LIQUID-PHASE ALKYLATION OF AROMATIC HYDROCARBONS[1]

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Results of the liquid-phase alkylation of aromatic hydrocarbons are affected profoundly by solvent extraction of the early reaction products in the catalyst layer. This accounts for some anomalous observations, such as premature formation of polyalkylbenzenes. Appropriate adjustments of physical conditions greatly increase the yields of monoalkylbenzenes. The alkylation is extremely rapid, perhaps even instantaneous; but delays are usually inherent in providing adequate contact among the two reagents and catalyst.

The alkylation reactions are not reversible because the equilibria are too far on the side of alkylation at moderate temperatures.

Alkyl groups have a negligible effect upon the rate of further alkylation. Their orienting effect can be considered "normal" (ortho and para directing), but it is so weak that, in view of the lability of the groups, it is readily superseded by the effect of thermodynamic stability, which may involve also steric effects. Meta isomers are formed probably by isomerization rather than dealkylation. Variations in the distribution of products with different catalysts are reconciled.

Friedel and Crafts announced their discovery of the alkylation of aromatic hydrocarbons in the liquid phase with aluminum chloride as catalyst seventy years ago (23). Innumerable investigations of this reaction have been made since that time. The process is extremely flexible, so that a wide variety of catalysts and alkylating agents is available under appropriate conditions, with corresponding variation in distribution of products. Results have already been reviewed so thoroughly by Calloway (16), Nightingale (46), Price (56, 57), and Thomas (73) that a comprehensive review is not now necessary. Yields of ethylbenzene have been summarized recently (22). This paper will consider only certain aspects not usually emphasized.

Variables in conditions are the identity and the amount of the aromatic hydrocarbon, alkylating agent, catalyst, and promoter; also temperature, time, pressure, degree of stirring, and manner of introduction of reagents. The products are distributed according to the relative amounts of mono-, di-, and poly-alkyl derivatives, unchanged and isomerized alkyl groups, and position isomers of di- and poly-alkyl derivatives.

It has been difficult to correlate the results with the conditions in all cases, partly because some of the analyses, which are difficult, may not be reliable (66), and partly because of the profound effect of some physical factors in the conditions, which are not entirely predictable.

An example of the latter is the selective solvent extraction of the hydrocarbon

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layer by the catalyst layer. This may result in a very considerable segregation of the early reaction products, so that subsequent reaction may depend as much on such physical effects as it does on chemical reactivity. Whether this factor is favorable or not depends upon the object of the reaction and on the manner of applying the alkylating agent, but it should not be neglected.

This factor is especially pertinent to the distribution of products between mono- and poly-ethylbenzenes. Usually the monoethylbenzene is desired because of its importance in making styrene, etc. The aim of a high yield of monoethylbenzene has resulted in many patents (*cf.* 22 for list) covering the use of a large excess of benzene over ethylene, or the idea of recycling the polyethylbenzenes, since it is possible to transfer some of the excess ethyl groups to another benzene molecule. But the recycling of either the benzene or the polyethylbenzenes involves additional expense in distillation, catalyst consumption, and effective capacity of equipment, so that it should be minimized.

The opinion has been general (9, 35, 45, 46, 57, 73) that benzene is less reactive in alkylation reactions than its alkyl derivatives, and this supposition has been blamed (57) for the accumulation of polyethylbenzenes. It is evident, however, that if the heavy catalyst layer has a selective solvent action, dissolving more ethylbenzene than benzene as has been shown (9, 39), and that if the only reaction takes place in that layer, a similar accumulation of polyalkylbenzenes would result.

This unfavorable consequence might be avoided either by eliminating the selective solvent action, or by changing conditions so that alkylation takes place in the hydrocarbon layer. Both have been tried with good results. The selective solvent effect was eliminated (22) by the use of a mutual solvent, ethyl ether, which rendered the reaction mixture homogeneous. The distribution of products corresponded exactly to that calculated on the assumption that the rate of ethylation of benzene is the same as that of each of its ethyl derivatives (except hexaethylbenzene). Other means of eliminating the unfavorable selection are high-speed stirring (9, 39, 42) and vapor-phase operation (at least twenty-five citations; for example, 52), which gave similar results.

