[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Reaction of Benzene and Toluene with Ethyl, Isopropyl and *t*-Butyl Bromides under the Influence of Aluminum Bromide; the Nature of the Transition State in Alkylation Reactions[1,2]

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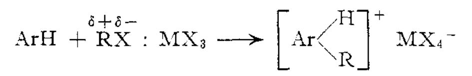
The reactions of benzene and toluene with ethyl, isopropyl and *t*-butyl bromides under the influence of molar quantities of aluminum bromide have been examined. The reactions proved to be extraordinarily rapid, being essentially complete within 0.005 sec. Under the alkylation conditions the products exhibit a marked tendency to undergo both isomerization and disproportionation, complicating the determination of the isomer distribution in the alkylation of toluene and the relative reactivities of toluene and benzene. By running the alkylation reactions with a contact time of 0.005 sec. it was possible to eliminate the disproportionation reaction in the ethylation and isopropylation of the aromatics, but not in the *t*-butylation reaction. It was, therefore, possible to obtain toluene/benzene reactivity ratios for ethylation and isopropylation. However, even at this short reaction time some isomerization occurred in the ethylation of toluene and extensive isomerization in the isopropylation and *t*-butylation of this aromatic. Consequently, isomer distributions could not be established. The toluene/benzene reactivity ratios are: methylation, 2.95; ethylation, 2.4; isopropylation, 1.65. An increase in the ratio would have been anticipated for a reaction involving an attack by carbonium ions of increasing stability: $CH_3^+ < C_2H_5^+ < (CH_3)_2CH^+$. It is considered that the aromatic must be involved in the rate-determining step of the alkylation reaction with a gradual increase in the degree of ionic character in the carbon–halogen bond in the transition state with increasing branching of the alkyl group R.

Considerable stereochemical evidence has been advanced[4-6] pointing to the intermediate formation of carbonium ions[5] in the alkylation of benzene with *sec*-butyl alcohol[4,6] and *sec*-butyl methyl ether.[6] Moreover, there is little doubt that isopropylation and *t*-butylation as carried out by Condon[7,8] with olefins using aluminum chloride in nitromethane or boron trifluoride etherate as catalysts must proceed by ionic mechanisms.

On the other hand, it was observed that the reaction of aromatics with substituted benzyl chlorides under the influence of aluminum chloride involves the aromatic in the rate expression.[9] More recently it has been observed that both the toluene/benzene reactivity ratio and the isomer distribution in the methylation of toluene varies with the nature of the halogen in the methyl halide.[10] Consequently, in these alkylation reactions involving primary halides, it is believed that the reaction cannot be purely ionic and must involve, instead, a displacement reaction by the aromatic on a polarized alkyl halide–metal halide addition compound.[9,10]



$$ArH + \overset{\delta+\delta-}{RX} : MX_3 \longrightarrow \left[Ar\begin{matrix} H \\ R \end{matrix}\right]^+ MX_4^-$$

With increased branching of the alkyl halide there should be observed an increased tendency for the formation and reaction of ionic intermediates. In order to obtain evidence on this point, we undertook an examination of the alkylation of aromatic compounds with ethyl, isopropyl and *t*-butyl bromides under conditions identical with those utilized in our study of the methylation reaction.[10]

Results

The initial experiments which attempted to apply the methylation technique to the reaction of the higher alkyl bromides revealed that, under the methylation conditions, the corresponding ethylation, isopropylation and *t*-butylation reactions are accompanied by considerable disproportionation, resulting in the formation of large quantities of polyalkylated products.[11] Significant isomerization of the reaction products was also observed.

Studies of the isomerization[12] and disproportionation[13] reactions suggested that these side reactions might be controlled by the use of short reaction times. Accordingly, we adopted a flow technique to obtain very short reaction periods.

