TABLE X

RETENTION TIMES OF MONOBROMOALKYLBENZENES ON PACKED COLUMN (COLUMN TEMPERATURE 150°)		RETENTION TIMES OF MONOBROMOALKYLBENZENES ON GOLAY CAPILLARY COLUMN (100°)	
Compound	Retention time, min	Compound	Retention time, min.
Bromobenzene	6	Bromobenzene	18
Bromotoluenes	10	*o*-Bromotoluene	26
o-Bromoethylbenzene	12	*p*-Bromotoluene	27
p-Bromoethylbenzene	14	3-Bromo-*o*-xylene	51
Bromo-*o*-xylenes	18	4-Bromo-*o*-xylene	53
Bromo-*m*-xylenes	17	2-Bromo-*m*-xylene	42
Bromo-*p*-xylene	16	4-Bromo-*m*-xylene	43
Bromomesitylene	26	Bromo-*p*-xylene	42
		Bromomesitylene	75

column although it was possible to separate the *ortho* from the combined *meta* and *para* isomers.

In order to separate the isomeric bromotoluenes, use was made of a high sensitivity Perkin–Elmer Model 226 vapor fractometer using a hydrogen flame ionization detector and a 150 ft. × 0.01 in. bifilar spiral Golay capillary column. The liquid phase was made up of 80% *m*-bis-(*m*-phenoxyphenoxy)-benzene and 20% Apiezon L. The column temperature was 60°. Helium was used as the carrier gas at a pressure of 20 p.s.i.; 2-μl. samples were injected. The isomeric bromotoluenes were separated with the following retention times: *o*-bromotoluene, 45 min.; *p*-bromotoluene, 48 min.; and *m*-bromotoluene, 48.5 min.

As the separation of isomeric bromotoluenes (and bromoethylbenzenes) represented difficulties even with the use of highly efficient capillary columns, they were also analyzed by infrared spectroscopy, reference being made to the characteristic out-of-plane hydrogen deformation absorption bands in the 12–14 μ region. Samples were weighed into carbon disulfide at two concentrations (10% and 2% wt./vol.) so that both weak and strong absorption bands could be measured accurately. The solutions were scanned on a double beam infrared spectrometer with sodium chloride optics. Analyses were carried out by the standard base line technique with suitable corrections made for the interference of any isomer on the others by use of an electronic computer. The following analytical wave lengths (μ) were used for the analyses: *o*-bromotoluene, 13.42; *m*-bromotoluene, 13.0; *p*-bromotoluene, 12.48; *o*-bromoethylbenzene, 13.4; *m*-bromoethylbenzene, 12.96; *p*-bromoethylbenzene, 12.22.

It was found advantageous for the infrared analyses to separate the combined bromotoluene or bromoethylbenzene fractions by preparative scale vapor phase chromatography, thus eliminating solvent and other aromatic interferences. Accuracy of the isomer ratios is within ±3 relative %, as checked with mixtures of known composition.

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Aromatic Substitution. XV.[1] Ferric Chloride Catalyzed Bromination of Halobenzenes in Nitromethane Solution

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The ferric chloride catalyzed bromination of benzene and halobenzenes with bromine in nitromethane solution was investigated at 25°. Relative reactivities and isomer distributions were determined in competitive experiments by gas–liquid chromatography.

Introduction

The electrophilic bromination of halobenzenes has been investigated in detail by Hollemann,[2] De la Mare,[3] Ferguson,[4] and one of us[5] in previous work. De la Mare and Ridd[6] have recently reviewed the field.

Results

Our investigations on the bromination of benzene and alkylbenzenes[1] have now been extended to the competitive bromination of benzene and halobenzenes. Brominations were carried out using anhydrous ferric chloride as catalyst in nitromethane solution, under conditions identical with those reported previously for the bromination of alkylbenzenes.[1]

Table I and II summarize data for the competitive bromination of benzene and halobenzenes, together with the corresponding isomer distributions, using neat bromine as brominating agent. (Analyses were carried out with gas–liquid chromatography, as described in the Experimental part.)

As in the related bromination of alkylbenzenes,[1] use of neat bromine presents difficulties in that local excesses of bromine promote dibromination to a certain degree, and it is consequently advisable to use nitromethane solutions of bromine instead of neat bromine. The data obtained are summarized in Table II.