The hydrocarbon layer was rendered catalytic for the ethylation by using a higher temperature, 100°C. (22), at which the solubility of aluminum chloride in benzene is sufficient. The selective solvent action of the catalyst layer then gave a favorable result. The ethylbenzene formed in the early part of the reaction was partly extracted and protected from further attack of the ethylene, which was applied under pressure from the vapor phase and never came into direct contact with the catalyst layer. These various modes of operation are illustrated in figure 1.

The above physical mechanism would account in considerable degree for many observations in the literature concerning low-temperature alkylation. Because of the low solubility of aluminum chloride in benzene (*cf.* 73, page 461) the only reaction at first is at the surface of the solid catalyst. This is the "incubation period" commonly observed (9, 39, 42, 73, 74). After some ethylated benzene is formed, a liquid complex with the catalyst results, giving a renewable surface of contact, which allows more rapid reaction. Still the only reaction is in the catalyst layer, which contains a relatively small amount of aromatic hydrocarbon. As ethylene is added, it gives effectively a large excess in the catalyst phase and readily forms hexaethylbenzene there, even with a mole fraction of much less than 1 mole of ethylene to 1 mole of total benzene (9, 21, 39, 42).

With more time the highly ethylated products are gradually reëxtracted by the benzene layer and partly deëthylated. This redistribution is facilitated by larger amounts of catalyst, by high-speed stirring, and by higher temperature (39, 42).

The view that the formation of hexaethylbenzene is the result of physical selection rather than of chemical mechanism is supported by the observation that none of it was found in any product made under conditions where the hydrocarbon layer was catalytically active and where the ethylene was added from the vapor phase (22). The homogeneous alkylation reaction is so rapid, however, that if ethylene is bubbled through the catalytic hydrocarbon layer, a little hexaethylbenzene is formed as a result of local excesses (22).

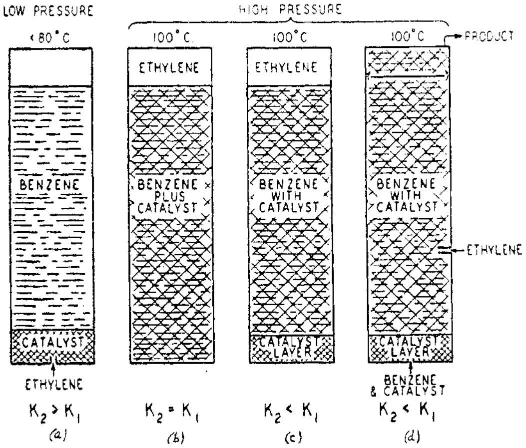


FIG. 1. Diagrammatic conditions for ethylation of benzene (22): (a) laboratory low-temperature operation; (b) homogeneous (solventized) liquid-phase ethylation; (c) ethylation with pressure and higher temperature (no homogenizing solvent); (d) semicontinuous operation. Crosshatching indicates catalyst dissolved in sufficient quantity for catalytic action. (Courtesy of *Industrial and Engineering Chemistry*.)

The "instantaneous" character of the real chemical reaction, thus demonstrated, seems in marked contrast to the long time commonly provided for the ethylation of benzene, usually 2–5 hr. (nineteen citations; for example, 3) or even more (fourteen citations; for example, 45). Speeding of the reaction requires adequate contact between the reagents and catalyst, which apparently can be attained only by solution of catalyst in the benzene. Even the 3-min. reaction time reached in one experiment (22) was probably slow compared with the chemical reaction, and like all ethylations was probably a measure of the rate of introduction of the ethylating agent into the system.

Factors which probably influenced this rate were the much larger volume in which the reaction was taking place, the much higher pressure of ethylene (100–300 lb. instead of only a few millimeters partial pressure when ethylene is bubbled through benzene at atmospheric pressure near the boiling point), and the retention of hydrogen chloride at pressures up to about half an atmosphere instead of allowing it to escape with unreacted hydrocarbon gases. The promoting effect of the hydrogen chloride upon aluminum chloride is well known qualitatively, but nothing seems to have been published on a relation between its partial pressure and its promoting effect. Thomas (73, page 79) even indicated that it should be withdrawn to avoid reversing the reaction with ethyl halide.

