralylethyl)-2,4-dimethyl-7-isopropylindene



1,2,3,4,5,6,6a,11a-Octahydro-10-isopropyl-7,11a-dimethylnaphtho(2,1-a)fluorene; i.e., 5,10-dimethyl-8-isopropyl-3,4,10,11,5',6',7',8'-octahydro-2',1'-naphtha-1,2-fluorene

The compound 2-methyl-1-phenethyl-3- α -naphthindene was treated in carbon disulfide solution with aluminum chloride, giving 5,6,6a,13a-tetrahydro-13a-methyldibenzo(ag)fluorene, as follows:



2-Methyl-1-phenethyl-3- α -naphthindene; i.e., 3- β -phenylethyl-2-methyl-4,5-benzindene

5,6,6a,13a-Tetrahydro-13a-methyldibenzo(ag)fluorene; i.e., methyltetrahydro-1,2,5,6-dibenzfluorene

The foregoing five cyclizations are in accordance with the principle of ring closure discussed previously under cycloölefins.

XI. AROMATICS WITH OTHER HYDROCARBONS

In addition to the reactions which individual aromatics undergo with aluminum chloride, there are others in which the aromatics react with paraffins, olefins, acetylene, cycloparaffins, cycloölefins, and other aro-

atics, as shown in tables 12 to 17, inclusive. The reactions of aromatics with other hydrocarbons lead to benzene, alkylated and condensed aromatics, arylated paraffins, olefins and cycloparaffins, cycloparaffinic aromatics, and paraffins. The gases formed are propane and butanes.

Because analyses of products were incomplete in many instances, the problem of isomerization has not been dealt with extensively. Many investigators have been satisfied to identify the presence of xylenes, the trimethylbenzenes, etc., without determining the particular isomers; still others merely determined the presence but not the amounts of the differ-

TABLE 12
Reactions of aromatics with paraffins

COMPOUNDS (a)	ADDITIONAL COMPOUNDS (b) (c)	TEMPERATURE		CONCENTRATION OF $AlCl_3$	RATIO a: b: c	PRODUCTS	REFERENCES
		$^{\circ}C.$	hours				
C_6H_6	iso- C_5H_{12} + HCl	125	23	10	1:1	Propane, 15 per cent; alkylated benzenes, 25 per cent	(80)
C_6H_6	C_6H_{14} + HCl	100	17	10	1:1	Butane, 30 per cent; paraffins below hex- ane, 15 per cent; al- kylated benzenes, 30 per cent (b.p. 90- 200 $^{\circ}C.$)	(80)
C_6H_6	2,2,4-(CH_3) $_3C_6H_9$ + HCl	25-40	4	5.7	1:0.86	Isobutane; traces of propane and pentane; mono- and di-terti- ary-butylbenzenes; traces of unsaturated compounds	(53)

ent isomers. However, a few observations appear to be sufficiently pronounced to be pointed out. The meta form appears to be the predominant disubstituted form, and the 1,3,5, the trisubstituted form. The latter would follow from the preference for the meta form. It was found that the *o*- and *p*-xylenes gave the meta form, while *m*-xylene was obtained from the 1,2,4- and 1,3,5-trimethylbenzenes (87), and *m*-diethylbenzene was produced from ethylbenzene (3, 4). When substituents differ by more than one methylene group, the above tendencies may not hold. For example, it was found that the above isomerization rules hold for benzene and propene, but not for toluene and propene (16).

