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Alkylaromatics. Part I. Friedel–Crafts Alkylation of Benzene and Alkyl-substituted Benzenes with *n*-Alkyl Bromides[1]

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A careful study of the aluminum bromide-catalyzed alkylation of aromatics with *n*-dodecyl and *n*-octyl bromide has shown that *n*-alkylaromatics can comprise up to 50% of the product with benzene and up to 88% with substituted benzenes. Decreasing the temperature decreases the amount of rearrangement accompanying alkylation. The secondary alkylbenzene products undergo isomerization under alkylation conditions, but no 1-phenylalkane is formed. Under more vigorous conditions, dealkylation of the secondary products occurs. A mechanism for rearrangement during alkylation is presented.

Introduction

The Friedel–Crafts alkylation of benzene with *n*-propyl and *n*-butyl halides repeatedly has been shown to give both *n*- and *sec*-alkylbenzenes.[2-13] There are some reports in the earlier literature of nearly exclusive production of one or the other of the two structures,[5,14] but mixtures usually have been obtained.

The effects of reaction variables upon product composition have received relatively little attention. Conflicting results are reported by two groups on the effect of temperature on the alkylation of benzene with *n*-propyl chloride. Ipatieff, Pines and Schmerling[2] observed that the ratio of *n*-propylbenzene to isopropylbenzene varied from 40:60 at 35° to 60:40 at −6°. Roberts and Shiengthong[7] reported a change in product composition of only 4% over the temperature range −18 to 80°. The influence of the aromatic has been pointed out by Brown and his co-workers.[15] In an excellent study of alkylation as an example of electrophilic aromatic substitution, they suggested that the reaction of primary derivatives displays many of the features characteristic of a displacement mechanism. The aromatic plays an important role in carbon–carbon bond formation in the transition state. Therefore, the degree of rearrangement accompanying attachment of the alkyl group to the ring should be a sensitive function of the nucleophilic character of the aromatic undergoing alkylation. They predict *n*-propyl-isopropylbenzene product compositions for the gallium bromide-catalyzed alkylation of a series of methylated benzenes with *n*-propyl bromide.[13]

In this paper, we describe a study of the alkylation of benzene and alkyl-substituted benzenes with *n*-octyl and *n*-dodecyl bromide using aluminum bromide as the catalyst. Special emphasis is given to those features which might be expected to exert an influence upon the amount of rearrangement obtained. The stability of the products plays an important role in the interpretation of the results and, therefore, is discussed at some length.

Results

Alkylation of Benzene.—Results of alkylations using benzene are presented in Table I. In these experiments, a solution of the alkyl halide (generally 0.02–0.08 mole) in 3 to 5 times its volume of solvent was added over a period of 0.25 to 2 minutes to benzene or a benzene–petroleum ether solution containing the aluminum halide catalyst. Samples were withdrawn periodically and quenched by hydrolysis. Products and unreacted alkyl halide were then determined by vapor-phase chromatography (v.p.c.). All of the possible straight chain alkylbenzene isomers were found in the product mixture.[16] In a number of cases, yields were determined by v.p.c. to be 85–95% through the use of an internal standard, *n*-hexadecane. These values were verified by preparative scale experiments. With the exceptions of runs J, K and M, the reaction systems were completely homogeneous.

Though no kinetic studies were undertaken, the method of analysis provided a qualitative measure of reaction rate. It can be seen in Table I that alkylation in excess benzene at 6° or above is rapid. In run D, analysis of a sample removed after 1.5 minutes showed that reaction was 91% complete, while after 4 minutes, conversion was 100%. In run N, using *n*-octyl bromide, conversion was 96% at 3 minutes and 100% at 6 minutes. The variation in other values given as maximum figures does not reflect differences in rate but merely that reaction was complete at the time the first sample was removed for analysis.

The isomer distributions reported in Table I are those measured when conversion of the alkyl halide to products was complete or nearly com-

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(1) Presented in part before the Division of Petroleum Chemistry, 141st Meeting of the American Chemical Society, March 20–29, 1962, Washington, D. C.

(2) V. N. Ipatieff, H. Pines and L. Schmerling, *J. Org. Chem.*, **5**, 253 (1940).

(3) M. I. Konowalow, *J. Russ. Phys.-Chem. Soc.*, **27**, 456 (1895); *Bull. soc. chim.*, **16**, 864 (1896).

(4) T. Estreicher, *Ber.*, **33**, 436 (1900).

(5) R. Heise, *ibid.*, **24**, 768 (1891).

(6) G. Gustavson, *ibid.*, **11**, 1251 (1878).

(7) R. M. Roberts and D. Shiengthong, *J. Am. Chem. Soc.*, **82**, 732 (1960).

(8) L. T. Diuguid, *ibid.*, **63**, 3527 (1941).

(9) A. M. Petrova, *Zhur. Obshchei Khim.*, **24**, 491 (1942); *C. A.*, **49**, 6150i (1955).

(10) R. D. Silva, *Bull. soc. chim.*, **43**, 317 (1885).

(11) P. Genvresse, *Compt. rend.*, **116**, 1065 (1893).

(12) B. A. Krentsel, A. V. Topchiev and L. N. Andreev, *Doklady Akad. Nauk S.S.S.R.*, **98**, 75 (1954); *C. A.*, **49**, 11574c (1955).

