the values of p_∞ calculated from equations 8 are consistent with the observed experimental values (Table VII).

$$\begin{aligned} n'_\infty &= a_1 p_\infty \\ n''_\infty &= a_2 p_\infty \qquad (8) \\ n'_\infty/a_1 &= n''_\infty/a_2 \end{aligned}$$

TABLE VII

PARTIAL PRESSURE OF HYDROGEN BROMIDE OVER THE REACTION MIXTURE AFTER THE COMPLETION OF THE ALKYLATION REACTIONS OF TOLUENE

Alkyl bromide	MeBr	EtBr	EtBr
Temp., °C.	0.0	0.0	−23.2
Apparent vol., cc.	43.2	46.5	48.8
Rm. temp., °C.	23.1	25.2	24.5
Henry's law const., mm.	4230	4250	1970
Toluene, mmoles	75.269	43.050	45.773
Alkyl bromide, mmoles	2.391	4.334	2.053
Ga_2Br_6, mmole	0.121	0.094	0.075
p_∞, calcd., mm.	116	317	76.1
p_∞, obsd., mm.[a]	117.0	313.2	77.6

[a] The values of p_∞, obsd., are obtained by subtracting the vapor pressure of the aromatic at the temperature investigated (6.70 mm. at 0° and 1.20 mm. at −23.2°) from the total pressure of the system measured after the completion of the reaction.

The value of a_1 can be calculated from the values of the apparent volume of the vapor phase of the system and the room temperature. The value of a_2 can also be calculated from the values of the total number of the moles of reactants introduced and the Henry's law constant for hydrogen bromide over the reaction mixture determined experimentally after the completion of the reaction by removing all the hydrogen bromide liberated by the reaction from the reaction mixture and by measuring the solubility of hydrogen bromide in the mixture of the reaction products. The above equation can then be solved for n'_∞, since $n''_\infty = n^\circ_{RBr} - n'_\infty$. Therefore, the values of p_∞ are calculated from equation 8.

Typical rate data are summarized in Table VIII.

TABLE VIII

RATE DATA FOR GALLIUM BROMIDE-CATALYZED REACTION OF ISOPROPYL BROMIDE WITH TOLUENE AT −45.3°

Time, min.	Press., mm. Run 1	Run 2	Run 3
0	0.40	0.35	0.40
0.5	3.40	..	..
1	6.40	2.65	1.50
2	10.40	5.00	2.65
3	11.85	7.25	3.70
4	...	9.30	4.80
5	14.00	10.70	5.90
7	...	12.40	8.05
10	...	13.65	11.20
15	...	...	15.15
∞	20.10	20.55	29.95
ArH, mmoles	61.63	84.71	39.97
RBr, mmoles	1.929	2.423	1.970
$GaBr_3$, mmole	0.0876	0.0681	0.0260
t_∞, min.[a]	3.28	8.78	26.9
V_1, ArH, cc.	6.125	8.419	3.972
V_1, RBr, cc.	0.173	0.218	0.177

[a] Run 1: $p_{obs} = 6.00t + 0.40$; 2: $p_{obs} = 2.30t + 0.35$; 3: $p_{obs} = 1.10t + 0.40$.

Relative Rate of Reaction, Toluene/Benzene.—A known quantity of gallium bromide was introduced into an empty storage tube in the vacuum line, and a known amount of toluene transferred into the tube. Dry nitrogen was introduced and the tube was sealed off and removed from the vacuum apparatus. The tube was then tilted in such a way that the solution flowed down into a thin-walled bulb which had been sealed previously to the tube. The thin bulb was sealed off at the constriction and placed in a 100-ml. round-bottom flask containing carefully measured quantities of benzene, toluene and isopropyl bromide. The reaction was started by breaking the fragile bulb containing the catalyst solution. After 30 seconds, the reaction mixture was quenched by pouring into ice-water. The organic layer was washed with bicarbonate solution, washed with water, and dried over Drierite. The reaction mixture of benzene, toluene, isopropylbenzene and isopropyltoluenes was analyzed by fractionation in a Podbielniak Micro Analyzer, using tetralin as the chaser. The results are summarized in Table III.