TABLE 13
Reactions of aromatics with olefins

COMPOUNDS (a)	ADDITIONAL COMPOUNDS (b) (c)	TEMPERATURE °C.	TIME	CONCENTRATION OF $AlCl_3$	RATIO a:b:c	PRODUCTS	REFERENCES
C_6H_6	C_2H_4	70-90	hours	per cent	1:7	Mono-, di-, and tri-ethylbenzenes	(10)
C_6H_6	C_2H_4	100	Several days	6*		Mesitylene	(49)
C_6H_6	C_2H_4	70-90	3-4	55*		Mono- to hexa-ethylated benzenes	(99)
C_6H_6	$C_2H_4 + HCl$	70-90	6	16	1:1	Monoethylbenzene (preferred)	(16)
C_6H_6	$C_2H_4 + HCl$	70-90	11	7	1:3	Triethylbenzene (preferred)	(16)
C_6H_6	$C_2H_4 + HCl$	70-75	12-14	11		Di-, tri-, and tetra-ethylbenzenes	(102)
$C_6H_6CH_3$	$C_2H_4 + HCl$	70-90	1.3	7		Ethylbenzene; ethyltoluene; higher products	(16)
$C_6H_6CH_3$	C_2H_4					<i>sym</i> -Diethyltoluene	(49)
$C_6H_6(CH_3)_2$	C_2H_4		1.5	5*		<i>sym</i> -Ethyltoluene	(49)
$C_{10}H_8$ (naphthalene).....	C_2H_4	240	80-85	5.3*		Mono- and di-ethylnaphthalenes	(150)
C_6H_6	$C_3H_6 + HCl$	70	12	7		Mono- to hexa-isopropylated benzenes	(16)
$C_6H_6CH_3$	$C_3H_6 + HCl$	70-90	1.3	7		<i>p</i> -Cymene; benzene; toluene; xylene; triethylbenzene; <i>m</i> -cymene (small)	(16)
$C_{10}H_8$ (naphthalene).....	$C_3H_6 + C_7H_{14}$ (hexahydro-toluene)	80		1.3	1:1.2	Diisopropylnaphthalene; less mono- and tetra-isopropylbenzenes	(74)
$C_{10}H_8$	$C_4H_8 + C_6H_{12}$ (hexahydro-benzene)	20		0.8	1:1.8:8	Tetrabutyl-naphthalene	(74)
$C_6H_6CH_3$	C_4H_{10}	25-30		3.3	2:5	Amyltoluene	(42)

* Calculated with C_2H_4 .

TABLE 14
Reactions of aromatics with acetylene

COMPOUNDS (a)	ADDITIONAL COMPOUNDS (b) (c)	TEMPERATURE	TIME	CONCENTRATION OF AlCl_3	RATIO a:b:c	PRODUCTS	REFERENCES
C_6H_6	C_2H_2	$^{\circ}\text{C}$.	hours	per cent	16:1	Diphenylalkanes; polymers	(21)
C_6H_6	C_2H_2	20	5	10	10:1	Styrene, 80 per cent; <i>as</i> -diphenylethane, 15 per cent; diphenyl, 5 per cent	(139)
C_6H_6	C_2H_2	Room	50	20*		Ethylbenzene; diphenyl; styrene	(109)
C_6H_6	C_2H_2	Room	Several days				
C_6H_6	C_2H_2	70-80	3	18		<i>as</i> -Diphenylethane; 9,10-dimethylanthracene hydride	(27)
$\text{C}_6\text{H}_5\text{CH}_3$	C_2H_2	70-80	3	18		Xylene; mesitylene; pseudocumene; <i>p</i> , <i>p'</i> -tolylethane; 2,7-dimethylanthracene; β -methylanthracene; 1,6-dimethylanthracene	(27)

* Calculated with C_2H_2 .