(13) C. R. Smoot and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 6249 (1956).

(14) J. Schramm, *Monatsh.*, **9**, 613 (1888).

(15) (a) H. C. Brown and M. Grayson, *J. Am. Chem. Soc.*, **75**, 6285 (1953); (b) H. C. Brown and H. Jungk, *ibid.*, **77**, 5584 (1955) and **78**, 2182 (1956); (c) H. Jungk, C. R. Smoot and H. C. Brown, *ibid.*, **78**, 2185 (1956).

(16) Although it is clear that hydride shifts occur, no evidence for skeletal rearrangement of the alkyl group was obtained. Roberts and Shiengthong,[7] using *n*-butyl chloride and aluminum chloride, found that isobutylbenzene was formed in small amounts but only at much higher temperatures and longer reaction times than were employed in the present work.

TABLE I

ALKYLATION OF BENZENE WITH n-ALKYL HALIDES[a]

Run	RX	Catalyst	Solvent	Temp., °C.	Products Primary, %[b]	Distribution of secondary isomers, %[c] 2-Ph	3-Ph	4- + 5- + 6-Ph	Reacn. time, min.
A	$n\text{-}C_{12}H_{25}Br$	Al_2Br_6 (0.23)	Benzene (49)	35	31.6[d] (35.1[e])	30.7	19.8	49.5	<1.25
B	$n\text{-}C_{12}H_{25}Br$	Al_2Br_6 (.09)	Benzene (56)	6	40.2	33.6	20.6	45.8	<2
C	$n\text{-}C_{12}H_{25}Br$	Al_2Br_6 (.12)	Benzene (38)	6	41.0	33.0	18.0	49.0	<8
D	$n\text{-}C_{12}H_{25}Br$	Al_2Br_6 (.25)	Benzene (55)	6	40.4	32.8	18.4	44.8	>1.5; <4
E	$n\text{-}C_{12}H_{25}Br$	Al_2Br_6 (.13)	48% benzene (35) 52% P.E.[f]	−15	46.5	33.0	21.6	45.4	71
F	$n\text{-}C_{12}H_{25}Br$	Al_2Br_6 (.12)	45% benzene (38) 55% P.E.	−15	47.8	31.2	18.0	50.8	90[i]
G	$n\text{-}C_{12}H_{25}Br$	Al_2Br_6 (.23)	30% benzene (35) 70% P.E.	−34	49.0	33.2	21.9	44.9	350
H	$n\text{-}C_{12}H_{25}Br$	Al_2Br_6 (.24)	30% benzene (36) 70% P.E.	−34	50.0	34.1	21.7	44.2	370
I	$n\text{-}C_{12}H_{25}Br$	Al_2Br_6 (.23)	30% benzene (34) 70% P.E.	6	37.0	33.0	18.8	48.2	*ca.* 22
J[g]	$n\text{-}C_{12}H_{25}Br$	Al_2Br_6 (.13)	14% benzene (4.8) 86% P.E.	6	30.0	32.5	21.7	45.8	82[j]
K[g,l]	$n\text{-}C_{12}H_{25}Br$	$AlCl_3$ (.07)	Benzene (32)	6	41.2	33.5	20.7	45.8	89[k]
L[l]	$n\text{-}C_{12}H_{25}Cl$	Al_2Br_6 (.08)	Benzene (53)	6	35.5	32.4	19.0	48.6	<4
M[g]	$n\text{-}C_{12}H_{25}Cl$	$AlCl_3$ (.17)	Benzene (54)	6	37.3	32.4	18.8	48.8	20
N	$n\text{-}C_8H_{17}Br$	Al_2Br_6 (.12)	Benzene (42)	6	40.0	49.0	51.0[h]		>3; <6
O	$n\text{-}C_8H_{17}Br$	Al_2Br_6 (.12)	45% benzene (38) 55% P.E.	−15	46.5	48.3	28.4	23.3[m]	80

[a] Numbers in parentheses indicate mole ratios of reactants relative to 1.0 mole of alkyl halide. [b] Accurate to ±1.5%. [c] Accurate to ±2%. [d] Calculated by the method described in the text. [e] Measured. [f] Petroleum ether. [g] Heterogeneous. [h] Sum of 3- + 4-phenyloctane. [i] 92% reaction. [j] 73% reaction in 4 minutes. [k] <5% reaction in 14 minutes. [l] Reactions probably complicated by halide exchange, see ref. 15b. [m] 4-Phenyloctane.

plete. Because of the instability of some of the products, these values are not those intrinsic to the alkylation reaction itself. 1-Phenyldodecane is not altered in 5 hours at 25° in the presence of aluminum bromide and hydrogen bromide. Hence, it is completely stable under all alkylation conditions employed. The secondary isomers, however, isomerize very rapidly to an equilibrium composition containing 32% 2-phenyl-, 20% 3-phenyl- and 48% of the 4-, 5-, 6-phenyldodecane combination. This behavior was first demonstrated by Olson[17] with 2-phenyldodecane which was allowed to react with aluminum chloride and hydrogen chloride in benzene at 50°. Our results show that the same equilibrium is reached in a matter of a few minutes when a mixture of secondary dodecylbenzenes rich in the 5- and 6-phenyl isomers is treated with aluminum bromide and hydrogen bromide in benzene or petroleum ether at 25°. It should be emphasized that no 1-phenyldodecane is formed.

