chloro- and bromobenzene, which are higher than those previously reported for electrophilic brominations,[4] can be explained by steric differences. The incipient bromonium ion in these brominations obviously is less space demanding than a polarized bromine molecule.

Experimental

Materials.—Benzene, halobenzenes, and bromohalobenzenes were commercial materials of highest available purity. They were purified by fractionation in a laboratory column rated at 50 theoretical plates or by repeated crystallization to constant m.p. Their purity was checked by gas–liquid chromatography. Nitromethane was purified as described previously.[1]

Competitive Brominations of Benzene and Halobenzenes. (a) Addition of Neat Bromine.—Competitive brominations were carried out by dissolving 0.125 mole (20 g.) of anhydrous ferric chloride in 50 g. of nitromethane and adding to this solution 0.25 mole each of benzene and the competing halobenzene. Bromine (0.05 mole, 8 g.) was then added dropwise to the stirred solution in a constant temperature bath at 25 ± 0.5°. The reaction mixture was stirred for 10 min. after the addition of the bromine was completed. The reaction mixture was then washed with water, three times with a 100-ml. portion of 5% NaOH solution, and again with water. After drying over $CaCl_2$, the solutions were analyzed by gas–liquid chromatography.

In order to avoid certain difficulties in separation of bromobenzene from bromofluorobenzenes and also to check the relative rate data by a second set of experiments, in addition to the direct competition of the halobenzenes with benzene, competition of chlorobenzene with fluorobenzene and that of chlorobenzene with bromobenzene were also determined.

Addition of neat bromine as brominating agent in the competitive brominations with benzene resulted in dibromobenzene also being formed, in amounts as high as 25% of that of bromobenzene. No dibromohalobenzenes were observed. Conversions based on bromine used were practically quantitative.

(b) Addition of Nitromethane Solution of Br_2 + $FeCl_3$.—Competitive brominations were carried out by dissolving 0.1 mole (16 g.) of anhydrous ferric chloride in 40 g. of nitromethane and adding to this solution 0.05 mole (8 g.) of bromine. This solution was then added dropwise to a stirred solution of 0.25 mole of each of benzene and the competing halobenzene in 40 g. of nitromethane. The reaction mixture was stirred for a total of 20 min. in a constant temperature bath at 25 ± 0.5°. The reaction mixture was then washed twice with water. After drying over $CaCl_2$, the solutions were analyzed by gas–liquid chromatography. No dibromobenzene or dibromohalobenzene formation was observed in any of the brominations. Conversions to monobrominated products, based on bromine used, were practically quantitative.

Analytical Procedure.—Gas–liquid chromatography was carried out on Perkin–Elmer Model 154-C and 154-D vapor fractometers, using thermistor and flame ionization detectors, respectively, equipped with Perkin–Elmer Model 194 electronic printing integrators. A 4-m. by 0.25-in. stainless steel column packed with polypropylene glycol (UCON LB 550-X) supported on diatomaceous earth or polypropylene coated 150 ft. by 0.01 in. Golay columns were used. The column temperature on the packed column was 180° for all bromohalobenzene determinations except for the determination of the isomer ratio of fluorobromobenzenes, which was carried out at 150°; 60 ml. of hydrogen per minute was used for carrier gas. Samples of 100 μl. were generally injected.

The column temperature of the capillary Golay column was 100° for all bromohalobenzene determinations. Helium was used as the carrier gas. Samples of 10 μl. were generally injected.

Relative response data were determined by making up known solutions of the halobromobenzenes with bromobenzene in excess benzene in ratios approximating those occurring in the reaction mixtures and determining the response per mole relative to bromobenzene.

Observed retention times of the bromohalobenzenes are given in Table VI.

TABLE VI

RETENTION TIMES OF THE BROMOHALOBENZENES

Compound, benzene	Retention times, min. Packed column at 180°	Retention times, min. Golay column at 100°
Bromo	7	18
o-Fluorobromo-	13 (at 150°)	19
p-Fluorobromo-	11	17
o-Chlorobromo-	16	46
p-Chlorobromo-	14	39
o-Dibromo-	26	76
p-Dibromo-	22	64

No *m*-isomers were detected by gas–liquid chromatography or by infrared spectroscopy (using the analytical wave lengths of 12.95 μ for *m*-bromofluorobenzene, 12.96 μ for *m*-bromochlorobenzene, and 12.98 μ for *m*-dibromobenzene). Therefore, even if present the amount of *m*-isomer must be less than 0.2%.

[CONTRIBUTION NO. 76 FROM THE EXPLORATORY RESEARCH LABORATORY, DOW CHEMICAL OF CANADA, LTD., SARNIA, ONTARIO, CAN.]

Aromatic Substitution. XVI.[1] Friedel–Crafts Isopropylation of Benzene and Methylbenzenes with Isopropyl Bromide and Propylene

BY GEORGE A. OLAH, SYLVIA H. FLOOD, STEPHEN J. KUHN, MARYANNE E. MOFFATT, AND NINA A. OVERCHUCK

RECEIVED AUGUST 31, 1962

Friedel–Crafts isopropylation of benzene and the methylbenzenes was investigated with isopropyl bromide and propylene. Competitive isopropylations with a variety of catalysts in homogeneous organic solutions (nitromethane, tetramethylene sulfone, sulfur dioxide, carbon disulfide) showed low substrate ($k_{toluene}:k_{benzene}$ = ~2), but higher positional selectivity. Relative rates and isomer distributions were determined by gas–liquid chromatography. The relative reactivities of the investigated methylbenzenes showed good agreement with π- but not with σ-complex stabilities of the substrates. The isomer distribution of the isopropyltoluenes formed was found to be *ortho* 44–60%, *para* 25–40%, while the amount of *m*-isomer in general was 14–18%. Isopropylation of *m*-xylene gave the 4- and 2-isopropyl isomers, with the amount of 5-isopropyl-*m*-xylene not exceeding 10%. $AlCl_3 \cdot CH_3NO_2$ catalyzed isopropylations with isopropyl bromide in nitromethane solution showed considerably increased steric requirements over similar alkylations with propylene. No 2-isopropyl-*m*-xylene was formed with the former alkylation system in isopropylation of *m*-xylene and the relative reactivity of mesitylene was less than one-tenth of that observed in isopropylation with propylene. A small secondary kinetic isotope effect was observed in the isopropylation of benzene-d_6. The reaction mechanism of the investigated isopropylations is discussed.

Introduction

For some time the alkylation of aromatics was believed to involve formation of alkyl carbonium ions, which then attacked the aromatic ring.[2]

More recently evidence has been accumulating which indicates that many alkylations, particularly those with primary alkyl halides, involve displacement by the aromatic ring of the α-carbon atom of the alkyl derivative–catalyst complex.[3]

Orientations in Friedel–Crafts alkylations were frequently considered to be anomalous.[2,4] For a long

(1) Part XV: *J. Am. Chem. Soc.*, **86**, 1044 (1964).

(2) C. C. Price, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946; C. C. Price, *Chem. Rev.*, **29**, 37 (1941).

(3) (a) H. C. Brown and M. Grayson, *J. Am. Chem. Soc.*, **75**, 6285 (1953); (b) L. Schmerling, *Ind. Eng. Chem.*, **45**, 1447 (1965); (c) H. C. Brown and H. Jungk, *J. Am. Chem. Soc.*, **77**, 3584 (1955); (d) H. Jungk, C. R. Smoot, and H. C. Brown, *ibid.*, **78**, 2185 (1956); (e) C. R. Smoot and H. C. Brown, *ibid.*, **78**, 6249 (1956).

time it was difficult to explain directive effects in alkylation of aromatics. Temperature, solvent, nature and amount of catalyst seem to have a large effect on the orientation of the products formed.