The ethylation of a mixture of benzene and toluene was carried out with a contact time of 0.5 sec. by mixing in the flow apparatus 8.61 g. (0.0790 mole) of ethyl bromide with a solution of 27.2 g. (0.301 mole) of toluene, 28.1 g. (0.360 mole) of benzene and 58.6 g. (0.110 mole) of aluminum bromide. Even with this short reaction time, the alkylation was complete. Moreover, fractionation of the reaction products indicated the formation of a maximum of 10% polyethyl derivatives. However, isopropylation of a mixture of benzene and toluene under identical conditions resulted in the formation of 40% of polyisopropyl derivatives. Clearly, a reaction time of 0.5 sec. was not satisfactory for the isopropylation reaction.

The flow apparatus was then modified to permit a contact time of 0.005 sec. Under these conditions ethylation and isopropylation proceeded essentially to completion, producing 95 and 87% of the monoalkylated products, respectively. The polyalkylated materials found in the products from these experiments presumably arose in part from dialkylation and in part from a disproportionation reaction.

Results at 0.005 sec. were applied to the determination of the relative reactivities of toluene and

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(1) The Catalytic Halides. XVI.

(2) Based upon a thesis submitted by Hans Jungk in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Standard Oil Company (Indiana) Fellow at Purdue University, 1952–1954.

(4) R. L. Burwell, Jr. and S. J. Archer, THIS JOURNAL, **64**, 1032 (1942).

(5) R. L. Burwell, Jr., L. M. Elkin and A. D. Shields, *ibid.*, **74**, 4570 (1952).

(6) C. C. Price and M. Lund, *ibid.*, **62**, 3105 (1940).

(7) F. E. Condon, *ibid.*, **70**, 2265 (1948).

(8) F. E. Condon, *ibid.*, **71**, 3544 (1949).

(9) H. C. Brown and M. Grayson, *ibid.*, **75**, 6285 (1953).

(10) H. C. Brown and H. Jungk, *ibid.*, **77**, 5584 (1955).

(11) D. A. McCaulay and A. P. Lien, *ibid.*, **75**, 2407 (1953).

(12) H. C. Brown and H. Jungk, *ibid.*, **77**, 5579 (1955).

(13) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 2176 (1956).

TABLE I

ALKYLATION OF BENZENE AND TOLUENE WITH ETHYL, ISOPROPYL AND *t*-BUTYL BROMIDES AT 25°

Reactants[a]					Contact time, sec.	Products[a, b]					Reaction, %	Polyalkyln., %	Relative rate[c]
$C_6H_5CH_3$	C_6H_6	Al_2Br_6	RBr	R		C_6H_6	$C_6H_5CH_3$	RC_6H_5	$RC_6H_4CH_3$	$R_nC_6H_{6-n}$			
0.301	0.360	0.110	0.0790	C_2H_5	0.5	0.162	0.178	0.0138	0.0373	0.006	110	10	2.40
.300	.335	.105	.0798	C_2H_5	.005	.162	.170	.009	.024	.002	92	5	2 30
.561	.561	.187	.126	C_2H_5	.005	.460	.376	.0229	.0471	.0067	82	8	2.40
.157	.157	.0522	.0696	*i*-C_3H_7	.5	.0536	.0529	....	.0115	.0076	96	40	
.592	.592	.197	.211	*i*-C_3H_7	.005	.353	.328	.0736	.1165	.020	96	13	1.65
.696	...	.116	.0830	C_2H_5	.005	....	.242	....	.033	.002	99	6	
.914	...	.161	.0880	*i*-C_3H_7	.005	....	.203	....	.023	.001	96	4	
.714	...	.119	.0420	*t*-C_4H_9	.005	....	.204	....	.014	.005	105	25	

[a] Moles. [b] Results of fractionation of a portion of the reaction products. [c] Calculated from the product distribution (footnote 14).

benzene.[14] Values of 2.40 for ethylation and 1.65 for isopropylation were obtained. Experimental data are summarized in Table I. An attempt was made to extend the study to *t*-butylation. However, even with this short reaction time extensive formation of poly-*t*-butylaromatics was observed.

The alkylation of toluene also was carried out in an attempt to establish the isomer distribution resulting from the alkylation reaction. However, it was observed that under the reaction conditions *p*-ethyltoluene is approximately 7% and *p*-isopropyltoluene is 52% isomerized.[12] Consequently, of the isomer distributions listed in Table II only that for ethylation can be considered to be closely representative of the isomer distribution resulting from the initial substitution reaction.