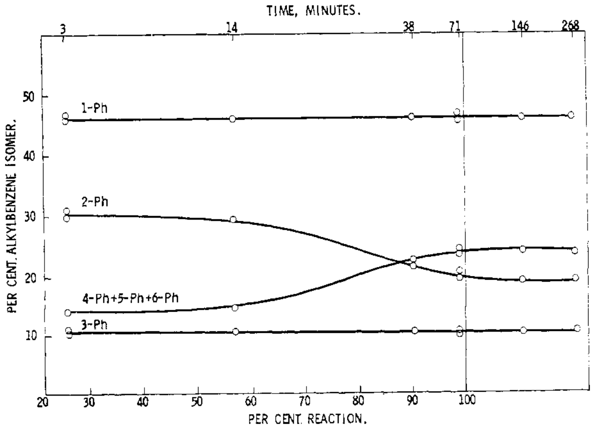

Fig. 1.—Alkylation of benzene at −15° (run E).

This isomerization is also apparent in Fig. 1. Alkylation product compositions at various stages of reaction are shown for run E performed at −15°. Throughout alkylation, the primary alkylbenzene content remained constant at about 46% since none was formed or destroyed by isomerization. The first product-forming reaction which leads to secondary isomers gave rise to the composition rich in 2-phenyldodecane shown in the figure at 24% reaction. Isomerization then occurred; by the end of the reaction, the equilibrium mixture, which contained less of the 2-phenyl isomer, had been obtained.

In the early stages, the relative rate of the product-forming reaction is high. Later, as this rate diminishes due to the multiple order of the reaction,[15] it no longer masks the isomerization reaction and the change in composition leading toward the equilibrium distribution can be seen. Clearly, the rate constants for alkylation and isomerization are of the same order of magnitude. Normalization to 100% of the values (pertaining only to secondary isomers) measured at the end of the reaction leads to the figures shown in Table I. A family of curves similar in shape to those of Fig. 1 was obtained for run G at −34°. The same processes thus occurred at this temperature and presumably at 6° and 35°, but because of the

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(17) A. C. Olson, *Ind. Eng. Chem.*, **52**, 833 (1960).

rapid rates at the higher temperatures, all samples reflected at least 91% reaction and nearly complete equilibration of the secondary isomers. The primary-secondary product ratio is unaffected by this isomerization.

Alkylation with 1-bromoöctane at −15° (run O) took a similar course as can be seen in Table II. Product composition data for alkylations with 2- and 4-bromoöctane under conditions identical with those of run O are also shown in this table. With the secondary octyl bromides, alkylation was at least 99% complete in 0.4 minute.

Table II

Alkylation with Octyl Bromides at −15°[a]

Time, minutes	Reaction, %	Products			
		Primary, %[b]	Distribution of secondary isomers, %		
			2-Ph[b]	3-Ph[c]	4-Ph[c]
Run O, 1-bromoöctane					
0.3	8	47.1	63.5	24.5	12.0
2.5	21	46.5	63.3	24.5	12.2
13	50	47.2	62.0	25.5	12.5
30	76	45.8	55.2	27.2	17.6
78	97	46.1	48.9	28.2	22.9
154	100	46.6	48.3	28.4	23.3
Run P, 2-bromoöctane					
0.35	>99	0.0	51.0	29.6	19.4
7	100	.0	50.3	29.0	20.7
25	100	.0	48.5	27.8	23.7
60	100	.0	48.5	28.2	23.3
Run Q, 4-bromoöctane					
0.4	>99	0.0	42.1	30.0	27.9
7	100	.0	44.1	29.4	26.5
30	100	.0	48.0	29.0	23.1
60	100	.0	48.0	28.7	23.3

[a] Conditions same as in run O, Table I; 0.024 mole RBr used, 0.25 min. addition time. [b] Accurate to ±0.6%. [c] Total of 3-Ph plus 4-Ph accurate to ±0.6%; value for either one accurate only to ±1.0% due to lack of complete resolution.

An additional side reaction reflecting the instability of the secondary isomers is dealkylation leading to a mixture of branched, saturated hydrocarbons corresponding in carbon content to the original side chain. This very interesting reaction, which we plan to study further, does not affect primary alkylbenzenes except under extreme conditions and is very slow relative to alkylation and isomerization. Cleavage does not occur to any measurable extent during the time required for complete alkylation at any given temperature; hence, the product compositions given in Table I have not been influenced by this reaction except in the case of run A.

Though not observed at −15° and −34°, dealkylation occurred at a measurable rate at 6° and very rapidly at 35°. Figure 2, depicting the course of run A at 35°, is illustrative. Alkylation was practically instantaneous. Dealkylation quickly followed as is shown by the appearance of dodecane in the top portion of the figure. The bottom series of curves shows the distribution of the remaining dodecylbenzenes. As degradation occurred, the quantity of 1-phenyldodecane remained constant. The secondary isomers were destroyed. Consequently, although the total quantity of alkylbenzenes decreased, the percentage of primary isomer in the remaining alkylbenzene component rose sharply because of the loss of secondary dodecylbenzenes.