TABLE 15
Reactions of aromatics with cycloparaffins

COMPOUNDS	ADDITIONAL COMPOUNDS (b) (c)	TEMPERATURE	TIME	CONCENTRATION OF AlCl_3	PRODUCTS	REFERENCES
C_6H_6	Cyclopropane + HCl	$^{\circ}\text{C}$.	hours	per cent		
$\text{C}_6\text{H}_5(\text{iso-C}_3\text{H}_7)$	Cyclohexane + HCl	Room	3	11.9	Propylbenzene; hexapropylbenzene	(54)
$\text{C}_6\text{H}_5(\text{sec-C}_4\text{H}_9)$	Cyclohexane + HCl	80	3	11.4	Propane, 33 per cent; phenylcyclohexane; methylcyclopentane; benzene; <i>p</i> -diisopropylbenzene	(84)
$\text{C}_6\text{H}_5(\text{tert-C}_4\text{H}_9)$	Cyclohexane + HCl	70	1	11.4	<i>n</i> -Butane, 35 per cent	(84)
$\text{C}_6\text{H}_5(\text{tert-C}_6\text{H}_{11})$	Cyclohexane + HCl	65-82	2	15.5	Isobutane, 61 per cent	(84)
$\text{C}_6\text{H}_5(\text{iso-C}_3\text{H}_7)$	Decahydronaphthalene + HCl	80	3	13.3	Isopentane, 60 per cent	(84)
$\text{C}_6\text{H}_5(\text{sec-C}_4\text{H}_9)$	Decahydronaphthalene + HCl	80	3	12.8	Propane, 53 per cent	(84)
$\text{C}_6\text{H}_5(\text{tert-C}_4\text{H}_9)$	Decahydronaphthalene + HCl	60-78	1.25	12.8	<i>n</i> -Butane, 71 per cent	(84)
					Isobutane, 94 per cent; benzene; decahydronaphthylbenzene	(84)

TABLE 16
Reactions of aromatics with cycloolefins

COMPOUNDS (a)	ADDITIONAL COMPOUNDS (b) (c)	TEMPERATURE	TIME	CONCENTRATION OF $AlCl_3$	RATIO S:D:C	PRODUCTS	REFERENCES
C_6H_6	C_6H_{10} (cyclohexene)	Room	3 hours	per cent 10	4:1	Cyclohexylbenzene, 70 per cent; 1,2-diphenylcyclohexane	(18)
C_6H_6	C_6H_{10} + HCl	55	5	9	1:1	Cyclohexylbenzene; high-boiling residue	(16)
$C_6H_6CH_3$	C_6H_{10} + CS_2	Room	3	5-6	4:1	<i>o</i> - and <i>p</i> -Cyclohexyltoluenes, 63 per cent	(18)
m - $C_6H_4(CH_3)_2$	C_6H_{10} + CS_2	Room	3	5-6	4:1	5-Cyclohexyl-1,3-dimethylbenzene, 35 per cent	(18)
p - $C_6H_4(CH_3)_2$	C_6H_{10} + CS_2	Room	3	5-6	4:1	2-Cyclohexyl-1,4-dimethylbenzene, 45 per cent; 1,4-dicyclohexyldimethylbenzene (small)	(18)
sym - $C_6H_3(CH_3)_3$	C_6H_{10} + CS_2	Room	3	4.2	5:1:5	2-Cyclohexyl-1,3,5-trimethylbenzene	(18)
p - $C_6H_4(CH_3)(iso-C_3H_7)$	C_6H_{10} + CS_2	Room	3	3	6:1:6	Cyclohexylisopropyl-1-methyl-4-benzene, 40 per cent; dicyclohexylisopropyl-1-methyl-4-benzene	(18)
$C_{10}H_8$	C_6H_{10} + CS_2	Room	3	4.4	1:2:1	Cyclohexyl-naphthalene; dicyclohexyl-naphthalene	(18)
$C_{10}H_{12}$ (tetralin).....	C_6H_{10} + CS_2	Room	0.66	4.4	1:2:1	Cyclohexyltetralin	(18)
$(C_6H_5)_2CH_2$	C_6H_{10} + CS_2	Room	3	4.3	1:2:1	<i>p</i> -Cyclohexyldiphenylmethane; <i>p</i> -benzyl-diphenyl	(18)
C_6H_6	$C_6H_9CH_3$	Room	3	10	1:3:5	Dimethyldicyclohexylbenzene; methylcyclohexylbenzene	(18)
$(C_6H_5)_2CH_2$	$C_6H_9CH_3$ + CS_2	Room	3	4.3	1:0.4:1	<i>p</i> -Methylcyclohexyldiphenylmethane	(18)
C_6H_6	Menthene	Room	3	12	2:1	Menthylbenzene	(18)