TABLE II

ISOMER DISTRIBUTION IN THE ALKYLATION OF TOLUENE WITH A CONTACT TIME OF 0.005 SEC.

Alkyl bromide	Isomer distribution, % *p*-	*m*-	*o*-
Ethyl	26.4	46.0	27.6
Isopropyl	14.5	85.5	..
t-Butyl	30.5	69.5	..

The absence of any *o*-isopropyltoluene in the reaction product is interesting in view of the large yields of the *ortho* isomer obtained in isopropylation under non-isomerizing conditions.[7,8] This suggests that the isomerization of the *ortho* isomer must be considerably more rapid than that of the *para*.

Discussion

It was pointed out previously that the methylation of toluene proceeds to completion in approximately 30 sec. at 0°.[10] Since the present reactions are essentially complete in 0.005 sec. at 25°, it would appear that the rates of reaction with ethyl, isopropyl and *t*-butyl bromides must be considerably greater than the rate with methyl bromide.

It should also be noted from Table I that significant amounts of polyalkyl products are obtained under conditions where methylation does not produce detectable amounts of polymethyl products.[10] The absence of significant dimethylation was attributed to the formation of a stable σ-complex which resisted further methylation. In view of the present results, it must be concluded that the failure of methyl groups to participate in a disproportionation reaction under the experimental conditions must also be an important factor in the high yields of monomethylated product.

By using a 0.5 sec. contact time for ethylation, the yield of polyethyl product was reduced to 10%. However, a contact time of 0.005 sec. was required to reduce the disproportionation of isopropyl groups to 4–13%. But even under these conditions, *t*-butylation yielded 25% of poly-*t*-butylated derivatives. Recalling that methyl groups fail to transfer even in much longer reaction times, it is apparent that the ease of disproportionation increases with increasing branching of the alkyl group.[15]

The results, therefore, indicate that the rates of alkylation, of isomerization and of disproportionation all increase sharply with increased branching of the alkyl group R. It is well known that the stability of the carbonium ions, R^+, also increases with increasing branching: $CH_3^+ < C_2H_5^+ < (CH_3)_2CH^+ < (CH_3)_3C^+$. It is, therefore, tempting to ascribe alkylation, isomerization and disproportionation to the participation of such carbonium ions in the mechanism.

However, considerable evidence has been presented previously that methylation cannot proceed through the formation of methylcarbonium ions.[10] Moreover, were carbonium ions involved in the alkylation reaction, the toluene/benzene reactivity ratio should be expected to increase with increasing stability of the carbonium ion.[16] In actual fact the reactivity ratio shows the opposite trend: methylation, 2.95; ethylation, 2.4; isopropylation, 1.65.

On the other hand, if the reaction were primarily a nucleophilic displacement by the aromatic, the rate of alkylation would be expected to decrease in the order: methylation > ethylation > isopropylation > *t*-butylation. However, the results clearly show the opposite trend.

It would appear, therefore, that the transition state is best described in terms of a nucleophilic attack by the aromatic on a strongly polarized alkyl bromide–aluminum bromide addition compound. In the case of methyl bromide, there must be a relatively large nucleophilic contribution by the aromatic, with the carbon–bromine bond in the

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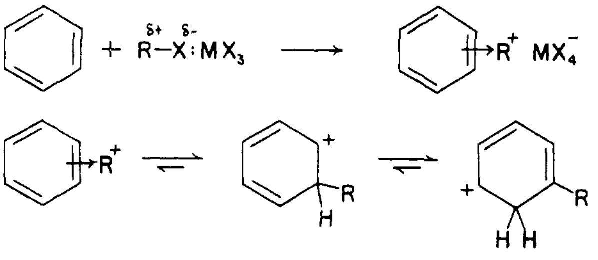
(14) The relative reactivities were calculated using the equation proposed by C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, *J. Chem. Soc.*, 1959 (1931): relative rate = $\log T_0/T/\log B_0/B$.

(15) D. A. McCaulay and A. P. Lien, THIS JOURNAL, **75**, 2411 (1953), have obtained quantitative data in the hydrogen fluoride–boron fluoride system that the rate of transfer of alkyl groups increases sharply in the series: $CH_3 < C_2H_5 < (CH_3)_2CH < (CH_3)_3C$.