REVERSIBILITY

It has often been stated that Friedel-Crafts alkylations are reversible (12, 16, 36, 38, 43, 46, 56, 57, 73). It is true that alkyl groups above methyl are readily transferred from one position to another in the same ring, and from one benzene nucleus to another, so that polyethylbenzenes react with benzene to give ethylbenzene. Isopropyl and *tert*-butyl groups are still more readily transferred, and one alkyl group can displace another (11, 15). Similarly, stirring pure ethylbenzene with aluminum chloride at room temperature for a few minutes gave substantial amounts of benzene and polyethylbenzenes (4, 22).

The methyl group is much more refractory in these rearrangements, so that toluene on long-time boiling under reflux with aluminum chloride gives little benzene and xylene (21), or is formed from them (12). Yet even methyl groups have been transferred in liquid-phase reactions (4, 5, 29, 36, 44, 46). Ethylation of toluene under vigorous conditions has given hexaethylbenzene (21). The byproduct, not isolated, might be an ethylated xylene.

True reversibility implies the dissociation of alkylbenzene into benzene and olefin, or the regeneration of some other ethylating agent. This does not take place with aluminum chloride or other catalysts at reaction temperatures for liquid-phase alkylation. Although benzene was distilled off rapidly from ethylbenzene heated under a column with aluminum chloride, no uncondensed gas (ethylene) appeared, and the residue was highly ethylated (22). Ethyl groups were shifted, but there was no reversal of ethylation.

The reason is that the thermodynamic equilibrium is so far on the side of alkylation at moderate temperatures that the partial pressure of ethylene is negligible. This is shown in table 1, calculated from equilibrium constants selected by the Bureau of Standards (2). The equilibrium is represented approximately by the equation $\log K = 5460/T - 6.56$.

Even at 300°C. hexaethylbenzene with zinc chloride or 97 per cent phosphoric acid failed to evolve appreciable amounts of ethylene (21). At the higher temperature of some vapor-phase processes there is a true equilibrium. Most of these processes operate at 300–500°C., at which the equilibrium is still favorable for alkylation. Transfer of alkyl groups at 454–538°C. was studied by Hansford, Myers, and Sachanen (28), and showed only a slight production of olefins in this temperature range. One patent (40) gives data from which can be calculated K = about 12 at 550–600°C., a value which is slightly higher than would be expected from the Bureau of Standards data (2). If this calculation is valid, it means a still lower equilibrium partial pressure of ethylene in table 1 in the high-temperature range.

The equilibrium between cumene, benzene, and propylene is not much more favorable to decomposition, the calculated partial pressure of propylene at 27°C. being only 10^{-3} mm. Diisopropyltoluene on heating at its boiling point (225°C.) with sodium aluminum chloride evolved no appreciable amount of propylene (21). A little gas which was produced proved to be propane (*cf.* 29, 32, 61). However, Schultze produced propylene and butenes by the decomposition of dialkylbenzenes at 400°C. or higher (62).

TABLE 1

Equilibrium constants

$C_6H_6 + C_2H_4 \rightleftharpoons C_6H_5C_2H_5$

TEMPERATURE	LOG K	PARTIAL PRESSURE OF ETHYLENE
°C.		*mm.*
27	11.6605	10^{-4}
127	7.0710	0.2
227	4.3417	5
327	2.5261	40
427	1.2382	145
527	0.2806	280

Alkylation with ethanol is calculated by combining the equation for the hydration of ethylene (from data of Aston (6))

$$\log K = 2400/T - 6.8$$

with the above equation for alkylation with ethylene, giving

$$\log K = 3060/T + 0.24$$

for $C_6H_6 + C_2H_5OH \rightleftharpoons C_6H_5C_2H_5 + H_2O$. Reversal would be negligible at all temperatures.