TABLE 17
 Reactions of aromatics with aromatics

COMPOUNDS (a)	ADDITIONAL COMPOUNDS (b) (c)	TEMPERATURE °C.	TIME hours	CONCENTRATION OF $AlCl_3$ per cent	RATIO R.D.C	PRODUCTS	REFERENCES
<i>m</i> - or <i>p</i> - $C_6H_4(CH_3)_2$	C_6H_6	100	6	0.9-0.5	10:1	Toluene	(20)
$C_6H_4(C_2H_5)_2$	C_6H_6	100	6	2	10:1	Ethylbenzene; residue	(20)
$C_6H_4(C_2H_5)_2 + C_6H_5(C_2H_5)_2$	C_6H_6	150-200	6	2	8:1	Ethylbenzene; residue	(20)
$C_6H_5-n(iso-C_3H_7)_n$	C_6H_6	100	6	0.65	10:1	Isopropylbenzene; residue	(20)
$C_6H_5(tert-C_4H_9)$	$C_6H_5C_2H_5 + HCl$	80	3	30	1:1	Isobutane, 75 per cent; diphenyl-ethylbenzene; higher boiling residues	(85)
$C_6H_5(tert-C_4H_9)$	$C_6H_6 + HCl$	85	3	30	2:3	Isobutane, 61 per cent; higher boiling residues	(85)
$C_6H_5-n(tert-C_4H_9)_n$	C_6H_6	100	6	2	10:1	<i>tert</i> -Butylbenzene; residue	(20)
$C_6H_5-n(tert-C_6H_{11})_n$	C_6H_6	100	6	0.9	10:1	<i>tert</i> -Amylbenzene; residue	(20)
<i>p</i> -(C_6H_4)(CH_3)(<i>iso</i> - C_3H_7).....	C_6H_6	100	10-6	2.5-0.4	10:1-1.5	Toluene; isopropylbenzene; residue	(20)
$C_{14}H_{10}$ (phenanthrene).....	C_6H_6	80	1	14.5	1:0.14	2,3,10,11-Dibenzoperylene	(26)
$C_{10}H_8$	$C_6H_5C_2H_5$	80	5	5.0	1:1	Diethylbenzene; benzene; di-ethylnaphthalene; higher products	(99)
$C_{10}H_8$	$C_6H_4(iso-C_3H_7)_2 + HCl$	90	4.5		1:0.48	Isopropyl-naphthalene, 4.3 per cent; higher boiling products	(16)
$C_6H_5C\equiv CC_6H_5$	$C_6H_6 + HCl$	Room	6	0.9	1:123	<i>sym</i> -Tetraphenylethane, 64 per cent	(1)
$C_6H_5C\equiv CC_6H_5$	$C_6H_6 + HCl$	Room	20	8	1:103	Dibenzyl, 32 per cent	(1)
$C_6H_5CH=CHC_6H_5$	$C_6H_6 + HCl$	Room	54			Dibenzyl, 20 per cent	(2)

$C_6H_5CH=CHC_6H_5$	$C_6H_6 + HCl$	Room	8	1.4	1:31	1,1,2-Triphenylethane, 49 per cent	(1)
$C_6H_5CH=C(C_6H_5)_2$	$C_6H_6 + HCl$	Room	20	0.71	1:89	s-Tetraphenylethane, 70 per cent	(1)
$C_6H_5CH=C(C_6H_5)_2$	$C_6H_6 + HCl$	Room	3 days	12.3	1:82	Dibenzyl, 28 per cent	(1)
$(C_6H_5)_2C=C(C_6H_5)_2$	$C_6H_6 + HCl$	Room	3	4.55	1:85	Dibenzyl	(1)
$(C_6H_5)_2C=C(C_6H_5)_2$	C_6H_6	80	3			9,10-Diphenylphenanthrene, 25 per cent; diphenylmethane	(17)
$C_6H_5CH_2-CH(C_6H_5)_2$	$C_6H_6 + HCl$	Room				Dibenzyl, 57 per cent	(1)
$(C_6H_5)_2CH-CH(C_6H_5)_2$	$C_6H_6 + HCl$	Room				Dibenzyl, 54 per cent	(1)