In this study the order with respect to the aromatic solvent could not be determined. We have assumed that the reaction is first order in solvent and utilized the usual equation employed for such reactions to calculate the reactivity ratio. Actually, the assumption that the reaction is first order in aromatic is not essential. If it is assumed that the order with respect to benzene and toluene is the same, it is possible to calculate the relative rate, using the expression $k_T/k_B = y/x$, providing that there is present in the reaction mixture the same number of moles of benzene and toluene. In these competitive experiments, the number of moles of the two aromatics was maintained sensibly equal. Use of this alternative equation yields the same value of k_T/k_B.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

Relative Rate and Isomer Distribution in the Gallium Bromide-catalyzed Benzylation of Benzene and Toluene[1]

BY HERBERT C. BROWN AND BRIAN A. BOLTO[2]

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Under the influence of gallium bromide, benzyl bromide undergoes an exceedingly rapid reaction with benzene and toluene. Attempts to measure the individual reaction rates failed. Utilizing a competitive method, the relative rate of benzylation of toluene and benzene at 25° was established as 4.0. The isomer distribution in the benzylation of toluene exhibited marked variation with the reaction times, even when these were quite short. The observed isomer distributions with reaction times of 10, 0.09, 0.03, 0.01 sec. were extrapolated to zero reaction time to obtain the isomer distribution in the absence of isomerization. From this isomer distribution, 41.1% *ortho*, 19.4% *meta* and 39.5% *para*, and the relative rate, k_T/k_B 4.0, the partial rate factors for the benzylation reaction were calculated: o_f 4.9; m_f 2.3; p_f 9.4. The data provide a fair fit with the Selectivity Relationship.

Methylation,[3] ethylation[3] and isopropylation[4] of toluene, under the catalytic influences of gal-

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[1] Directive Effects in Aromatic Substitution. XXXV.

[2] Post-doctorate research associate, 1956–1957, on a grant-in-aid provided by the American Cyanamid Co.

[3] C. R. Smoot and H. C. Brown, THIS JOURNAL, **78**, 6245, 6249 (1956); H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

[4] S. U. Choi and H. C. Brown, *ibid.*, **81**, 3315 (1959).

lium bromide, has been previously shown to follow the Selectivity Relationship.[5,6] It was of interest to extend this study to the benzylation reaction. In this case it would be possible to examine the utility of the electrophilic substituent constants[7] in correlating both the effect of substituents in the aromatic undergoing substitution and their effect in the benzyl halide undergoing reaction.

The reaction of several substituted benzyl chlorides with representative aromatics under the influence of aluminum chloride in nitrobenzene has been examined earlier.[8] However, there is growing evidence that aluminum chloride in nitrobenzene is a complex system.[9,10] On the other hand, gallium bromide has yielded relatively simple kinetics in a number of alkylation reactions,[3,4] and its use avoided the incursion of serious side-reactions, *e.g.*, isomerization and disproportionation, encountered in the use of aluminum bromide.[11,12] Accordingly, we decided to examine the reaction of benzyl bromide with benzene and toluene under the influence of gallium bromide.

Results and Discussion

Attempts were made to measure the rate of reaction of benzyl bromide with benzene (excess aromatic serving as solvent) under the influence of gallium bromide using the same techniques as those previously applied to methyl and ethyl bromide.[3] However, the reaction proved to be very fast, far too fast to follow even when the concentration of gallium bromide was markedly reduced.

We then attempted to reduce the activity of the catalyst by adding small quantities of nitrobenzene to the reaction mixture. In the case of ethyl bromide, a reaction mixture 0.0240 M in gallium bromide and 0.040 M in nitrobenzene, reacted 200 times slower than an identical reaction mixture which did not contain nitrobenzene. However, even this expediency failed to bring the rate of benzylation to a range practical for measurement by our analytical methods.