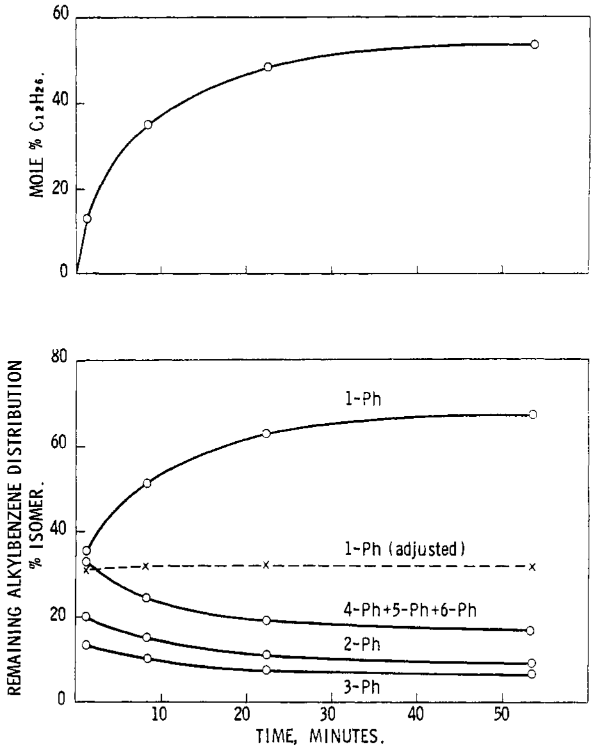

Fig. 2.—Alkylation–dealkylation at 35° (run A).

As in other experiments at lower temperatures, the distribution of the secondary isomers did not vary from the known equilibrium composition during dealkylation. This result is required since equilibration is exceedingly fast relative to dealkylation.

Due to the presence of selective dealkylation, the primary–secondary product ratio of alkylation at 35° could not be determined directly. Since all the dodecane was derived from degradation of only the secondary isomers, this ratio could be calculated. The measured mole percentage of dodecane was added to the measured mole percentage of the secondary isomers. From the resulting figures, the primary–secondary product ratio was determined for each of the four samples analyzed. The agreement was excellent, 31.6 ± 1.2% 1-phenyldodecane.

No rearranged alkyl bromide was found in samples removed from reactions which had not reached 100% conversion. The v.p.c. method used was capable of detecting 0.01% of secondary bromide in the studies of the octyl system.

Variation in the mole ratio of aluminum bromide to alkyl bromide in the range studied (0.09–0.25: 1.0) slightly altered reaction rate but had no effect upon product composition. This is shown in runs B, C and D. In additional experiments using mole ratios of approximately 0.01:1.0, complete reaction occurred in only a fraction of the runs; but in cases where a significant amount of product was formed, the composition was normal. Run

J, using 14% benzene–86% petroleum ether and a mole ratio of benzene to alkyl bromide of only 4.8:1, is the only case where the solubility limit of the bromide catalyst was exceeded. Alkylation was abnormal in that 73% reaction occurred in 4 minutes, but complete conversion required 82 minutes. The primary–secondary product ratio was seriously reduced, possibly because heterogeneous catalysis had an anomalous effect.

Alkylation of Substituted Benzenes.—A number of alkyl-substituted benzenes were alkylated with *n*-dodecyl bromide using aluminum bromide as the catalyst. The proper assignment of structures to the v.p.c. peaks and thus the determination of the primary–secondary product ratio was greatly simplified as a result of the work of Olson.[17] He showed that the alkylation of benzene with 1-dodecene produces no 1-phenyldodecane. With each of the substituted aromatics, we ran two parallel alkylation experiments, one using *n*-dodecyl bromide and one using 1-dodecene. The v.p.c. trace of the products of the former reaction showed all the peaks found in the olefin alkylation system plus a new, well-defined peak (or set of peaks) with greater retention time, clearly representing the unrearranged product (or products if ring-positional isomers were possible).[18]

The product composition of these alkylation reactions is shown in Table III. The determination of primary–secondary product distribution of the reaction with cumene was complicated by the fact that this aromatic produces benzene (and diisopropylbenzenes) by disproportionation to the extent of 10–20% under the conditions employed for alkylation. Some fraction of the benzene so produced underwent alkylation. The v.p.c. peaks representing primary and some of the secondary dodecylbenzenes were intimately mixed with and could not be differentiated from those of secondary dodecylcumenes. The apparent percentage of secondary alkylcumenes was thus high by the amount of alkylbenzene produced in the reaction. Hence, the value given for percentage primary alkylcumene produced by alkylation is low. More nearly correct values were obtained by a method of alkyl group transfer described in Part II.[19] All of the dodecyl derivatives were converted to a mixture of dodecylbenzenes, and the composition was accurately measured. Since it is certain that no rearrangements to give new primary attachments occurred, measurement of the fraction of 1-phenyldodecane established a minimum value for the percentage of 1-dodecylcumene produced in the original alkylation.[20]