Alkylation with ethyl chloride is calculated by combining the equation for its dissociation (from the experimental data of Rudkovskiĭ and coworkers (60) and of Tilman (75)),

$$\log K = -3334/T + 5.75$$

with that for alkylation with ethylene, giving

$$\log K = 2126/T - 0.81$$

for $C_6H_6 + C_2H_5Cl \rightleftharpoons C_6H_5C_2H_5 + HCl$. The maximum equilibrium partial pressure of ethyl chloride below the boiling point of ethylbenzene would be about 2 mm. Jacobsen (36) claimed to have reversed the corresponding methylation by evolving methyl chloride very slowly from *m*-xylene or more highly methylated benzenes with aluminum chloride at reflux temperatures, using a stream of dry hydrogen chloride. However, the high yields of higher alkylbenzenes obtained by Simons and Hart (65) with alkyl chlorides and hydrogen chloride under high pressure and moderately high temperature proves that the equilibrium is almost entirely on the side of alkylation, with alkyl halides. The same conclusion applies to methylation with dimethyl ether (26), and to alkylation with esters.

At moderate temperatures, although the alkylations might be considered reversible kinetically, they are scarcely more reversible thermodynamically than is the formation of water from hydrogen and oxygen.

ISOMERIZED ALKYL GROUPS

This subject has been discussed extensively (16, 18, 24, 33, 34, 56, 57, 73). However, neglect of the possibility of isomerization of the alkyl group has resulted in much misidentification of alkylbenzenes in the early literature and quoted recently (*cf.* 20 for about sixteen illustrations). In the products of Friedel–Crafts reactions the resulting alkyl groups above ethyl are rarely primary except from cycloparaffins (27, 34, 64) and primary alcohols (34), and under mild conditions from primary esters or halides (13, 34), especially with a long chain (25). They are usually secondary from straight-chain olefins and other reagents, and tertiary from reactants having a branch adjacent to the functional group. The phenyl group frequently assumes a position different from that occupied by the functional group of the reagent (31, 76).

On alkylation with aluminum chloride and secondary alcohols the position of the phenyl group usually can be predicted by postulating preliminary decomposition of the alcohol to olefin, followed by addition of the aromatic to one side of the double bond according to Markovnikov's rule (*cf.* 31, 78). With sulfuric acid the double bond may shift before alkylation (33, 34). This would be required in order to produce *tert*-amyl derivatives from isoamyl reagents.

Intermediate formation of olefins is not the only mechanism, however, since it is inapplicable to alkylation with methyl and benzyl (13) and neopentyl radicals (34, 54). Moreover, Price and Lund (59), Burwell and Archer (14), and Tsukervanik (76) have shown that some optical activity in the alkylating agent may be retained in the alkylbenzene.

As noted by Ipatieff, Pines, and Schmerling (34) the carbon skeleton is rarely isomerized in alkylating aromatic hydrocarbons, as stated by Calloway (16) and by Linstead (38), except with neopentyl derivatives (54). However, under vigorous isomerization a *sec*-butyl group has been rearranged to a tertiary structure (47). Moreover, Legge (37) has identified products with isopropyl and *tert*-amyl groups on per-alkylation with isobutene.

ORIENTATION IN ALKYLATION

Since alkyl groups are uniformly ortho and para directing in nitration, halogenation, and sulfonation reactions, it is usual to consider *p*-dialkylbenzenes as the "normal" products and *m*-dialkylbenzenes as "abnormal" (56, 57). The ortho isomer is not usually considered an important product except in methylation (35, 50), although recent observations on distribution for the cymenes (66) show 31–38 per cent of the ortho isomer. Sometimes the para isomer is the main product, especially with phosphoric acid (76), sulfuric acid (77), and boron fluoride (67, 78), but just as frequently, especially with a vigorous catalyst like aluminum chloride, the meta isomer is the predominant product (table 2).

Similarly, the trialkylbenzenes formed by alkylation are commonly the 1,2,4-derivatives when mild conditions are used (67), and the 1,3,5-isomers with a vigorous catalyst (50, 61, 70), but apparently no vicinal trialkylbenzene (1,2,3-) has ever been positively identified in the products of a Friedel–Crafts alkylation. This may be the result of steric influences.