Alkylation of alkyl aromatics with alkyl halides, olefins, and other alkylating agents in the presence of Lewis acid type metal halide catalysts (aluminum, gallium halides, etc.) generally leads to the formation of considerable amounts of the *m*-dialkyl isomers.[5] The formation of larger quantities of *m*-isomers than those obtained at thermodynamic equilibrium were found in alkylations using molar or larger quantities of catalysts.[6] It was proposed that the large yield of the *m*-isomer arises from isomerization of the *o*- and *p*-isomers to the more stable σ-complexes formed by the *m*-dialkylbenzenes.[7]

Brown has suggested that the relatively high proportions of *m*-isomers in the Friedel–Crafts alkylation of toluene and other alkylbenzenes under nonisomerizing conditions is a consequence of a high reactivity resulting in a low selectivity aromatic electrophilic substitution reaction.[5d,e] Based on available data, it was suggested that the relative yields of *m*- isomer vary in a regular and predictable manner with the *activity* of the attacking agent. In a sense then, the high yields of the *m*-isomer are not an anomalous property of the Friedel–Crafts alkylation, but a consequence of the low selectivity (both substrate and positional) substitution reaction.

Data obtained with alkylation systems were used to establish the linear free energy relationship known as the "selectivity relationship."[5d,e,8]

In a previous study of the benzylation of alkylbenzenes with benzyl[9] chloride we were able to show that low substrate selectivity alkylation does not necessarily mean a low positional selectivity. We demonstrated that *ortho–para* direction (only relatively small amounts of *m*-isomer were formed) was maintained in these low substrate selectivity Friedel–Crafts benzylations.

Similar results were also obtained for the nitronium tetrafluoroborate nitration of alkylbenzenes in tetramethylene sulfone solution.[10]

To investigate further the question of positional and substrate selectivity in electrophilic aromatic substitution, the Friedel–Crafts isopropylation of benzene and toluene has been studied with isopropyl bromide and propylene in the presence of different catalysts and solvents. An attempt was made to carry out the reactions with the smallest possible degree of isomerization.

Results and Discussion

The experimentally reported isomer distribution in the isopropylation of toluene with the lowest *m*-isomer ratio according to the kinetic work of Brown and co-workers,[5e] using gallium bromide as catalyst in excess toluene or 1,2,4-trichlorobenzene as solvent and isopropyl bromide as alkylating agent at 25°, was 26.2% *o*-, 26.6% *m*-, and 47.2% *p*-isopropyltoluene. The same isopropylation showed also low substrate selectivity $k_{\text{toluene}}:k_{\text{benzene}} = 1.82$.

Allen and Yats[11] recently reviewed the present status of concurrent alkylation and isomerization of alkylbenzenes with alkyl halides, olefins, and alcohols in excess aromatics as solvent (diluent). They concluded that all isopropylations of toluene investigated could have been obtained by alkylations producing the isomeric mixtures with an average "nonisomerized" isomeric composition of 42% *o*-, 21.5% *m*-, and 36.5% *p*- isomer and subsequent isomerization of the mixtures.

Allen came to the conclusion that in the alkylation of toluene the particular catalysts and alkylating agents used influence the extent of isomerization that accompanies the alkylation. For the isomer distributions investigated, the ratio of *para* to *meta* substitution is constant within experimental error, indicating that methylation, ethylation, and isopropylation have the same positional selectivity.

The comparison of many reported alkylation data with varying amounts of *m*-isomer support the conclusions of Allen insofar as accompanying isomerization seems to be a major factor in all reported isopropylations of alkylbenzenes. The calculated, "nonisomerized" isomer distribution values, however, when compared with other typical electrophilic aromatic substitutions, still indicate, due to relatively high *m*- and low *o*-isomer values, that the influence of concurrent or consecutive isomerization was probably not completely absent. The *o*-isomer value (42%) seems to be too low, whereas the *m*-isomer value (21.5%) seems too high for a typical electrophilic aromatic substitution of toluene where steric hindrance is not of major importance.

Both Brown's and Allen's alkylations were carried out in systems using excess of aromatics as solvent or a very weakly basic solvent, as 1,2,4-trichlorobenzene. Even if these systems are homogeneous (as in the case of gallium halide catalysts) they are very well suited for the formation of ternary aromatic–reagent–catalyst complexes (σ-complexes). It has been proved that activated states of the same nature are involved in the isomerization of dialkylbenzenes leading to increased amounts of *m*- and decreased amounts of *o*-isomers.

Isomer distributions could be seriously influenced by concurrent isomerization, as well as by steric factors involving heterogeneous systems with bulky catalyst–reagent complexes. To prove this point, a synthetic mixture of benzene, toluene, and isomeric cymenes (containing 43.6% *o*-, 13.8% *m*-, and 42.6% *p*- isomer) was treated in 1,2,4-trichlorobenzene solution with aluminum chloride at 25° for 15 min. (in concentrations used in the present alkylation work). After recovery of the material, gas–liquid chromatographic analysis showed an isomer distribution of 1.5% *o*-, 60.4% *m*-, and 38.1% *p*-cymene with a substantial (52%) amount of higher alkylates present (probably due to disproportionation). As a result of isomerization, the amount of *m*-isomer substantially increased, whereas that of the *ortho* decreased. Intermolecular transalkylations were also observed. This experiment clearly indicated the difficulties involved in obtaining rate data from isopropylation systems using a weakly basic solvent or only excess aromatics as solvent (where similar substantial isomerization is observed). In connection with the $AlCl_3 \cdot CH_3NO_2$ catalyzed benzylation of aromatics with benzyl chloride[9] we have expressed our view of factors influencing isomerization in alkylation systems. The proper choice of catalyst and solvent are essential in these systems and excess aromatics or very weakly basic solvents generally seem insufficient to provide nonisomerizing conditions.

(4) A. W. Francis, *Chem. Rev.*, **43**, 257 (1948).

(5) (a) K. T. Serijan, H. F. Hipsher, and L. C. Gibbons, *J. Am. Chem. Soc.*, **71**, 873 (1949); (b) J. H. Simons and H. Hart, *ibid.*, **69**, 979 (1947); (c) F. E. Condon, *ibid.*, **71**, 3544 (1949); (d) H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953); (e) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956); (f) S. U. Choi and H. C. Brown, *ibid.*, **81**, 3315 (1959).

(6) D. A. McCaulay and A. P. Lien, *ibid.*, **74**, 6246 (1952).

(7) (a) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951); (b) H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).

(8) (a) K. L. Nelson, *J. Org. Chem.*, **21**, 145 (1956); (b) L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **81**, 3323 (1959).

(9) G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **84**, 1688 (1962).

(10) G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **83**, 4571 (1961).

(11) R. H. Allen and L. D. Yats, *ibid.*, **83**, 2799 (1961).

In continuation of our work we have carried out isopropylation of toluene and benzene with isopropyl bromide and propylene in the solvents nitromethane, tetramethylene sulfone, sulfur dioxide, and carbon disulfide, and in the presence of a variety of catalysts. The data obtained are summarized in Tables I and II (for ratios of reagents and experimental details see Experimental part). All data were taken from an average of at least three parallel experiments.

Table I

Competitive Isopropylation of Toluene and Benzene with Isopropyl Bromide at 25° (Homogeneous Conditions)

Catalyst	Solvent	$k_T:k_B$	Isopropyltoluene, %: o-	m-	p-	ortho:para
$AlCl_3$	CH_3NO_2	2.03	46.7	14.7	38.6	1.20
$GaCl_3$	CH_3NO_2	1.68	46.9	17.4	35.7	1.31
$FeCl_3$	CH_3NO_2	2.21	44.8	15.5	39.7	1.12
$TiCl_4$	CH_3NO_2	2.19	43.6	13.6	42.8	1.02
$SnCl_4$	CH_3NO_2	2.77	46.0	17.2	36.8	1.25
$AgClO_4$	CH_3NO_2	2.24	46.9	15.5	37.6	1.24
$AgBF_4$	CH_3NO_2	2.19	46.1	14.6	39.3	1.15
$AgPF_6$	CH_3NO_2	2.03	44.6	18.0	37.4	1.19
$AgSbF_6$	CH_3NO_2	1.93	47.2	14.5	38.2	1.24
$AgAsF_6$	CH_3NO_2	1.82	46.2	16.6	37.2	1.24
$AlCl_3$	TMS[a]	1.92	42.4	18.4	39.2	1.08
$SnCl_4$	TMS	2.88	39.4	14.3	46.3	0.85
$AgSbF_6$	TMS	2.35	47.8	14.8	37.4	1.28
$AlCl_3$	SO_2[b]	1.41	46.6	12.3	41.1	1.13
$TiCl_4$	CS_2	2.54	56.2	13.5	30.3	1.86

[a] TMS = tetramethylene sulfone. [b] At −10°.