TABLE III

ALKYLATION OF SUBSTITUTED BENZENES WITH *n*-DODECYL BROMIDE

Aromatic	Primary isomer, %[a]	Temp., °C.	Reaction, % (time, min.)	Primary isomer, % predicted[b]
Benzene	41	6	100 (4)	28.2 (28[c])
Toluene	68	2	85–95 (20)	49.2 (47[c])
	78	−15	93 (210)	
	ca. 84[d]	−20		
Ethylbenzene	*ca.* 70	−20	70 (5)	..
			84 (65)	
Cumene	72[e]	−15	84 (8)	..
			98 (35)	
p-Xylene	73	14	90 (5)	53.6
			100 (58)	
m-Xylene	71	8	76 (16)	74.2
			76 (36)	
Mesitylene	88	10	77 (16)	90.7
			78 (61)	
Pentamethylbenzene	..	..	...	95.7

[a] Accurate to ±2%. [b] Predicted by Smoot and Brown for alkylations with *n*-propyl bromide and gallium bromide at 25°; ref. 13. [c] Found, ref. 13. [d] Alkylation with *n*-propyl bromide. [e] Calculated by method described in the text; measured values in two duplicate runs were 66%.

Discussion

The data of Table I as well as the observations of Brown and his co-workers[15] demonstrate that alkylation with aluminum bromide above 0° is exceedingly fast, even with primary derivatives. Reactions using aluminum chloride and alkyl chloride are also rapid, as can be seen from run M in which alkylation was complete in 20 minutes at 6°. From the literature, it is apparent that such chloride alkylation mixtures commonly have been maintained for several hours at temperatures up to 80°. Yields often have been low, probably because of these unnecessarily long heating periods, which we have shown cause dealkylation in chloride as well as bromide systems. Furthermore, it is quite likely that some of the discrepancies in data concerning primary–secondary product distribution result from selective destruction of the secondary isomers. With an aluminum bromide to alkyl bromide ratio of 3:1 at a temperature of 4°, alkylation with *n*-dodecyl bromide was followed by complete degradation of the secondary isomers in less than 90 minutes, leaving 1-phenyldodecane as the only surviving alkylbenzene. The primary isomer was also destroyed in 24 hours at 25°. This selective destruction suggests a convenient laboratory preparation of primary alkylbenzenes.

The primary–secondary product ratio intrinsic to alkylation alone is sensitive to temperature change. This fact is established by the data obtained in runs A–H, N and O. A change in temperature from 35° to −34° caused an increase in the percentage of primary alkylbenzene product from about 31% to approximately 50%. A plot of percentage primary isomer formed against reaction temperature shows a rather good straight line, indicating an increase in primary alkylbenzene content of approximately 3% per 10° reduction in temperature. A sensitivity to temperature is also shown in the alkylation of toluene with *n*-dodecyl bromide.

Dilution of benzene with petroleum ether in these runs reduced reaction rate but had very

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[18] In all straight chain alkylbenzene mixtures studied, the nearer the phenyl group was to the end of the chain, the greater was the retention time of the compound on the v.p.c. column used. A typical v.p.c. trace of the products of alkylation of cumene is reproduced in ref. 19.

[19] S. H. Sharman, Part II, *J. Am. Chem. Soc.*, **84**, 2951 (1962).

[20] No significant disproportionation of ethylbenzene or the methylated benzenes occurred under our alkylation conditions.

little effect upon product distribution as is evident from comparison of runs G and H with run I. If anything, these variations in media mask slightly the temperature sensitivity. Dilution of benzene with petroleum ether caused a minor reduction of the fraction of primary alkylbenzene produced; hence, if it were possible to perform the alkylation at −34° in pure benzene, the percentage of 1-phenyldodecane probably would increase only 1 to 2%.

The effect of other reaction variables is seen in Table IV which gives samples of alkylation selected from this work and from the literature. The primary-secondary product ratio seems to be slightly smaller in alkyl chloride-aluminum chloride than in alkyl bromide-aluminum bromide alkylations and smaller yet when gallium bromide is used to catalyze reactions of alkyl bromides. A most interesting feature is that no primary alkylbenzene is formed in the alkylation of benzene with primary alcohols and boron trifluoride.[21]

Increase in the nucleophilic character of the aromatic results in a dramatic rise in the amount of unrearranged product obtained. This rise was predicted by Smoot and Brown.[13] They suggested that alkylation with *n*-propyl bromide and gallium bromide occurs through two concurrent reactions: (1) a displacement-type reaction to give unrearranged product in which the rate-determining step involves nucleophilic attack by the aromatic nucleus upon a polarized primary bromide–gallium bromide complex and (2) rearrangement of the *n*-propyl complex to an isopropyl complex followed by extremely rapid alkylation to give isopropyl derivatives. Presumably, this isopropyl complex is the same as that which would arise if alkylation were carried out with isopropyl bromide. They reasoned that the use of more nucleophilic aromatics should cause an increase in the rate of the displacement reaction but have little effect upon the rate of isomerization of the alkyl bromide. Therefore, the primary–secondary product ratio should increase. Table III shows values which they predicted for alkylation of a series of methylated benzenes. Although the catalyst and the reaction conditions were different in our study, the results show a trend similar to that predicted.