TABLE 18
Aluminum chloride addition compounds

FORMULA OF COMPLEX	CHARACTERISTIC PROPERTIES		REFERENCES
	Color and physical state	Stability	
$\text{AlCl}_3 \cdot 2\text{C}_2\text{H}_2 \cdot 2\text{H}_2\text{O}$	Colorless crystals	Unstable	(67)
$\text{AlCl}_3 \cdot 3\text{C}_2\text{H}_4 \cdot \text{H}_2\text{O}$	Colorless crystals	Unstable	(67)
$2\text{AlCl}_3 \cdot \text{C}_3\text{H}_{16}$		Stable	(58, 60, 61, 62)
$2\text{AlCl}_3 \cdot \text{C}_8\text{H}_{16} \cdot 6\text{C}_6\text{H}_6$		Unstable	(60, 61)
$\text{AlCl}_3 \cdot 3\text{C}_6\text{H}_6$	Fuming liquid	Very unstable	(55, 59)
$\text{AlCl}_3 \cdot 3\text{C}_6\text{H}_5\text{CH}_3$	Fuming liquid	Very unstable	(55, 59, 60)
$2\text{AlCl}_3 \cdot \text{C}_6\text{H}_4(\text{CH}_3)_2$		Stable	(60)
$2\text{AlCl}_3 \cdot \text{C}_6\text{H}_4(\text{CH}_3)_2 \cdot 6\text{C}_6\text{H}_6$		Stable	(60)
$2\text{AlCl}_3 \cdot \text{C}_6\text{H}_4(\text{CH}_3)_2 \cdot 5\text{C}_6\text{H}_5\text{CH}_3$		Stable	(60)
$2\text{AlCl}_3 \cdot 5\text{C}_6\text{H}_4(\text{CH}_3)_2$		Stable	(60)
$2\text{AlCl}_3 \cdot \text{C}_6\text{H}_4(\text{CH}_3)_2 \cdot 3\text{C}_6\text{H}_3(\text{CH}_3)_3$		Stable	(60)
$2\text{AlCl}_3 \cdot 3\text{C}_6\text{H}_4(\text{CH}_3)(\text{CHMe}_2)_2$	Heavy liquid		(56)
$2\text{AlCl}_3 \cdot \text{C}_6\text{H}_3(\text{C}_2\text{H}_5)_3$	Liquid		(60, 61, 62)
$2\text{AlCl}_3 \cdot \text{C}_6\text{H}_3(\text{C}_2\text{H}_5)_3 \cdot \text{C}_6\text{H}_6$			(63)
$2\text{AlCl}_3 \cdot \text{C}_6\text{H}_3(\text{C}_2\text{H}_5)_3 \cdot 6\text{C}_6\text{H}_6$			(60, 61)
$2\text{AlCl}_3 \cdot \text{C}_6\text{H}_3(\text{C}_2\text{H}_5)_3 \cdot 5\text{C}_6\text{H}_5\text{CH}_3$			(60, 61)
$2\text{AlCl}_3 \cdot \text{C}_6\text{H}_3(\text{C}_2\text{H}_5)_3 \cdot 4\text{C}_6\text{H}_4(\text{CH}_3)_2$			(61)
$2\text{AlCl}_3 \cdot \text{C}_6\text{H}_3(\text{C}_2\text{H}_5)_3 \cdot 4\text{C}_6\text{H}_5\text{C}_3\text{H}_6$			(60)
$2\text{AlCl}_3 \cdot \text{C}_6\text{H}_3(\text{C}_2\text{H}_5)_3 \cdot 3\text{C}_6\text{H}_3(\text{CH}_3)_3$			(60, 61)
$2\text{AlCl}_3 \cdot \text{C}_6\text{H}_3(\text{C}_2\text{H}_5)_3 \cdot 3\text{C}_6\text{H}_5\text{C}_3\text{H}_7$			(60)
$2\text{AlCl}_3 \cdot \text{C}_6\text{H}_3(\text{C}_2\text{H}_5)_3 \cdot \text{C}_6\text{H}_3(\text{CHMe}_2)_3 \cdot \text{HCl}$	Yellow crystals	Unstable	(63)
$\text{AlCl}_3 \cdot \text{C}_6\text{H}_3(\text{C}_2\text{H}_5)_3$	Yellow crystals	Unstable	(60, 61)
$2\text{AlCl}_3 \cdot 2\text{C}_6\text{H}_3(\text{C}_2\text{H}_5)_3 \cdot \text{HCl}$			(62, 63)
$2\text{AlCl}_3 \cdot \text{C}_6\text{H}_3(\text{C}_2\text{H}_5)_3 \cdot 3\text{C}_6\text{H}_2(\text{C}_2\text{H}_5)_4$			(60)
$2\text{AlCl}_3 \cdot \text{C}_6\text{H}_3(\text{CHMe}_2)_3$			(62, 63)
$2\text{AlCl}_3 \cdot \text{C}_6\text{H}_3(\text{CHMe}_2)_3 \cdot \text{C}_6\text{H}_6$	Green liquid	Unstable	(62, 63)
$2\text{AlCl}_3 \cdot \text{C}_6\text{H}_3(\text{CHMe}_2)_3 \cdot 6\text{C}_6\text{H}_6$	Liquid		(62, 63)
$2\text{AlCl}_3 \cdot 2\text{C}_6\text{H}_3(\text{CHMe}_2)_3 \cdot \text{HCl}$	Yellow crystals	Unstable	(62, 63)
$2\text{AlCl}_3 \cdot 2\text{C}_6\text{H}_3(\text{CMe}_2)_3 \cdot \text{HCl}$	Yellow crystals	Unstable	(62)
$2\text{AlBr}_3 \cdot \text{C}_6(\text{C}_2\text{H}_5)_6$	Colorless crystals		(83)