Table II

Competitive Isopropylation of Toluene and Benzene with Propylene at 25°

Catalyst	Catalyst concn., mole	Solvent	Reaction time, min.	$k_T:k_B$	Isopropyltoluene, %: o-	m-	p-
$AlCl_3$	0.02	CH_3NO_2	15	1.96	46.1	15.1	38.8
$FeCl_3$	.02	CH_3NO_2	15	2.01	44.4	16.9	38.8
$SnCl_4$	.02	CH_3NO_2	15	1.96	43.9	15.3	40.8
$GaCl_3$	.02	CH_3NO_2	15	1.78	43.9	16.4	39.7
100% H_2SO_4	.02	CH_3NO_2	15	2.67	45.1	14.8	40.1
70% $HClO_4$	.05	CH_3NO_2	30	2.70	45.7	15.7	38.6
100% HF	.1	CH_3NO_2	60	2.08	44.1	18.3	37.6
100% H_2SO_4	.1	TMS	30	3.27	47.2	17.0	35.8
100% H_2SO_4 (−10°)	.02	SO_2	15	1.45	44.2	14.4	41.4

In acetonitrile solution the isopropylation of toluene with $AlCl_3$ catalyst gave an isomer distribution of 62.4% *o*-, 12.3% *m*-, and 25.2% *p*-cymene. However, the more basic the solvent, the lower the yields obtained. The acetonitrile solvent system gives difficulties in reproducibility and in many runs failed to give even vapor phase chromatographically detectable alkylation products.

The isomer distributions and relative rates (obtained from competitive experiments) were determined by gas–liquid chromatography, using a Golay-type capillary column and hydrogen flame ionization detector. Details of the analytical determination and the alkylation conditions are described in the Experimental part. Using a homogeneous alkylation system (in which no separate alkylate layer was formed) and a constant large excess of aromatics, little di- or higher alkylation was observed to take place (no more than 5% of monoalkylates in any of the investigated cases).

Based on data obtained on mixtures of known compositions (see Table IX), our analytical method—even considering the difficulty to separate dialkylbenzene isomers—was reliable to ±5 relative per cent for the *o*- and *p*-isomers, but the error of determination is higher (in certain instances as high as 20 relative per cent) for the *m*-isomer present in smaller amounts.

Another condition which needs to be carefully checked is the homogeneity of the alkylation systems. Using slightly higher catalyst concentrations than those in the experiments of Table I (0.1 mole or higher instead of 0.05 or 0.02 mole, respectively) gave with certain silver salts, such as $AgSbF_6$, heterogeneous reaction conditions. Under these conditions the *ortho*:*para* ratio was generally higher than in related homogeneous systems. A typical $AgSbF_6$–*i*-C_3H_7Br system gave the isomer distribution: *ortho* 59.6%, *meta* 14.7%, and *para* 25.7%. It must be concluded that in homogeneous solution the solvation of the alkylating agent (*i*-C_3H_7Br:$AgSbF_6$) is more complete and, owing to increased steric requirements, gives somewhat lower *o*-isomer ratios.

Competitive isopropylation of benzene, toluene, xylenes, and trimethylbenzenes was investigated in detail both with isopropyl bromide and propylene in nitromethane solution at 25°, using $AlCl_3 \cdot CH_3NO_2$ as catalyst. The data obtained are summarized in Tables III and IV.

Table III

$AlCl_3 \cdot CH_3NO_2$ Catalyzed Isopropylation of Benzene and Methylbenzenes with Isopropyl Bromide in Nitromethane Solution at 25°

Aromatic	$k_{Ar}:k_{benzene}$	Isomeric isopropylmethylbenzenes,[a] %
Benzene	1.00	
Toluene	2.03	1,*2*-, 46.7; 1,*3*-, 14.7; 1,*4*- 38.6
o-Xylene	2.21	1,2,*4*-, 54.2; 1,2,*3*-, 45.8
m-Xylene	2.80	1,3,*4*-, 89.4; 1,3,*5*-, 10.6
p-Xylene	2.70	1,*2*,4-, 100
Benzene		
1,2,3-Trimethyl-	4.31	1,2,3,*4*-, 65.2; 1,2,3,*5*-, 34.8
1,2,4-Trimethyl-	3.25	1,2,4,*5*-, 58.5; 1,2,4,*6*-, 41.5
1,3,5-Trimethyl-	0.35	1,*2*,3,5-, 100

[a] Position of isopropyl group italicized.

Table IV

$AlCl_3 \cdot CH_3NO_2$ Catalyzed Isopropylation of Benzene and Methylbenzenes with Propylene in Nitromethane Solution at 25°

Aromatic	$k_{Ar}:k_{benzene}$	Isomeric isopropylmethylbenzenes,[a] %
Benzene	1.00	
Toluene	1.95	1,*2*-, 46.1; 1,*3*-, 15.1; 1,*4*-, 38.8
o-Xylene	1.73	1,2,*4*-, 59.9; 1,2,*3*-, 40.1
m-Xylene	2.49	1,*2*,3-, 15.8; 1,3,*4*-, 74.0; 1,3,*5*-, 10.2
p-Xylene	2.29	1,*2*,4-, 100
Benzene		
1,2,3-Trimethyl-	3.98	1,2,3,*4*-, 67.8; 1,2,3,*5*-, 32.2
1,2,4-Trimethyl-	2.75	1,2,*3*,4-, 24.5; 1,2,4,*5*-, 44.4 1,2,4,*6*-, 31.1
1,3,5-Trimethyl-	3.31	1,*2*,3,5-, 100

[a] Position of isopropyl group italicized.

The method of competitive reaction rate determination can be applied only if the observed relative rates are dependent on the aromatic substrate. Since the observed relative rates showed only small substrate selectivity, it could have been attributed, as discussed in previous papers of this series, to a fast reaction influenced rather by statistical factors than real competition. In order to clarify this possibility and also to determine the accuracy of the method used, we carried out experiments to establish whether real competition actually occurs under the experimental conditions. Changing the concentration of either of the

aromatic components in competitive experiments in nitromethane solution from the 1:1 ratio to 9:1 and 1:9, respectively, showed that the relative rate ratio remains almost unchanged if a first-order dependence in aromatics is accepted (Tables V and VI).

TABLE V

CONCENTRATION VARIATION IN COMPETITIVE ISOPROPYLATION OF TOLUENE–BENZENE WITH ISOPROPYL BROMIDE + $AlCl_3 \cdot CH_3NO_2$ IN NITROMETHANE SOLUTION AT 25°

Ratio of toluene:benzene		Obsd. relative rate	$k_T:k_B$
1	9	0.19	1.71
1	4	.51	2.04
1	2	.95	1.89
1	1	2.03	2.03
2	1	4.00	2.00
4	1	8.40	2.10
9	1	20.25	2.25
		Average	2.01

TABLE VI

CONCENTRATION VARIATION OF TOLUENE AND BENZENE IN COMPETITIVE ISOPROPYLATION WITH PROPYLENE + $AlCl_3 \cdot CH_3NO_2$ NITROMETHANE SOLUTION AT 25°

Ratio of toluene:benzene		Obsd. relative rate	$k_T:k_B$
1	9	0.19	1.74
1	4	0.46	1.84
1	2	1.02	2.04
1	1	1.95	1.95
2	1	3.74	1.87
4	1	8.64	2.16
9	1	20.61	2.29
		Average	1.98

Consequently it can be stated that the observed relative rates are real and represent direct competition of the substrates (toluene–benzene).

In nitromethane solution, as well as in the other basic solvents, isopropylation reactions are considerably slower than those carried out in excess aromatics or 1,2,4-trichlorobenzene solution. In order to carry out competitive alkylations, a 10:1 aromatics:isopropyl bromide ratio was used. It was found that the amount of $AlCl_3$ catalyst needed in nitromethane solution to obtain a sufficient (~30%) conversion was equimolar with that of the isopropyl bromide. Using a smaller amount of catalyst decreased the amount of product (Table VII) without affecting, however, either relative rates or isomer distributions.