TABLE IV

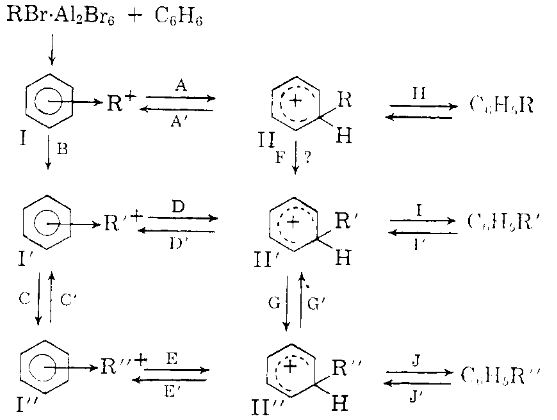
PRIMARY–SECONDARY PRODUCT DISTRIBUTION IN FRIEDEL–CRAFTS TYPE ALKYLATION

Aromatic	RX	Catalyst	Primary isomer, %	Ref.
Benzene	*n*-$C_8H_{17}Br$	Al_2Br_6	40	
Benzene	*n*-$C_{12}H_{25}Br$	Al_2Br_6	40	
Benzene	*n*-$C_8H_{17}Cl$	$AlCl_3$	37	
Benzene	*n*-C_3H_7Cl	$AlCl_3$	33–35	7
Benzene	*n*-C_4H_9Cl	$AlCl_3$	32–36	7
Benzene	*n*-C_3H_7Br	$GaBr_3$	28	13
Benzene	*n*-$C_5H_{11}OH$	BF_3	0	21
Toluene	*n*-$C_{12}H_{25}Br$	Al_2Br_6	68	
Mesitylene	*n*-$C_{12}H_{25}Br$	Al_2Br_6	88	

Smoot and Brown did not report the composition of unreacted bromides. Although we could detect no secondary alkyl bromide at partial conversion, the mechanism proposed by these authors is not invalidated. Since the rates of isomerization and displacement are of the same order of magnitude and the rate of reaction of secondary alkyl bromides is extremely fast, no significant concentration of these bromides could develop.

We have obtained evidence, however, that, at least in part, alkyl aromatics produced in alkylations using primary halides develop by a route different from that described above. By an argument presented earlier, it can be concluded from Fig. 1 and the data from run O (Table II) that the rates of isomerization of secondary alkylbenzenes and alkylation with *n*-alkyl halides are of the same order of magnitude. The alkylation reaction at −15° has a half-life of some 13 minutes. The rate of isomerization of secondary alkylbenzenes, therefore, cannot be extremely fast at this temperature. This statement is verified by the data of runs P and Q and leads to the conclusion that the product compositions of these runs with secondary octyl bromides at −15° measured at reaction times of about 0.4 minute are very nearly those of the first formed products. Very little isomerization could have occurred in this short time. Furthermore, these compositions are far different from the composition of the secondary isomers first formed in the alkylation with primary halides. Thus, at least a significant fraction of the secondary alkylbenzene product formed from primary alkyl bromides is derived from intermediates which are different from those through which alkylation with secondary alkyl bromides proceeds.

The observed reduction in rearrangement accompanying increase in the nucleophilic character of the aromatic undergoing alkylation can be explained by the mechanism shown below, in which the aromatic nucleus becomes involved in the early stages of reaction.



This scheme suggests that the formation of both primary and secondary products reflects a competition between reactions A and B. Both reactions may be very fast but must be similar in rate. Increase in the nucleophilicity of the aromatic should increase the rate of A and have little effect upon B. This follows from data summarized by Brown and Nelson[22]

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(21) A. Streitwieser, Jr., D. P. Stevenson and W. D. Schaeffer, *J. Am. Chem. Soc.*, **81**, 1110 (1959).

(22) H. C. Brown and K. L. R. Nelson, Chapter 56 in B. T. Brooks, S. S. Kurtz, Jr., C. E. Boord and L. Schmerling, "The Chemistry of Petroleum Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., Vol. 3, p. 465.

on the stability of σ-complexes as a function of nucleophilic character of the aromatic. This scheme provides for rearrangement of the side chain (by path B) with involvement of the aromatic in a π-complex and does not require that collapse to a secondary bromide occur or that the intermediates be the same as those encountered when alkylations are carried out with secondary bromides.

The mechanism proposed by Streitwieser, Schaeffer and Andreades for the alkylation of benzene with alcohols and boron trifluoride[23] would be consistent with the present observations if alkylation with secondary bromides proceeds through an elimination step followed by reaction of the aromatic with the olefin thus formed. It is possible, however, that rearrangement and alkylation do occur through the bromides themselves but that the intermediate complexes require less involvement or a different type of participation by the aromatic nucleus than is the case in reactions with primary halides. Such behavior would not be surprising since ionization of the C–Br bond would be expected to take place much more readily with the secondary derivatives. It is interesting to note in runs P and Q, Table II, that the first formed products of alkylation using 2- and 4-bromoöctane contain all the possible secondary isomers. Although the compositions of these initial products are slightly different in the two cases, they very nearly reflect the distribution at equilibrium (shown at 60 minutes).