TABLE I

FERRIC CHLORIDE CATALYZED COMPETITIVE BROMINATION OF BENZENE AND HALOBENZENES IN NITROMETHANE SOLUTION AT 25° (NEAT BROMINE ADDED)

Aromatic, benzene	$k_{halobenzene}:k_{benzene}$	—Isomer bromohalobenzene, %— *o*-	*m*-	*p*-
Benzene	1.0	10.5		
Fluoro-	0.69	10.5	<0.2	89.5
Chloro-	.35	20.3	< .2	79.7
Bromo-	.30	23.6	< .2	76.4

TABLE II

FERRIC CHLORIDE CATALYZED COMPETITIVE BROMINATION OF BENZENE AND HALOBENZENES IN NITROMETHANE SOLUTION AT 25° (CH_3NO_2 SOLUTION OF Br_2 ADDED)

Aromatic, benzene	$k_{halobenzene}:k_{benzene}$	—Isomer bromohalobenzene, %— *o*-	*m*-	*p*-
Benzene	1.0			
Fluoro-	0.27	10.5	<0.2	89.5
Chloro-	.12	22.1	< .2	77.9
Bromo-	.10	26.0	< .2	74.0

As nitromethane itself is capable of promoting high selectivity brominations, the bromination of benzene and halobenzenes was carried out using a nitromethane solution of bromine and excess ferric chloride in order to minimize the effect of solvent. Table III summarizes data from competitive brominations with this system.

The competitive method of relative rate determination could be used conveniently in these investigations, since the concentration variation of benzene and halobenzenes, as investigated in the case of chloro-

(1) Part XIV: *J. Am. Chem. Soc.*, **86**, 1039 (1964).
(2) A. F. Hollemann, *Chem. Rev.*, **1**, 187 (1925).
(3) P. B. D. De la Mare, *J. Chem. Soc.*, 4450 (1954).
(4) L. N. Ferguson, A. Y. Garner, and J. S. Mack, *J. Am. Chem. Soc.*, **76**, 1250 (1954).
(5) G. Olah, A. Pavlath, and G. Varsanyi, *J. Chem. Soc.*, 1823 (1957).
(6) P. B. D. De la Mare and J. H. Ridd, "Aromatic Substitution, Nitration and Halogenation," Academic Press, Inc., New York, N. Y., 1959.

TABLE III

FERRIC CHLORIDE CATALYZED COMPETITIVE BROMINATION OF BENZENE AND HALOBENZENES IN NITROMETHANE SOLUTION AT 25° (CH_3NO_2 SOLUTION OF Br_2 + $FeCl_3$ ADDED)

Aromatic, benzene	$k_{halobenzene}:k_{benzene}$	Isomer bromohalobenzenes, %- o-	m-	p-
Benzene	1.0			
Fluoro-	0.48	11.9	<0.2	88.1
Chloro-	.20	25.1	< .2	74.9
Bromo-	.16	27.2	< .2	72.8

TABLE IV

FIRST-ORDER DEPENDENCE OF THE Br_2 + $FeCl_3$ BROMINATIONS IN AROMATICS

Ratio of chlorobenzene:benzene	Obsd. relative rate	$k_{Cl}:k_B$
5:1	1.05	0.21
2:1	0.44	.22
1:1	.20	.20
1:2	.09	.18
	Average	0.20

benzene in competitive experiments at 25°, showed first-order dependence of relative rates on aromatic substrates (Table IV).

Discussion of Results

The observed relative reactivities of halobenzenes and benzene show fair agreement with relative stabilities of complexes of halobenzenes with Ag^+, Br_2, I_2, ICl, SO_2, picric acid, tetracyanoethylene, HCl, and HF, which are considered to be π-complex-forming agents.

Table V shows a comparison of the relative rates of bromination with Br_2 + $FeCl_3$ with relative stabilities of complexes of halobenzenes and with previously investigated nitration and benzylation rates. Differences may be due partly to varying steric factors.

No data are available on the σ-complex forming ability of halobenzenes (HF + BF_3). It seems that under conditions where the alkylbenzenes give stable benzenonium ions, no similar complex formation takes place with halobenzenes.