TABLE VII

EFFECT OF CONCENTRATION VARIATION OF ALUMINUM CHLORIDE ON PRODUCT YIELD IN COMPETITIVE ISOPROPYLATION OF TOLUENE AND BENZENE IN CH_3NO_2 SOLUTION AT 25°

Toluene, mole	Benzene, mole	$AlCl_3$, mole	Isopropyl bromide, mole	$k_T:k_B$	—Isomer cymenes, %— o-	m-	p-	Conversion to monoalkylate, %
0.25	0.25	0.0125	0.05	2.02	44.8	14.8	40.8	6.6
.25	.25	.025	.05	2.18	45.3	13.5	41.2	14.2
.25	.25	.05	.05	2.07	45.2	14.5	40.5	30.5

The 1:1 halide:catalyst ratio seems to represent conditions suitable for the formation of the R–Br–$AlCl_3$ complex (solvated in nitromethane). However, it should pointed out that no free aluminum chloride capable of coordination with isopropyl bromide is present in the system. $AlCl_3$ in nitromethane solution forms the stable complex $CH_3NO_2 \cdot AlCl_3$. Therefore, any interaction with the reagent must involve the catalyst–solvent complex. The linear change of conversion with catalyst concentration does not unambiguously mean first-order dependence of the reaction on the isopropyl bromide–aluminum chloride complex because, owing to competition of complexing of the aluminum halide with CH_3NO_2, the reagent–catalyst complexing may be very incomplete even in the case of the 1:1 ratio (as indicated by the relatively low, 30% conversion).

Isopropylations with propylene gave even lower conversions (based on propylene) than those with isopropyl bromide, probably due to the higher volatility of the reagent at the reaction temperature. The applied higher propylene:aromatic hydrocarbon ratios, therefore, represented not more than 10–15% conversion, with the amount of dialkylate again being less than 5% of the monoalkylate.

The effect of reaction time on the isopropylation reactions was also investigated in the case of the $AlCl_3$-catalyzed competitive isopropylation of toluene and benzene with isopropyl bromide in nitromethane solution of 25°. The data are summarized in Table VIII.

TABLE VIII

EFFECT OF REACTION TIME ON THE $AlCl_3 \cdot CH_3NO_2$ CATALYZED ISOPROPYLATION OF TOLUENE AND BENZENE WITH ISOPROPYL BROMIDE IN NITROMETHANE SOLUTION AT 25°

Reaction time, min.	$k_{toluene}:k_{benzene}$	—Isomer distribution, %— o-	m-	p-	Conversion to monoalkylate, %
20	2.12	44.1	15.3	40.5	65.9
15	2.06	44.3	14.6	41.1	30.5
10	2.12	46.2	13.3	40.5	24.7
5	1.94	45.8	13.8	40.4	11.6
3	1.91	44.8	14.3	41.9	3.5
1	1.95	43.0	15.4	41.6	1.1

Neither the relative reactivities nor isomer distributions changes significantly by varying the reaction time from 1 to 20 min. At the same time, over-all conversion (as measured against an internal reference of known concentration, cyclohexane) increases from 1 to 66%.

The material balance of the isopropylation of toluene and benzene with 15-min. reaction time was established both from gas–liquid chromatographic analysis (using the internal reference method) and by mass spectroscopic analysis. Besides the product cymenes (present in about 30% conversion) there was about 1.5% (or 5% of the monoalkylate) of diisopropyltoluenes, but practically no higher alkylates or condensates. The remainder was unchanged toluene, benzene, and isopropyl bromide. It was possible to account for almost 98% of the over-all material.

Aluminum chloride in nitromethane solution (or related basic solvents) is incapable of effecting isomerization of cymenes. When a synthetic reaction mixture approximating the average composition was treated in nitromethane solution with aluminum chloride (in the presence of added co-catalytic amount of HCl) for the usual reaction time, no isomerization was observed. After recovery of the aromatic material it was analyzed by gas–liquid chromatography. In Table IX the observed composition after $AlCl_3$ treatment is compared with the original composition of the mixture.

The data of Table IX also indicate the accuracy of the analytical method. The largest source of error is in the determination of relatively small amounts of *m*-cymene in the presence of the *o*- and *p*-isomers.

TABLE IX

EFFECT OF $AlCl_3$ ON SYNTHETIC REACTION MIXTURE IN NITROMETHANE SOLUTION AT 25°

	Compn. of synthetic mixt., mole %	Compn. of mixt. based on g.l.c. analysis, mole %	Compn. of mixt., based on g.l.c. analysis, after treatment with $AlCl_3$ in CH_3NO_2 soln., mole %
Benzene	34.6	35.9	34.3
Toluene	36.7	36.8	38.1
Cumene	9.8	9.6	9.3
Total cymenes	18.9	17.7	18.3
% *o*-	43.6	44.5	44.5
% *m*-	13.8	11.6	11.3
% *p*-	42.6	44.9	44.0
Diisopropylated products	None	None	None

A possible source of error in the competitive isopropylations of benzene and alkylbenzenes could be due to formation of a certain amount of diisopropylated products (generally not more than 5% of the monoalkylate). If one of the isomeric isopropyl alkylbenzenes should react substantially faster than the others to form the diisopropylated product, this could lead to a substantial decrease of the isomer in the reaction mixture. Thus, for example, if during the isopropylation of toluene the *m*-cymene should react faster than the *o*- and *p*-isomers (as is expected on a theoretical basis) there would be a substantial decrease in the amount of *m*-cymene in the alkylation mixtures. To evaluate the effect of the difference in alkylation rates of the isomeric cymenes we have determined their reactivities (relative to benzene) in the $AlCl_3$·CH_3NO_2 catalyzed isopropylations with isopropyl bromide. The data obtained are summarized in Table X.

TABLE X

$AlCl_3$·CH_3NO_2 CATALYZED COMPETITIVE ISOPROPYLATION OF CYMENES AND BENZENE WITH ISOPROPYL BROMIDE IN NITROMETHANE AT 25°

Aromatic	$k_{Ar}:k_{benzene}$	Isomer distribution of diisopropyltoluenes,[a] %
Benzene	1.00	
o-Cymene	3.42	*1*,2,4-, 36.5; *1*,2,-3, 37.4; 1,2,5-, 26.1
m-Cymene	3.50	*1*,3,6-, 20.3; *1*,3,4-, 61.2; 1,3,5-, 18.5
p-Cymene	2.82	*1*,2,4-, 94.4; *1*,3,4-, 5.6

[a] Position of methyl group italicized.

Accordingly, although *p*-cymene reacts slightly more slowly, *o*-cymene is isopropylated at practically the same rate as *m*-cymene. The error caused by secondary selective alkylation of *m*-cymene consequently cannot be significant.

As may be seen from the data of Tables I and II the choice of both catalyst and solvent markedly influences isomer distributions and relative rates. Using only an excess of aromatics as solvent causes both intra- and intermolecular isomerization (disproportionation). Table XI summarizes the isomer distribution of isopropyltoluenes found in alkylations with isopropyl bromide with a variety of 44 catalysts using only excess of toluene as solvent.

Whereas strong Lewis acids like aluminum, ferric, and zirconium halides cause substantial isomerizations (as indicated by increased amounts of *meta* and decreased amount of other isomers), weaker acid catalysts gave isomer ratios comparable with those obtained in homogeneous nitromethane solutions.

Because of substantial intermolecular isomerization (transalkylation) no attempt was made to determine the relative reactivities over benzene in these systems.