The additional possibility that product composition is determined by a competition between reactions H and F deserves some consideration. Since path H involves merely the removal of a proton from the σ-complex II, the presence in the medium of increasingly basic substances might increase the ratio of rates $k_H:k_F$ and thus raise the fraction of primary alkyl aromatic produced. Such behavior was observed as the basicity of the aromatic hydrocarbon undergoing alkylation was increased (Table II). On the other hand, the development of additional base strength through formation of the more highly substituted products might be expected to lead to an increase in the primary–secondary product ratio as the reaction progresses. An increase of this kind was not detected. Furthermore, alkylation using a 9:1 mixture of benzene and toluene in large excess gave an alkyl aromatic product in which the alkylbenzene fraction displayed an isomer distribution typical of alkylations in pure benzene.[24] It is difficult to predict how large these effects would be. We do not, therefore, consider our failure to detect them as strong evidence against the operation of a product determining competition between reactions F and H.

Experimental

Materials.—Aluminum bromide (Matheson, Coleman, and Bell, technical grade) was distilled in vacuum under anhydrous conditions through a 46-cm. Vigreux column (b.p. 114° (10 mm.)). A large center cut was collected in a resin flask. Within a nitrogen-filled dry-box, the bromide was broken into chunks about 1 cm.^{3} in volume and transferred to weighed vials for storage. The material was pure white to very light brown in color. Since aluminum bromide is soluble in all the media used, it was possible to use large chunks, thus minimizing surface area exposed during transfer. Aluminum chloride (Baker and Adamson, anhydrous sublimed) was used without further purification.

n-Dodecyl bromide (1-bromododecane, Matheson, Coleman, and Bell) was redistilled under vacuum (b.p. 180–181° (50 mm.)). The material was assumed to be >98% primary isomer since it gave products identical with those formed from a sample prepared in these laboratories and shown by a kinetic method to have the indicated purity.[25] *n*-Dodecyl chloride and 1- and 2-bromoöctane (Matheson, Coleman, and Bell) as well as *n*-dodecyl bromide were shown by v.p.c. to contain no more than 2% impurities. 4-Bromoöctane (K and K Laboratories) was approximately 96% pure. All alkyl bromides were treated with silica gel shortly before use. 1-Dodecene (Humphrey Wilkinson) was used as supplied.

Benzene and toluene (Baker analyzed reagent grade) were used as supplied. Additional purification had no significant effect upon reaction or product characteristics. The addition of water, up to a water to aluminum bromide (Al_2Br_6) mole ratio of 2:1, had no effect other than a slight decrease in alkylation rate. Ethylbenzene and cumene (Eastman Kodak Co., white label) were treated with silica gel. In addition, cumene was redistilled (b.p. 88.9–89.1° (102 mm.)). *p*-Xylene (Oronite Division, California Chemical Co.) was shown by the freezing point method to be 99.8% pure. *m*-Xylene (Phillips Petroleum Co., research grade, 99.92 mole per cent.) was used without purification. Mesitylene (Eastman Kodak Co., white label) was treated with silica gel and redistilled through a 20-plate column. A center cut (b.p. 99.0–99.8° (100 mm.)) was shown by infrared and v.p.c. analysis to be greater than 99% pure. Petroleum ether (Baker and Adamson, b.r. 30–60°) was used as supplied. It contained no olefin as shown by infrared and bromine number.

Analysis of Product Mixtures.—Distribution of the various isomeric alkylbenzenes in product mixtures was determined by the vapor phase chromatographic method of Olson[17] who generously supplied authentic samples of the dodecylbenzenes. Resolution was excellent except among those isomers having the phenyl group near the middle of the chain. The 4-phenyldodecane was well but not completely separated from the 5- and 6-phenyl isomers which themselves were unresolved. There were no extraneous peaks or shoulders which might represent branched chain dodecylbenzenes, although the presence of very small quantities cannot be ruled out. Analysis of products in the studies involving other aromatics was by the method described in a previous section. Identification of the saturated hydrocarbon produced by dealkylation was by mass spectrometer, infrared, bromine number and boiling point.

Alkylations.—All but one of the small-scale analytical alkylations were performed in the same general manner, using appropriate changes in conditions. The following depicts a typical experiment.

Benzene (140 ml.) was placed in a flask equipped with a mechanical stirrer, thermometer and adding funnel. The system was protected by a drying tube. After cooling to 6°, aluminum bromide (2.80 g., 0.00525 mole) was added by rapid mechanical transfer from its storage vial. The mixture was stirred for 1–2 minutes during which time the catalyst dissolved, giving a very light yellow solution. A solution of *n*-dodecyl bromide (12.50 g., 0.050 mole) in 35 ml. of benzene then was added over a period of about 2 minutes. Precooling of the alkyl bromide solution and rapid stirring minimized local heating. Upon addition of the first few drops of the bromide solution, the color of the reaction mixture changed to a yellow-orange. At 1, 5, 16 and 60 minutes (time zero being taken at the instant addition was half complete), 15-ml. samples were withdrawn by pipet and immediately quenched in 50 ml. of 3 *N* hydrochloric acid contained in a separatory funnel. Immediately upon contact with the aqueous system, the color of the organic

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[23] A. Streitwieser, Jr., W. D. Schaeffer and S. Andreades, *J. Am. Chem. Soc.*, **81**, 1113 (1959).

[24] An alkylation of benzene in the presence of the very basic aromatic hydrocarbon hexamethylbenzene was attempted. No reaction occurred, presumably because the activity of the aluminum bromide catalyst was seriously reduced through complex formation with the methylated benzene.