It is usual to account for meta derivatives by postulating the preliminary formation of the 1,2,4-trialkyl derivative, followed by dealkylation of the group in the 1-position (5, 36, 43, 56, 57, 58). The reason for selective removal of the 1-alkyl group (58)—namely, that it is ortho to one alkyl group and para to the other—may be open to some question. The 1-alkyl group is in a preferred position for stability. In analogous cases it has been shown by Holleman and others (*cf.* 19) that the most labile substituent is the one "most out of place with respect to the directive influence of the other substituents". In the table given in reference 19 (page 259) opposite trichlorobenzenes, in the 1,2,4-isomer, the 2 should have been printed in bold type, signifying the one displaced (30).

Meta isomers might arise also by direct isomerization of para isomers, since this reaction has been accomplished (7, 29, 44, 51). Symmetrical trialkylbenzenes have been considered to result either from the dealkylation of first-formed hexaalkylbenzenes (39), or the isomerization of the 1,2,4-isomer (7, 39, 47, 61, 72), which has been accomplished.

If an isomerization occurs, giving more than 50 per cent of an isomer, it is evident that that one is the most stable thermodynamically and has the lowest free energy under the conditions of the experiment. Probably the distribution of products on isomerization is near to thermodynamic equilibrium. The same distribution is probable among isomers from alkylation under vigorous conditions (e.g., with aluminum chloride). This would be a necessary consequence if alkylation were considered reversible kinetically (even though it is not so thermodynamically); that is, that the products are sufficiently interactive.

This hypothesis can be tested for the xylenes by direct comparison with the equilibrium percentages of isomers, which were investigated by Pitzer and Scott (55), showing 12 per cent *o*-, 71 per cent *m*-, and 17 per cent *p*-xylenes, almost independent of temperature. It is quite likely that the equilibrium percentage of the ortho isomer is less for higher alkyl derivatives because of greater steric hindrance. In fact, such a difference is indicated in thermodynamic data on methylethylbenzenes from the Bureau of Standards (2).

Table 2 summarizes the isomer distribution of products in several investigations of the alkylation of benzene and alkylbenzenes in the liquid phase; and table 3 shows some isomerization studies. These tables are by no means complete (*cf.* the lists in references 57, 73) but include those with more quantitative

TABLE 2

Orientation in alkylation

REAGENTS		TEMPERATURE	PRODUCTS*			REFERENCES
Aromatic	Aliphatic		Ortho	Meta	Para	
(a) Catalyst: aluminum chloride						
		°C.				
Benzene	CH_3Cl			95	5 xylenes	(1)
Toluene	CH_3Br	−3	44.5	28	27.5 xylenes	(50)
Toluene	CH_3Br	94	8	83	9 xylenes	(50)
Toluene	CH_3Cl	0	53.5	27.3	19.2 xylenes	(50)
Toluene	CH_3Cl	55	12.2	87.1	0.7 xylenes	(50)
Toluene	CH_3Cl	106	1.8	98.2	0 xylenes	(50)
m-Xylene	CH_3Cl	100	87 Mesitylene			(50)
Xylene (technical)	CH_3Cl	130 to 140	60 1,2,3,5- Tetramethylbenzenes 40 1,2,4,5- Tetramethylbenzenes			(68)
Benzene	CH_3Cl	−40 to 0	Pseudocumene			(50)
m-Xylene	C_2H_5Br	−10 to 0	1,3-Dimethyl-5-ethylbenzene			(50)
Toluene	C_2H_5Br	−12 to −8	1-Methyl-3,5-diethylbenzene			(50)
Benzene	C_2H_5Br	−50 to 0	1,3,5-Triethylbenzene			(50)
Benzene	C_2H_5Cl	70 to 75	86 1,3,5-Triethylbenzene 14 1,2,4-Triethylbenzene			(70)
Benzene	C_2H_5Cl	70	50 1,2,3,4- Tetraethylbenzenes 50 1,2,4,5- Tetraethylbenzenes			(70)
Toluene	Propylene	70	*p*-Cymene			(9)
Benzene	Propylene	70	65 *m*-Diisopropylbenzene			(9)
Benzene	Propylene	70	75 1,3,5-Triisopropylbenzene			(9)
Benzene	Ethylene	70 (little $AlCl_3$)	48 1,3,5-Triethylbenzene			(39)
Benzene	Ethylene	70 (much $AlCl_3$)	62–65 1,3,5-Triethylbenzene			(39)
Benzene	Ethylene	55	15 1,3,5-Triethylbenzene			(39)
Benzene	Ethylene	95	62–65 1,3,5-Triethylbenzene			(39)
Toluene	*n*-C_4H_9Cl	0 to 5	75 *m*-, 25 *p*-*sec*-Butyltoluene			(63)
Toluene	Iso-C_4H_9Br	0 to 5	70 *m*-, 30 *p*-*tert*-Butyltoluene			(63)
Toluene	*tert*-C_4H_9Cl	0 to 5	62 *m*-, 38 *p*-*tert*-Butyltoluene			(63)
Toluene	*tert*-C_4H_9Cl (with $C_6H_5NO_2$)	0 to 5	67 *m*-, 33 *p*-*tert*-Butyltoluene			(63)
Toluene	*tert*-C_4H_9Cl		Mostly *m*-*tert*-butyltoluene			(8, 15, 49, 53)