TABLE XI

ISOMER DISTRIBUTION OF THE ISOPROPYLATION OF TOLUENE WITH ISOPROPYL BROMIDE AT 25° (HETEROGENEOUS REACTION CONDITIONS, EXCESS TOLUENE AS DILUENT)

	Isopropyltoluene, %				Isopropyltoluene, %		
Catalyst	*o*-	*m*-	*p*-	Catalyst	*o*-	*m*-	*p*-
$AlCl_3$	3	61	36	$SbCl_5$	46	20	34
$AlBr_3$	2	64	34	$SbBr_3$	28	12	60
AlI_3	9	57	34	$SnCl_4$	44	19	37
$AuBr_3$	44	14	42	$TaCl_5$	39	21	40
$AuCl_3$	44	29	37	$ThCl_4$	32	12	56
BBr_3	54	14	32	TiF_4	45	18	37
BI_3	42	21	37	$TiCl_4$	42	21	37
$BeCl_2$	34	17	49	$TiBr_4$	44	20	36
$BiCl_3$	47	21	32	$TiCl_3$	44	20	36
$CdCl_2$	38	18	44	$ZnCl_2$	45	17	38
$CdBr_2$	37	17	46	$ZnBr_2$	48	17	34
$FeCl_3$	47	15	38	ZnI_2	42	21	37
$FeBr_3$	27	30	43	$ZrCl_4$	36	36	28
FeI_3	43	20	37	$ZrBr_4$	37	28	35
$GaCl_3$	3	67	30	ZrI_4	43	21	36
$HfCl_4$	44	15	41				
$InCl_3$	42	23	35	HBr	50	11	39
$InBr_3$	42	22	36	I_2	30	11	59
InI_3	34	29	37	$AgBF_4$	45	14	41
$MoCl_5$	44	17	39	$AgClO_4$	42	13	45
$NbCl_5$	40	21	39	$AgPF_6$	46	15	39
$RuCl_3$	44	14	42	$AgSbF_6$	7	53	40
$SbCl_3$	28	14	58				

The observed relative reactivities of benzene and methylbenzenes obtained in competitive isopropylations in nitromethane solution show good agreement with relative stabilities of complexes of alkylbenzenes with Ag^+, Br_2, I_2, ICl, SO_2, tetracyanoethylene, picric acid, HCl, and HF, which are considered as π-complex-forming agents, but not with relative stabilities of HF + BF_3, $AlCl_3$ + HCl, $AlBr_3$ + HBr complexes, considered as σ-complex-forming agents (corresponding basicity data were summarized in previous publications of this series).

It thus appears that isopropylation of methylbenzenes in homogeneous solutions gives relative rates which correspond to relative π-complex but not to σ-complex stabilities.

Isopropylations of toluene carried out in homogeneous organic solutions show *ortho–para* directing effects, the amount of *m*-isomers being in general 14–18% (Tables III and IV). The directing effects of isopropylations of xylenes and trimethylbenzenes show also predominant *ortho–para* orientation.

No disproportionation was observed in any of the systems, and dialkylation, although not entirely excluded in all cases, was less than 5% of over-all alkylation, thus not affecting the results seriously. Concurrent intramolecular isomerization may be affecting, in the case of isopropylation of methylbenzenes, the observed isomer ratios, and is difficult to exclude on the basis of the available experimental data. (The probability of consecutive isomerization can be fairly well excluded based on the data of Tables VIII and IX.)

Our values for the relative reactivity of toluene and benzene in isopropylation show close correspondence with Brown's data, both indicating low substrate selectivity. Our data of isomer distributions, however, show higher positional selectivity.

There is one basic difference between the isopropylation procedure used by Brown and co-workers and that reported herein. We have employed sufficiently basic solvents, *e.g.*, nitromethane, to avoid the possibility of stable σ-complex formation and subsequent isomerization. It was observed that in these solvents no

stable σ-complexes were formed from any of the polyalkylbenzenes with strong acids, such as HF + BF_3, which are otherwise well known to be capable of ring protonation. This technique in our opinion helped to eliminate product isomerization, but at the same time may here also affect the activity or selectivity of the potential dimethylcarbonium ion or its precursors. This is clearly indicated by the slowness of the isopropylation reactions in nitromethane, as compared with measured fast reactions (Brown and co-workers) using excess aromatics or 1,2,4-trichlorobenzene as solvent.[12] The second-order rate constants of the aluminum chloride catalyzed isopropylation of toluene, and benzene with isopropyl bromide in nitromethane solution at 25° are k_2(toluene) = 2.8×10^{-4} l. mole^{-1} sec.$^{-1}$ and k_2(benzene) = 1.7×10^{-4} l. mole^{-1} sec.$^{-1}$, respectively.[13]

Consequently, we should not attempt to draw a parallel between the isomer distribution in our system and those obtained from other systems, wherein the activity of the carbonium ion may have been much higher, resulting in a direct kinetically controlled, but much less discriminate alkylation to produce more *m*-isomer.

Isopropylation of di- and trimethylbenzenes also shows low substrate (as compared with benzene), but higher positional selectivity, following predominantly the *ortho–para* directing effect of the methyl groups. Comparison of data obtained in isopropylations with isopropyl bromide with those resulting from alkylations with propylene—in otherwise identical systems—points to some substantial differences in the isomer distributions. In alkylations of toluene with isopropyl bromide the amount of *o*-cymene is comparable with that obtained in isopropylation with propylene. Thus the steric *ortho* effect of a methyl group does not substantially differ in alkylations either with isopropyl bromide or propylene. However, in isopropylation of *m*-xylene no 2-isopropyl-*m*-xylene is formed with isopropyl bromide, as there is no 3-isopropylpseudocumene formed in the isopropylation of pseudocumene (1,2,4-trimethylbenzene). In contrast, these isomers are formed in propylations with propylene. The very substantially decreased reactivity of mesitylene in propylation with isopropyl bromide (about one tenth of that observed with propylene) and the absence of isomers containing isopropyl groups in vicinal position to two methyl groups in isopropylation of *m*-xylene and pseudocumene can be sufficiently explained by steric factors. It is suggested that the isopropyl bromide–aluminum chloride–nitromethane adduct, which must be considered the effective alkylating agent, is bulkier than the propylene–catalyst adduct. In the latter case the alkylating agent must be closer in nature to the dimethylcarbonium ion, formed through protonation of propylene and thus effecting less steric hindrance.

In the isopropylation of *m*-xylene both with isopropyl bromide and propylene about 10% of the 1,3,5-isomer was formed. It is again difficult to exclude the possibility that some of this is due to concurrent isomerization of the primarily formed 1,3,4- or 1,2,3-isomers, but the degree of isomerization must be small.

In all of the investigated isopropylations the amount of di- and polyalkylates were less than 5% of the monoalkylate. No intermolecular isomerization (transalkylation) exceeding 2% of the amount of monoalkylates could be found in control experiments with pure isomeric isopropylxylenes and trimethylbenzenes in excess benzene with the same catalyst system. It is therefore suggested that the observed relative reactivities and isomer distributions are reliable within ±5%. However the isomer distributions could be affected somewhat more by intramolecular isomerizations. According to Allen's data[11,14] the isomerization of cymenes takes place to about 86% through intermolecular and to 14% by intramolecular isomerization. If these data can be extrapolated to di- and trimethylisopropylbenzenes, then an indication of the possible extent of isomerization affecting the observed isomer distributions can be suggested.

Kinetic Isotope Effect.—Because of the difficulty in avoiding hydrogen exchange in systems involving strong acid catalysts, no kinetic isotope effect has been reported for Friedel–Crafts alkylations, with the exception of the previously investigated benzylation.[14] Using the described technique of competition between benzene and benzene-d_6, the i-C_3H_7Br + $AgClO_4$ alkylation in nitromethane solution was found suitable for the determination of the kinetic isotope effect of the reaction. Mass spectroscopy has shown only slight hydrogen exchange, as compared with substantial hydrogen exchange when stronger acid catalysts like $AlCl_3 \cdot CH_2NO_3$ were employed.