[25] E. Clippinger, unpublished results.

mixture disappeared. After vigorous shaking, 25 ml. of pentane was added to minimize emulsion formation; and shaking was continued. The organic layer was washed with 5% sodium bicarbonate solution and water and dried with Drierite. The bulk of the solvent was slowly boiled off on a steam plate. Independent experiments showed that no loss of products or reactants occurred. The remaining solution was analyzed by v.p.c. In some cases, 0.200 ml. of *n*-hexadecane was added during washing as an internal standard for determination of yield by v.p.c.

The one exception to the general procedure occurred in the alkylation of cumene where a two-step alkylation was required to ensure complete reaction.[26] Cumene (50 ml.) was placed in flask equipped as above. After cooling to −15°, aluminum bromide (2.26 g., 0.00424 mole) was introduced. One-half minute thereafter, *n*-dodecyl bromide (6.00 g., 0.0241 mole) was added over a period of 15 seconds. The temperature rose to −11° but returned to −15° within 0.5 minute. After 8 minutes, a 5-ml. sample was removed and analyzed by the above procedure. Reaction was 84% complete. After 11 minutes, the entire mixture was quickly transferred to a freshly prepared solution of aluminum bromide (4.62 g., 0.00866 mole) in 65 ml. of cumene at −15°. Twenty-four minutes later, a sample was removed for analysis. Reaction was 98% complete.

Several preparative scale alkylations were run in the manner just described. The products were distilled. In the case of dodecylbenzene studies, the boiling range was 118–159° (2 mm.). The yields were 88–90%.

Isomerization of Secondary Dodecylbenzenes.—Mixtures of secondary dodecylbenzenes were isomerized to the equilibrium composition in both benzene and petroleum ether. The following describes the study in benzene. A mixture of composition 20.0% 2-phenyl-, 17.1% 3-phenyl- and 62.9% 4- + 5- + 6-phenyldodecane (2.00 g., 0.00812 mole) was placed in 25 ml. of benzene at 25° contained in a flask fitted with a stirrer, thermometer and drying tube. Aluminum bromide (1.017 g., 0.0019 mole) then was added. Hydrogen bromide gas was bubbled through the solution for 1 minute. Samples were withdrawn by the above technique at 13, 100 and 370 minutes. Analysis by v.p.c. showed that all samples had the equilibrium composition. Dealkylation also occurred.

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(26) In the alkylations using these substituted benzenes, the initial reaction was very rapid; but as product was formed, a sharp deceleration or complete cessation of alkylation occurred. Data included in Table III illustrate this behavior. The stability of aluminum halide–aromatic complexes increases as additional alkyl substitution is introduced.[23] Presumably, this rapid decrease in rate reflects a reduction in the efficiently of the catalyst as it becomes complexed with the more highly substituted products.

[CONTRIBUTION FROM CALIFORNIA RESEARCH CORPORATION, RICHMOND 1, CALIF.]

Alkylaromatics. Part II. A Study of the Transfer of Alkyl Groups by Aluminum Bromide–Hydrogen Bromide Catalysis[1]

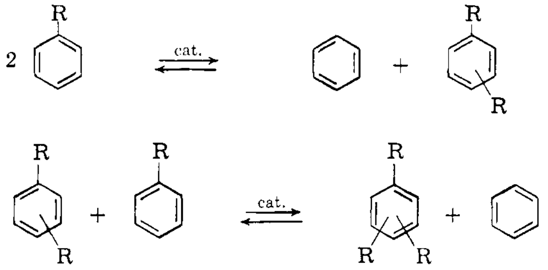
BY SAMUEL H. SHARMAN

RECEIVED MARCH 6, 1962

Dodecylcumenes and dodecylethylbenzenes of high primary isomer content have been prepared by Friedel–Crafts alkylations with *n*-dodecyl bromide. Treatment of these products with aluminum bromide and hydrogen bromide in a large excess of benzene causes selective transfer of secondary alkyl groups. Dodecylcumenes were converted completely to dodecylbenzenes.

Introduction

Disproportionation of alkylbenzenes in the presence of aluminum halide–hydrogen halide or other Lewis acid-type catalysts has long been known.[2] Numerous investigators have reported that under relatively mild conditions, migration of straight chain alkyl groups occurs without rearrangement.[3-9] Brown and Smoot[7] demonstrated that transfer of secondary alkyl groups is much faster than that of primary side chains, *i.e.*, isopropyl >> *n*-propyl. The previous paper in this series[10] reported that Friedel–Crafts alkylation of aromatics occurs with relatively little rearrangement if alkyl-substituted benzenes are employed. In the present work, we have made use of these facts to produce, by a two-stage process, alkylbenzenes with increased primary side chain attachment.



Results and Discussion

Aluminum bromide catalyzed alkylation of ethylbenzene at −20° with *n*-dodecyl bromide produced a dodecylethylbenzene mixture in which about 70% was *n*-dodecylethylbenzene.[10] This alkylation mixture was mixed with a large excess of benzene at 6° containing aluminum bromide and hydrogen bromide. Reaction was followed by v.p.c. analysis of samples withdrawn periodically and quenched by hydrolysis. Alkyl transfer was significant within 7 minutes as shown by the ap-

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(1) Presented in part before the Division of Petroleum Chemistry, 141st Meeting of the American Chemical Society, March 20–29, 1962, Washington, D. C.

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