Toluene and ethylbenzene did not undergo reactions similar to those just given, indicating stability of the bond between phenyl and both methyl and ethyl groups.

When benzene and cyclohexene reacted in the presence of aluminum chloride and carbon disulfide, it was indicated that the cyclohexyl radical formed added to the benzene ring; when several groups were present, the 1,3,5-position was the preferred one (18, 19). The carbon disulfide used as solvent did not appear to change the nature of the reaction. The phenylmethanes with cyclohexene formed the cyclohexylphenylmethanes. Menthene and benzene formed menthylbenzene.

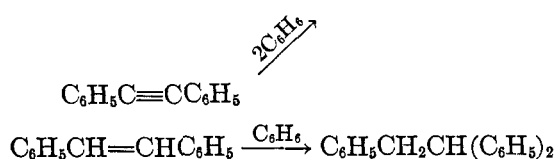
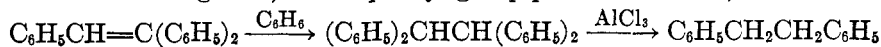
TABLE 19
Hydrocarbon group reactions with aluminum chloride

	PARAF- FINS	OLEFINS	ACETYL- ENES	CYCLO- PARAF- FINS	CYCLO- OLEFINS	TER- PENES	ARO- MATIC
A. Reactions:							
1. Dissociation.....	+	+	-	+	-	+	+
2. Dehydrogenation.....	-	+	-	+	+	+	+
3. Alkylation.....	+	+	+	+	-	-	+
4. Isomerization.....	+	+	-	+	+	-	+
5. Cyclization.....	-	+	+	-	+	-	+
6. Polymerization.....	-	+	+	-	+	+	+
7. Hydrogenation.....	-	+	-	-	+	+	+
8. Addition compounds with AlCl ₃	-	+	+	-	-	-	+
B. Products formed:							
1. Paraffins.....							
2a. Butanes.....	+	+	-	+	-	-	+
b. Higher and lower.....	+	+	-	+	-	+	+
3. Olefins (unsaturates).....	+	+	+	+	-	+	+
4. Cycloparaffins.....	+	+	-	+	+	+	+
5. Aromatics.....	-	+	-	+	+	+	+
6. Carbon.....	+	+	-	-	-	-	+
7. Liquids of unknown constitu- tion.....	+	+	+	+	-	+	+
8. Chlorinated compounds.....	+	+	-	+	-	+	+