Mass spectroscopic analysis of the $C_6H_5C_3H_7 : C_6D_5C_3H_7$ ratios gave a kinetic isotope effect of $k_H : k_D$ = 1.15 ± 0.03. As a check on the reproducibility of the small observed kinetic isotope effect, competitive isopropylation of toluene–benzene and toluene–benzene-d_6 was also carried out with i-C_3H_7Br + $AgClO_4$ in nitromethane solution. In this case gas–liquid chromatography could be used to determine the relative ratios which were found to be

$$k_{\text{toluene}} : k_{\text{benzene}} = 2.24$$
$$k_{\text{toluene}} : k_{\text{benzene-}d_6} = 1.91$$
$$k_H : k_D = 1.17 \pm 0.04$$

The kinetic isotope effects determined from direct competition of C_6H_6–C_6D_6 and from competition of $C_6H_5CH_3$–C_6H_6 and $C_6H_5CH_3$–C_6D_6 gave good agreement. The effects causing a small secondary isotope effect, similar to that observed in the previous benzylation work, have been discussed and do not need to be repeated.[9]

The observation of only a small secondary isotope effect during the Friedel–Crafts isopropylation of deuterated benzene is in accordance with the observation that the rate-determining step involves an activated state closer in nature to an oriented π- than a σ-complex. In the latter case, a primary isotope effect should be observed, as in the acetylation of deuterated benzene and toluene with $CH_3CO^+SbF_6^-$. In this case rate data point to the activated state being in nature closer to a σ-complex than a π-complex and a primary isotope effect of $k_H : k_D$ = 2.20 was observed.[15]

The absence of a primary kinetic isotope effect in the isopropylation of deuterated benzene indicates that fast proton elimination is not of major kinetic importance in the investigated alkylations.

Aspects of the Reaction Mechanism.—The present investigation has provided a good correlation of the relative isopropylation rates of methylbenzenes and benzene with relative π-, but not with σ-complex stabilities of the methylbenzenes. To account for a low substrate but high positional selectivity substitution of aromatics it is suggested that activated states corresponding in nature both to π- and σ-complexes play

(12) H. C. Brown and H. Jungk, *J. Am. Chem. Soc.*, **78**, 2182 (1956); S. U. Choi and H. C. Brown, *ibid.*, **81**, 3315 (1959).

(13) Unpublished results.

(14) R. H. Allen, T. Alfrey, Jr., and L. D. Yats, *J. Am. Chem. Soc.*, **81**, 42 (1959).

(15) G. A. Olah, S. J. Kuhn, and S. H. Flood, Abstract Papers, XVIII International Congress of Pure and Applied Chemistry, Montreal, Canada, 1961, A-1, p. 78.

important roles, the first being the dominant in the rate-determining step, whereas the latter effects the isomer distribution (and can account for possible isomerizations).

The potential energy diagram of a typical aromatic substitution reaction involving a strongly electrophilic substituting agent can in our view be represented as shown in Fig. 1, where T_1 represents the transition state corresponding to a π-complex and T_2 corresponds to the transition state of σ-complex nature. T_2 indeed must be composed of separate transition states corresponding to the *m*-, *p*-, and *o*-positions involved, from which that leading to the *m*-position represent the highest, energy barrier. The proton elimination side of the reaction coordinate is substantially symmetrical with that of the reagent attack side, the relative heights of the activated states being barely affected by the very small secondary kinetic isotope effect.

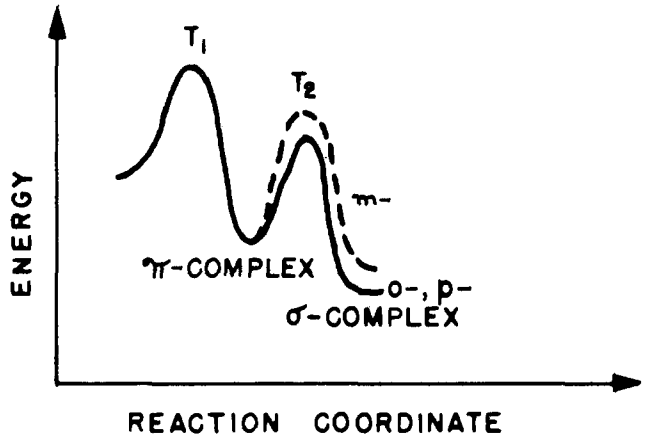


Fig. 1.—Energy diagram of a typical aromatic substitution involving a strong electrophile (irreversible π-complex formation).

When considering formation of a π-complex type activated state as the rate-determining step with subsequent "localization" of the entering substituent into individual positions (thus positional discrimination), it is necessary that T_1 be *higher* than T_2, *i.e.*, the formation of the π-complex is *irreversible*.

Although it is customary to consider π-complexes as weak, reversible interactions of aromatics with neutral or slightly polarized reagents (*e.g.*, molecular halogens) or with ions (*e.g.*, Ag^+) not capable of effecting irreversible changes (substitution), it is possible that strong electrophiles, capable of effecting substitutions (*e.g.*, NO_2^+, R^+, Br^+), could, however, form irreversible π-complexes as the once-complexed cation is passing over the *lower* energy barrier (T_2) leading to the σ-complex and consequently to substituted product instead of climbing back through the *higher* barrier (T_1) for reversing. When, on the other hand, T_2 is higher than T_1, the formation of the π-complexes becomes reversible and *both* substrate and positional selectivity are determined by the activation energy needed for formation of the σ-complex (Fig. 2). In this case it is easily understood why the substrate and positional selectivities show good correlation (Brown's selectivity relation). By the same reasoning it is also understandable that, when π-complex formation is the rate-determining step, the substrate and positional selectivities may become independent of each other and low substrate selectivity may be obtained simultaneously with high positional selectivity. In the latter case the two are determined by separate transition states, whereas in the first case by the same one.

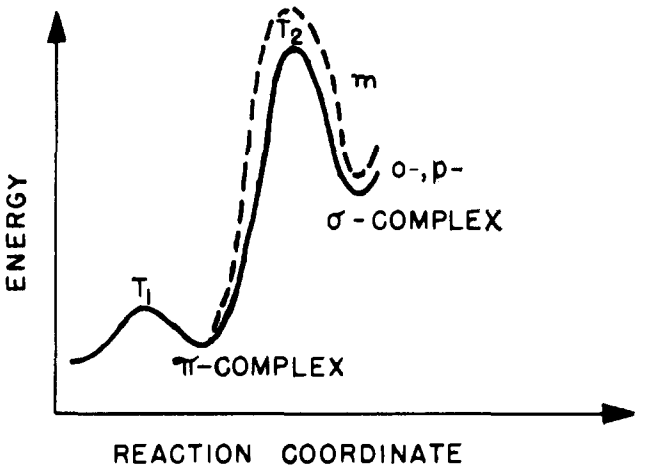
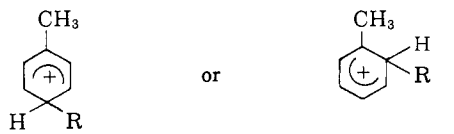


Fig. 2.—Energy diagram of a typical aromatic substitution involving a weak electrophile (reversible π-complex formation).

The energy resisting the formation of an irreversible π-complex of aromatics with strong electrophiles is ascribable to the fact that no free separated ions (*e.g.*, NO_2^+, R^+, Br^+, etc.) are present in any of the reaction media of the Friedel–Crafts reactions. Even in the case of isolated, stable ion salts (like $NO_2^+BF_4^-$) it was proved that in the used solvent systems they are present predominantly as solvated ion pairs (or higher conglomerates) and *not* as separated ions. This is believed also the case in alkylation, halogenation, etc., systems, where no free, separated alkyl carbonium or halonium ions can be detected. Consequently, to pull away the cation from the strong coulombic interaction of its ion-pair or ion-conglomerate interaction, which in turn is further strengthened by solvation, and bring it onto the unchanged aromatic molecule involves substantial energy.

The nature of the π-complexes involved in the electrophilic substitution of alkylbenzenes has been discussed previously.[10] It was suggested in accordance with Melander's and Brown's previous suggestions that the nature of π-complexes between electrophiles and a nonsymmetrical aromatic hydrocarbon must be an oriented one, in contrast to Dewar's original suggestion of a symmetrical π-complex. The oriented nature of the primary π-complex would affect the overall reaction picture in that it could slightly lower the $\pi \rightarrow \sigma$ transition energies in the *o*- and *p*-positions.