(16) H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953).

alkyl bromide retaining a large measure of covalent character. As the alkyl group is changed to ethyl, isopropyl and finally to *t*-butyl, the carbon–halogen bond must become more and more ionic in the transition state with a correspondingly decreasing covalent contribution from the aromatic.[17] At some point in this series we should expect to approach the condition designated by Winstein[17a] as "limiting" with the reaction proceeding through an essentially free carbonium ion.[18]

In the isomerization[12] and disproportionation[13] studies it appeared desirable to postulate a localized π-complex as an intermediate in the reactions. The general similarity between the effect of the structure of R on the rate of alkylation, isomerization and disproportionation suggests the possibility that a similar localized π-complex[19] may be an intermediate in the alkylation reaction. That is to say, the transfer of the alkyl group from the alkyl bromide–metal bromide complex may first occur to form a high energy localized π-complex which then isomerizes to the more stable σ-complex.



(plus isomers)

If the rate of formation of this intermediate represents the rate-determining step in the alkylation reaction and the same intermediate is involved in the isomerization and disproportionation reactions, as previously proposed,[12,13] we should have at hand a simple explanation for the apparent marked similarity in the effect of the structure of the alkyl group R on the rates of the alkylation, isomerization and disproportionation reactions. We hope to investigate this question further.

Experimental Part

Materials.—The alkyl halides were the purest grade materials available commercially. They were fractionated through a column packed with $^1/_{16}''$ glass helices, rated at 50 plates, and stored over Drierite in amber bottles. The material exhibited the following constants: b.p. 38.3° at 746 mm., n^{20}_D 1.4239; isopropyl bromide, b.p. 59.8° at 747 mm., n^{20}_D 1.4247; *t*-butyl bromide, b.p. 73.4° at 744 mm., n^{20}_D 1.4278.

The purification of benzene and toluene has been described previously.[10,12] The purification and handling techniques for aluminum bromide were the same as those reported earlier.[12]

Alkylation Procedure.—The flow reaction device described for the isomerization study[12] was used for the alkylation experiments. By controlling the pressure on the reservoirs containing the reactants and modifying the length of the path between the mixing and quenching chambers, it was possible to obtain reaction times from 0.5 to 0.005 sec.

For the determination of the toluene/benzene reactivity ratio, the aluminum bromide was dissolved in a mixture of benzene and toluene. This solution was mixed in the flow apparatus with the desired alkyl halide and rapidly quenched. The details of operation of the flow apparatus, the quenching procedure, and the methods used in working up the products are similar to those used in the isomerization studies.[12] The distributions of products were determined by fractionating an aliquot of the reaction product in a micro Todd column.

For the determination of the isomer distributions, the same procedure was followed. In these experiments, toluene was the only aromatic present. After fractionation to establish the product distribution, a separate reaction sample was analyzed by infrared to establish the isomer distribution. A compensating technique was used to blank out the excess toluene in the samples.

Experimental details are summarized in Table I.

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[17] According to this interpretation the situation would be quite similar to other nucleophilic displacement reactions of alkyl halides as discussed by (a) S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951), and (b) C. G. Swain and W. P. Langsdorf, *ibid.*, **73**, 2813 (1951).

[18] A more detailed analysis of the nature of the transition state in aromatic alkylation is presented in the following paper: H. Jungk, C. R. Smoot and H. C. Brown, *ibid.*, **78**, 2185 (1956).

[19] M. J. S. Dewar ["Electronic Theory of Organic Chemistry," Oxford University Press, New York, N. Y., 1949, p. 432] originally introduced the concept of a non-localized π-complex as an intermediate in aromatic substitution. As was pointed out earlier (ref. 12) the non-localized structure does not account for the observed characteristics of the isomerization reaction. To account for the phenomena it appears necessary to postulate the participation of a localized π-complex. We wish to emphasize that we consider this π-complex to be a high energy intermediate of considerably lower stability than the σ-complex. On this point our views diverge from those expressed by Dewar.