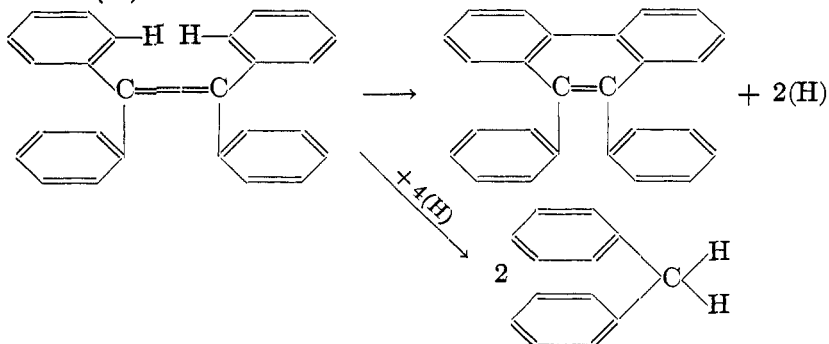
Alkylated benzenes in the presence of benzene redistributed the alkyl groups so that only one alkyl group remained on each benzene ring. From this, it appears that monosubstituted benzene is the most stable. In all redistributions of ethyl groups, it is interesting to note that the ethyl group did not change to a higher or lower alkyl radical. Ethylbenzene was found to act as hydrogen donor in the scission of tertiary-butylbenzene (85). It has been suggested (84) that important applications of similar hydrogen donor reactions are to be found in determining the structure of

alkyl groups attached to an aromatic nucleus, and the relative stability of bonds in hydrocarbons.

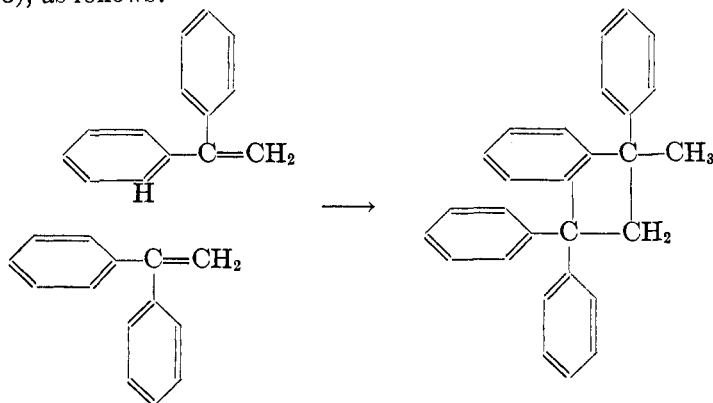
Polyarylated acetylenes, ethylenes, and ethanes formed dibenzyl, as a result of the action of benzene and aluminum chloride. This indicates a redistribution of phenyl groups so that two phenyls remain on each two-carbon atom fragment, or one phenyl group per carbon atom, as follows:



Tetraphenylethylene upon refluxing with benzene and aluminum chloride dehydrogenated to form 9,10-diphenylphenanthrene and diphenylmethane (17):



The compound *as*-diphenylethylene upon prolonged contact with aluminum chloride in the presence of benzene polymerized to a saturated dimer, to which was ascribed the structure of 1,1,3-triphenyl-3-methylindan (15), as follows:



It was thought desirable to tabulate, as far as possible, the reactions which occur to the greatest extent in the case of the hydrocarbon groups studied. The plus signs in table 19 indicate that the hydrocarbons dissociate, dehydrogenate, hydrogenate, isomerize, cyclize, polymerize, alkylate, and form addition compounds, or undergo a combination of some of these reactions. The detailed data are given in the preceding tables.

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