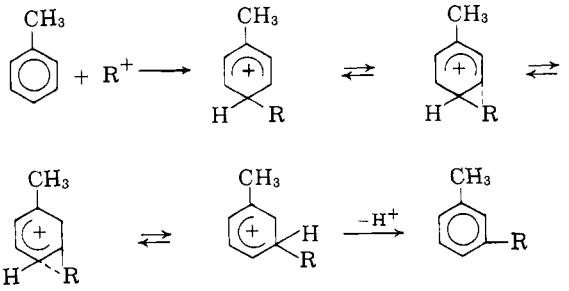
If alkylation of alkylbenzenes should involve only a σ-complex type rate-determining transition state, the attachment of the attacking alkyl species must be primarily at the *o*- and *p*-positions relative to the alkyl group on the ring, because only in these positions is the intermediate benzenonium ion conjugatively stabilized.



The formation of the *m*-isomer must involve a 1,2-shift of the alkyl group within the benzenonium ion, prior to the loss of the proton.

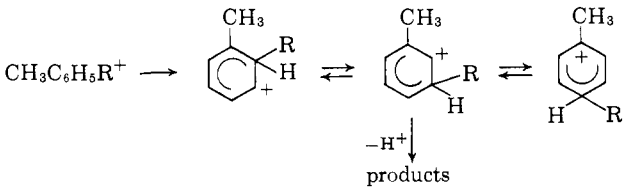
We suggest that the driving force for the alkyl shift to the *m*-position is thermodynamic rather than kinetic and consequently is the equivalent of a concurrent, intramolecular isomerization.

Professor H. C. Brown, however, considers that migration of the alkyl group within the σ-complex prior to loss of the proton cannot be considered as an isom-



erization of the products.[16] Thus the orientation is determined after the σ-complexes are formed, but before they are deprotonated.

$$CH_3C_6H_5 + R^+ \rightleftarrows CH_3C_6H_5R^+$$



However, even when this point of view is accepted, the shift of the alkyl groups from the conjugatively stabilized *o*- and *p*-positions of the benzenonium ions into the nonstabilized *m*-position must be considered as thermodynamically, and not kinetically, influenced.

It is not questioned that direct kinetically controlled alkylation also takes place to a certain degree in the *m*-positions. The quantity of the *m*-isomer formed in the direct alkylation step and that produced by consecutive or concurrent isomerization cannot be accurately established.

As to the nature of the effective alkylating species, the data of the present investigation do not allow final conclusion. The dependence of the isopropylation on the aromatic substrates, as well as the seeming dependence on the 1:1 catalyst:alkylating agent composition and the slowness of the reactions indicate that the isopropylations in nitromethane solution are in effect nucleophilic displacement reactions, by the aromatic substrate, of the catalyst–reagent complexes, as suggested by Brown for alkylations involving primary halides.[17] In the fairly basic solvent the ionization of the alkyl halide or the protonation of the olefin are not favored (in contrast to when only excess aromatic is used as reaction media) because of the competing donor effect of the solvent. However, an equilibrium of the carbonium ion cannot be excluded, in which case there would be the possibility of two different alkylating agent (the donor–acceptor complex and the carbonium ion) reacting simultaneously, but obviously with different velocity and selectivity.

In suggesting for these and related electrophilic aromatic substitutions involving strong electrophiles, separate substrate and positional selectivity determining transition states corresponding in nature to oriented π- and σ-complexes, we wish finally to stress that reactions generally do not follow entirely one limiting case or the other. Obviously aromatic substitutions must go through a continuous transition from a weak interaction of the reagent with the substrate (outer complex) to a strong one (inner complex), in which the reagents became bonded onto the ring. We can only postulate the nature of the transition states from kinetic data. With the present alkylation system the data suggest that the rate-determining step involves an activated state which is closer to an oriented π-complex than to a σ-complex type intermediate. The σ-complex itself, as proved by isolation of a substantial number of stable arenonium BF_4^-, SbF_6^-, PF_6^-, AsF_6^-, and $AlCl_4^-$ salts, is in certain cases indeed an intermediate proper and therefore is represented by a minimum on the potential energy diagram. Many previous investigations have established for a variety of electrophilic aromatic substitutions a mechanism in which π-complexes are unimportant and both substrate and positional selectivities are determined in the same σ-complex type transition state. Between these two limiting cases any degree of transition is possible and indeed reactions were observed which point to an intermediate type. Generally, the stronger the electrophile, the closer the rate-determining activated state can come to an oriented π-complex. In other words, against a strong acid aromatics can show π-basicities proportioned to the donor properties of the unopened π-sextet. With weaker electrophiles the weak donor–acceptor interaction becomes reversible and is followed by a higher energy level transition state corresponding in nature more to a σ-complex or arenonium ion, which then determined both substrate and positional selectivity.

It is fully realized that suggesting a substrate selectivity-determining step involving a π-complex type transition state is not easy to accept. Alternate explanations for the low substrate, high positional selectivity reactions have been offered.[18]

However, we feel that the data are best explained with the reaction mechanism suggested and that the possibility of aromatic hydrocarbons acting as π-donor entities against strongly acidic reagents in the substrate selectivity-determining step is not unreasonable. It also should be mentioned that in view of the low substrate selectivity of the Friedel–Crafts alkylation of benzene and alkylbenzenes, Brown and co-workers[19] once considered a somewhat similar mechanism, but later seemingly abandoned it because in their view a high reactivity but low selectivity reaction involving a σ-complex type transition state sufficiently well explained the reaction in accordance with the selectivity relationship. Observed deviations from the selectivity relationship in cases were π-complex formation can play a kinetic role made consideration of the suggested mechanism necessary.

(16) Personal communication by Professor H. C. Brown.

(17) H. C. Brown and M. Grayson, *J. Am. Chem. Soc.*, **75**, 6285 (1953); H. Jungk, C. R. Smoot, and H. C. Brown, *ibid.*, **78**, 2185 (1956).

(18) A referee of this paper, for example, suggested that each aromatic substrate may react by two paths. One path is "selective" with a displacement mechanism, the other is "nonselective" involving the more reactive carbonium ion pair, according to the equilibria

$$Me_2CHBr + RNO_2AlCl_3 \rightleftarrows Me_2CHBr\cdot AlCl_3 + RNO_2$$

$$Me_2CHBr\cdot AlCl_3 \rightleftarrows Me_2CH^+BrAlCl_3^-$$

The rate-determining steps should be

$$ArH + Me_2CHBr\cdot AlCl_3 \longrightarrow \sigma\text{-complex} \qquad k$$

$$ArH + Me_2CH^+BrAlCl_3^- \longrightarrow \sigma\text{-complex} \qquad k^1$$

$$\frac{\text{rate toluene}}{\text{rate benzene obsd.}} = \frac{[k_T(Me_2CHBr\cdot AlCl_3) + k^1_T(Me_2CH^+BrAlCl_3^-)][T]}{[k_B(Me_2CHBr\cdot AlCl_3) + k^1_B(MeCH^+BrAlCl_3^-)][B]}$$

It is expected that $k_T(Me_2CHBr\cdot AlCl_3)/k_T(Me_2CH^+BrAlCl_3^-)$ will not be equal to $k_B(MeCHBr\cdot AlCl_3)/k^1_B(Me_2CH^+BrAlCl_3^-)$ and therefore the isopropylation results may be interpreted in the context of this mechanism if $k_T > k^1_T$ while k_B and k^1_B both contribute to the total rate of alkylation of benzene.

In our view the above suggestions still leaves unanswered the question of why if the rate-determining step involves δ-complexes of benzene and toluene is their reactivity difference so small ($\sim$2), because the stability differences of the complexes $C_6H_7^+$ and $CH_3C_6H_6^+$ are substantial (>100).

(19) H. C. Brown and H. Jungk, *J. Am. Chem. Soc.*, **78**, 2182 (1956); H. Jungk, C. R. Smoot, and H. C. Brown, *ibid.*, **78**, 2185 (1956).