The reason for this must be not only the lower π-electron density of the ring in halobenzenes, but the absence of alkyl groups capable of stabilizing through conjugation (in the *o*- and *p*-positions) benzenonium ion formation.

The recent observation of a stable benzenonium complex in the system fluorobenzene + HF + SbF_5[7] is in agreement with the fact that the fluorine substituent can effect, through conjugation, considerable stabilization of the benzenonium ion in the *p*-position.

The stabilities of the π-complexes do not vary greatly with the nature of the halogen substituents (see data of Table V). Thus the reactivities observed in these brominations should be of the same order of magnitude for benzene and halobenzenes if the halobenzenes take part with their π-sextet as entities in a rate-determining π-complex-forming step. This order of selectivity of the aromatic substrate is different from that in reactions where relative stabilities of intermediate σ-complexes in individual positions are involved. In halobenzenes, these frequently show relative reactivities orders of magnitude smaller than that of an individual benzene position.

It is suggested that the isomer distributions obtained represent the nonisomerized, kinetically controlled distributions. The very low amount of *m*-isomers present substantiate this view, in comparison with our previous investigations of the Friedel–Crafts isomerization of dihalobenzenes.[8]

The greater the reactivity of an electrophilic substituting agent, the smaller its selectivity.[9] This means low selectivity with different aromatics and also a simultaneous change of the isomer distribution toward the statistical value (40% *ortho*, 40% *meta*, and 20% *para*, representing two *o*-, two *m*-, and one *p*-position in a monosubstituted benzene). This generally is demonstrated by an increase in the concentration of the *m*-isomer. This is explained by the decreasing role of small activation energy differences of different individual positions compared to the over-all activation energy of the reaction. This, again, is valid only if the reaction is dependent on the relative stability of σ-complexes involving competition of individual positions (according to relative σ-complex stability). If, however, competition involves π-donor entities, a low substrate selectivity with different aromatics (halobenzenes in the present investigation) is possible without necessarily involving low positional selectivity, *i.e.*, a change of the isomer distribution in the direction of statistical distribution (demonstrated by an increase of the *m*-isomer).

TABLE V

COMPARISON OF RELATIVE STABILITIES OF COMPLEXES OF HALOBENZENES WITH BROMINATION AND OTHER ELECTROPHILIC SUBSTITUTION RATES

Aromatic, benzene	Ag^+	Br_2	I_2	ICl	$C_2(CN)_4$	SO_2	HCl	$NO_2^+BF_4^-$	$C_6H_5CH_2Cl$ + CH_3NO_2·$AlCl_3$	Br_2 + $FeCl_3$ in CH_3NO_2
Benzene	1.00	1.00	1.00	1.00	1.0	1.00	1.00	1.00	1.00	1.0
Fluoro-	0.18						0.74	0.45	0.46	0.48
Chloro-	.29	0.86	0.50		0.39	0.58	.50	.14	.24	.20
Bromo-	.40	1.13	0.86	0.59	0.31		.41	.12	.18	.16

Our competitive brominations showing relatively low substrate selectivity of the halobenzenes gave at the same time isomer distributions of the monobromo products showing only an insignificant amount of the *m*-isomers.

Concerning the directing effect in the bromination of halobenzenes the $-I > +T$ effect of the halogen atom results, in the region of the *o*-positions, in some degree of neutralization of the two opposed effects. Since the inductive effect diminishes with distance, in the *p*-position the conjugative effect becomes predominant. This is best shown by comparing the *ortho*:*para* ratios of bromo-halobenzenes obtained, which give a sequence opposed to the expected steric *ortho* effect, based on radii of halogens.

	ortho:*para*
Fluorobenzene	0.12
Chlorobenzene	.25
Bromobenzene	.31

The over-all effect can be increased further by polarization by the strong electrophilic reagent. The *o*-isomer values obtained in these brominations of

(7) G. A. Olah, W. S. Tolgyesi, and R. E. A. Dear, *J. Org. Chem.*, **27**, 3441 (1962).

(8) G. A. Olah, W. S. Tolgyesi, and R. E. A. Dear, *ibid.*, **27**, 3455 (1962).

(9) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953); M. J. S. Dewar, *Ann. Repts.*, **53**, 132 (1956).

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°	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%.

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

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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**, 5584 (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).