(b) Other catalysts

AROMATIC	ALIPHATIC	CATALYST	PRODUCTS	REFERENCES
Benzene	Propylene	BF_3, H_2SO_4	98 *p*-, 2 *o*-Diisopropylbenzene	(67)
Benzene	Propylene	BF_3, H_2SO_4	1,2,4-Triisopropylbenzene	(67)
Benzene	Propylene	BF_3, H_2SO_4	1,2,4,5-Tetraisopropylbenzene	(67)
Toluene	*tert*-C_4H_9Cl	$FeCl_3$	67 *m*-, 33 *p*-*tert*-Butyltoluene	(63)
Toluene	*tert*-C_4H_9Cl	$FeCl_3$	Mostly *p*-*tert*-butyltoluene	(10, 15, 49, 53)
Benzene	Propylene	H_3PO_4	7 *o*-, 43 *m*-, 50 *p*-Diisopropylbenzene	(41)

* Numbers are percentages adjusted to total 100 per cent for the group of isomers comprising the fraction.

analyses, for illustration. Divergencies from equilibrium composition seem to be on the side of directive influence, and probably indicate incomplete redistribution. Several such differences appear to result from differences in temperature or other factors in vigor of reaction. The very substantial difference between the results using aluminum chloride and ferric chloride in forming *tert*-butyltoluenes is doubtless due to the greater vigor of the former catalyst. It gives largely the meta isomer (8, 15, 49, 53), while ferric chloride gives mostly the para isomer (10, 15, 49, 53), more nearly according to directive influence. On the other hand, Shoesmith and McGechen (63) found little difference between the results with the two catalysts, perhaps because they compensated in some way for the difference in activity of the catalysts.

TABLE 3

Isomerization of alkylbenzenes

ALKYLBENZENE	PRODUCT*	REFERENCES
(a) Catalyst: aluminum chloride		
o-Xylene	18.7 *m*-Xylene	(50)
p-Xylene	64.3 *m*-Xylene	(50)
p-Xylene	Mostly *m*-xylene	(44)
o- and *p*-Xylenes	Mostly *m*-xylene	(29)
Prehnitene	83 Isodurene, 17 durene	(48)
1,2,4-Triethylbenzene 1,3,5-Triethylbenzene	20 1,2,4-Triethylbenzene† 80 1,3,5-Triethylbenzene†	(48)
1,2,3,4-Tetraethylbenzene	50 1,2,3,5-Tetraethylbenzene 50 1,2,4,5-Tetraethylbenzene	(48)
p-Di-*n*-propylbenzene	65 *m*-Di-*n*-propylbenzene	(7)
m-Di-*n*-propylbenzene	Mostly *m*-di-*n*-propylbenzene	(7)
1,2,4-Tri-*n*-propylbenzene	Mostly 1,3,5-tri-*n*-propylbenzene	(7)
1,3-Dimethyl-4-*n*-butylbenzene	1,3-Dimethyl-5-*sec*-butylbenzene	(47)
1,3-Dimethyl-4-*sec*-butylbenzene	1,3-Dimethyl-5-*tert*-butylbenzene	(47)
1,3-Dimethyl-4-*tert*-butylbenzene	1,3-Dimethyl-5-*tert*-butylbenzene	(47)
(b) Catalyst: oleum (Jacobsen reaction)		
Durene Isodurene	Only prehnitene	(43, 69)
1,2,3,5-Tetraethylbenzene 1,2,4,5-Tetraethylbenzene	Only 1,2,3,4-tetraethylbenzene	(71)