Experimental

The benzene, methylbenzenes, and isopropyl bromide used were commercially available products of the highest purity. If necessary they were redistilled on a Podbielniak column or purified by preparative scale gas chromatography. Average purity was 99+% as analyzed by analytical gas–liquid chromatography. Propylene (Matheson Chemical Co.) was used without further purification. We are grateful for samples of pure isomeric cymenes, 2-isopropyl-*p*-xylene, and 5-isopropyl-*m*-xylene to Drs. R. H. Allen (The Dow Chemical Co., Midland, Mich.), B. S. Friedman (Sinclair Research Inc., Harvey, Ill.), and D. A. McCaulay (American Oil Co., Whiting, Ind.), respectively. Reference isomeric cymenes were also obtained from the National Bureau of Standards, Washington, D. C. Other isomeric isopropyldi- and trimethylbenzenes were prepared by known methods in this laboratory. The purity of all standard isomers used was controlled by gas–liquid chromatography and infrared spectroscopy. Nitromethane used was purified as described previously[20] by use of the method of Winstein and Smith. Anhydrous acidic halide catalysts were commercial products purified by standard methods (sublimation, azeotropic distillation, treatment with thionyl halides) or halides prepared by known methods in this laboratory.

Commercial "anhydrous" silver perchlorate was dehydrated in a manner similar to that described recently by Radell, Connelly, and Raymond[21] by azeotropic distillation with benzene.

Anhydrous silver tetrafluoroborate,[22] hexafluoroantimonate,[23] hexafluoroarsenate,[23] and hexafluorophosphate[23] were prepared as described.

Benzene-d_6 was purchased from Ciba Limited, Basel, Switzerland.

Competitive Isopropylation of Benzene and Methylbenzenes with Isopropyl Bromide.—To a solution of 0.05 mole of catalyst in 50 g. of solvent (see Tables I and III) were added 0.25 mole each of methylbenzene and benzene in a three-necked reaction flask equipped with a thermometer, reflux condenser (connected through a drying tube to a hydrogen halide absorber), and dropping funnel. The reaction flask was then placed in a constant temperature bath at 25 ± 0.5°. With vigorous stirring (magnetic stirrer) 0.05 mole (6 g.) of isopropyl bromide in 30 g. of solvent was added dropwise. The addition took approximately 10 min. and the reaction was then allowed to proceed for another 5 min. Thereafter the solution was washed with water, three times with 200-ml. portions of 5% NaOH (to remove nitromethane), and again with water. The organic layer was separated, dried over $CaCl_2$, and analyzed by gas–liquid chromatography. The data obtained are summarized in Tables I and III.

Competitive Isopropylation of Benzene and Methylbenzenes with Propylene.—To a solution of 0.02 mole (except where otherwise indicated) of catalyst in 50 g. of solvent (see Tables II and IV) were added 0.10 mole each of toluene and benzene. The reaction flask fitted with thermometer, reflux condenser, and gas inlet tube was then placed in a constant temperature bath at 25 ± 0.5° and, with stirring, propylene gas was introduced at a constant rate (75 ml./min.) for 15 min. The solution was then washed with water, 5% NaOH solution, and again with water. The organic layer was separated, dried, and analyzed by gas–liquid chromatography as previously. The data obtained are summarized in Tables II and IV.

Concentration Variation of Toluene and Benzene in Competitive Isopropylations.—The concentration variations were carried out in the same manner as the competitive studies varying only the relative amounts of toluene and benzene. The data obtained are summarized in Tables V and VI.

Isopropylation of Toluene with Isopropyl Bromide under Heterogeneous Reaction Conditions, Excess Toluene as Diluent.—Isopropylations of toluene with isopropyl bromide were carried out by mixing the catalyst (0.1 mole) and toluene (1.0 mole) and then adding 0.1 mole of isopropyl bromide to the stirred reaction mixture at 25°. The reaction mixture was generally allowed to react for 5 min. Mixtures with less reactive catalysts where no product formation was observed (as evidenced by hydrogen bromide evolution) under these conditions, were allowed to react for longer periods of time (up to several hours) in order to obtain alkylation of 10–15%, a suitable amount for analysis. The solutions were then washed, dried, and analyzed by gas–liquid chromatography, as in previous experiments.

Determination of Kinetic Isotope Effect. (a) Isopropylation of C_6D_6 + C_6H_6.—Benzene-d_6 (0.1 mole), benzene (0.1 mole), and 0.02 mole of anhydrous $AgClO_4$ were dissolved in 30 g. of nitromethane. Into this stirred solution kept at 25 ± 0.5°, 0.02 mole of isopropyl bromide dissolved in 5 g. of nitromethane was added dropwise and reacted as in previous experiments. The reaction mixture was washed twice with 50 ml. of water, the organic layer dried over $CaCl_2$ and analyzed by mass spectroscopy.

(b) Isopropylation of $CH_3C_6H_5$ + C_6H_6 and $CH_3C_6H_5$ + C_6D_6.—Toluene (0.1 mole) and 0.1 mole of benzene or benzene-d_6 together with 0.02 mole of anhydrous $AgClO_4$ were dissolved in 30 g. of nitromethane. To the stirred solutions kept at 25 ± 0.5°, 0.22 mole of isopropyl bromide dissolved in 5 g. of nitromethane was added dropwise. The reactions were then carried out as in previous experiments. The mixtures were washed twice with 50 ml. of water, dried over $CaCl_2$, and analyzed by gas–liquid chromatography.

Gas–Liquid Chromatographic Analysis.—The analyses of all isopropylations were carried out by gas–liquid chromatography on a Perkin–Elmer Model 154-D vapor fractometer equipped with a Golay type capillary column (150 ft.) coated with propylene glycol and using a hydrogen flame ionization detector. Peak areas were directly obtained by the use of Perkin–Elmer Model 194 and Infotronics Model CRS-1 electronic printing integrators. The general column conditions were: temperature = 100°, helium pressure 10 p.s.i.g., with characteristic retention times for a column given in Table XII.

TABLE XII

RETENTION TIME OF ISOPROPYLBENZENE AND ISOPROPYLMETHYLBENZENES AT 100° ON A CAPILLARY COLUMN

Compounds	Retention time, min.
Isopropylbenzene	10.0
o-Isopropyltoluene	14.9
m-Isopropyltoluene	13.3
p-Isopropyltoluene	13.7
5-Isopropyl-*m*-xylene	19.4
4-Isopropyl-*m*-xylene	21.8
2-Isopropyl-*m*-xylene	24.0
2-Isopropyl-*p*-xylene	20.4
4-Isopropyl-*o*-xylene	22.9
3-Isopropyl-*o*-xylene	26.2
2-Isopropylmesitylene	39.8
3-Isopropylpseudocumene (1,2,4-trimethylbenzene)	45.8
5-Isopropylpseudocumene	38.6
6-Isopropylpseudocumene	40.2
5-Isopropylhemimellitene (1,2,3-trimethylbenzene)	43.2
4-Isopropylhemimellitene	52.4

Relative response data of isopropylbenzene and isopropylmethylbenzenes were determined according to Messner, Rosie, and Argabright.[24]

Improved separation of *m*- and *p*-isopropyltoluenes was achieved using a *m*-bis-(*m*-phenoxyphenoxy)-benzene coated 150 ft. capillary column, the liquid phase being modified with 20% Apiezon L grease. Using a Perkin–Elmer Model 226 gas chromatograph with above column at 80° with average carrier gas He pressure of 20, H_2 pressure of 35, and air pressure of 40 p.s.i., the following characteristic retention times were observed: isopropylbenzene, 11.9 min.; *m*-isopropyltoluene, 20.8 min.; *p*-isopropyltoluene, 21.3 min.; and *o*-isopropyltoluene, 24.5 min. Peak areas on this instrument were determined with the use of a high speed Infotronics Model CRS-1 integrator.

(20) G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *J. Am. Chem. Soc.*, **86**, 1039 (1964).

(21) J. Radell, J. W. Connelly, and A. J. Raymond, *ibid.*, **83**, 3960 (1961).

(22) G. A. Olah and H. W. Quinn, *J. Inorg. Nucl. Chem.*, **14**, 295 (1960).

(23) G. A. Olah, S. J. Kuhn, W. S. Tolgyesi, and E. Baker, *J. Am. Chem. Soc.*, **84**, 2733 (1962).

(24) A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).