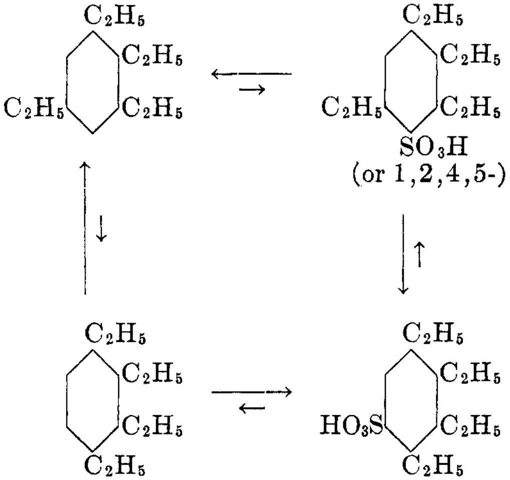
* Numbers are percentages adjusted to total 100 per cent for the group of isomers comprising the fraction.

† Average value.

If the distribution of products under vigorous alkylation is governed largely by equilibria, it is no longer necessary to postulate an arbitrary indirect mechanism. However, some anomalous observations require explanation.

The tetraalkyl isomer to be expected from directive influence is the 1,2,4,5-structure, and this is generally present. It is the only isomer identified from the propylation of benzene (9, 27, 67); but isomerization studies on the tetraethylbenzenes (48) with aluminum chloride catalyst indicate that at equilibrium the 1,2,3,5-isomer is present in equal amount, and for the tetramethylbenzenes it constitutes 83 per cent. The vicinal isomer, 1,2,3,4-, is practically absent in all cases. On the other hand, the Jacobsen rearrangement with oleum catalyst gives almost exclusively the vicinal isomer with both methyl (69) and ethyl groups (71). These observations seem mutually contradictory.

However, it has been shown (43, 69, 71) that it is the sulfonic acid and not the hydrocarbon which isomerized in the Jacobsen reaction. To reconcile the much higher thermodynamic stability of the sulfonic acid of the vicinal derivative than those of its isomers with the much lower stability of the free hydrocarbon (or of its aluminum chloride complex), it is necessary to postulate a much higher equilibrium in sulfonating the vicinal, as indicated by the length of arrows in the following scheme:



Another example of the effect of strong sulfuric acid in modifying the reaction is the production of 2,6-diisopropyltoluene (17), an isomer which could hardly be expected from aluminum chloride catalysis. The latter rarely gives vicinal isomers if it is possible for the alkyl groups to be further apart. Presumably a sulfonic acid had blocked off the para position and augmented directive influence to the 2- and 6-positions.

Closely related to orientation is the effect of substituents on the absolute rate of further substitution. It is well known that toluene and other alkylbenzenes are more readily nitrated or halogenated than benzene. Aniline, phenol, and their derivatives are still more reactive. On the other hand, a nitro or carboxyl group greatly retards substitution. This effect is not quite parallel with directive influence, since halogen substituents make a benzene ring less reactive although they are ortho–para directing. Moreover, in a mixture of toluene and chlorobenzene the former is much more reactive to nitration (79), although in *o*-chlorotoluene the directive power of chlorine predominates over that of methyl. The distinction has been discussed previously (19, pages 277–80).

Similar effects have been noted in alkylation, to such an extent that it has not been found possible to alkylate nitrobenzene or benzoic acid (16). *p*-Dichlorobenzene was found sufficiently inert (50) to aluminum bromide for molecular weight determinations of toluene complexes with the catalyst, although it has been ethylated (21). Ethylation of 1,2,4-trichlorobenzene was effected to only a slight extent under conditions giving high-speed ethylation of benzene (21). The effect of ethyl groups upon the rate of further ethylation has been shown in this paper and previously (22) to be almost negligible. However, propylation was found to be slightly accelerated by alkyl groups in the molecule (16a).

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