Consequently, we decided to examine the vacuum line technique utilized by Dr. Choi for the study of the isopropylation of toluene at low temperatures.[4] However, we observed that the rate of benzylation of toluene was too rapid for measurement by that technique even at $-80°$. Consequently, we abandoned our efforts to measure the individual rates, and undertook to determine the relative rate of reaction of toluene and benzene by competitive methods.[4]

Experiments revealed that both isomerization and disproportionation of the reaction products were very fast reactions at 25°. As described below, we observed that with reaction times as low as 0.01 second isomerization was greatly reduced. Accordingly, in order to minimize the complications resulting from these side reactions, the competitive alkylation was carried out in a flow reactor with a reaction period of 0.01 second. We were unable to analyze the mixture of diphenylmethane and methyldiphenylmethanes satisfactorily by fractional distillation or by infrared spectroscopy. However, vapor phase chromatography provided partial separation of the diphenylmethane and the methyldiphenylmethanes and permitted a reasonably good analysis of known mixtures. The results of two competitive experiments indicated values of the relative rates of 3.85 and 4.10. On this basis, the relative rate, k_T/k_B, may be taken as 4.0.

To determine the isomer distribution, a 1 M solution of benzyl bromide in toluene was treated with gallium bromide, 0.04 M ($GaBr_3$). After a reaction time of 10 seconds, the reaction mixture was quenched. Analysis of the product by infrared spectroscopy indicated the presence of 45.7% of *m*-methyldiphenylmethane. It was suspected that the large amount of the *m*-isomer must be the result of considerable isomerization, in spite of the short reaction time. Accordingly, the alkylation was carried out in a flow reaction, utilizing reaction times ranging from 0.09 to 0.01 sec. The results are summarized in Table I.

TABLE I

ISOMER DISTRIBUTIONS IN THE BENZYLATION OF TOLUENE WITH BENZYL BROMIDE AND GALLIUM BROMIDE AT 25°

Reactants		Reaction time,	Methyldiphenylmethane, %		
[$C_6H_5CH_2Br$]	[$GaBr_3$]	sec.	*o*-	*m*-	*p*-
0.985	0.0538	10	23.1	45.7	31.2
1.01	.0448	0.09	33.8	31.4	34.8
0.927	.0408	.03	38.7	22.6	38.7
0.985	.0408	.01	40.2	21.1	38.7
		.00	(41.1)[a]	(19.4)[a]	(39.5)[a]

[a] Extrapolated value.

The variation in the isomer distribution observed even with these short reaction times of 0.09 to 0.01 second supports the conclusion that isomerization is influencing the isomer distribution. The similarity in the results at 0.03 and 0.01 second suggests that isomerization is no longer a major factor in the benzylations with these short reaction periods. Consequently, it appeared safe to extrapolate the isomer distribution data obtained in the flow experiments (0.09, 0.03 and 0.01 sec.) to zero reaction time in order to estimate the isomer distribution in the absence of isomerization. This approach leads to the estimated formation of 41.1% *ortho*, 19.7% *meta* and 39.5% *para* substitution in the benzylation of toluene at 25°.

From the relative rate, k_T/k_B, of 4.0 and the isomer distribution, the following partial rate factors can be calculated: o_f 4.9; m_f 2.3; p_f 9.4. These partial rate factors provide only a fair fit with the Selectivity Relationship.[13]

The data are of considerable interest in permitting a comparison of the relative rates and isomer distributions realized in the benzylation reaction with the corresponding data for the methylation,[3] ethylation[3] and isopropylation[4] reac-

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(5) H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953).

(6) H. C. Brown and C. W. McGary, *ibid.*, **77**, 2300 (1955).

(7) H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957); H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

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(9) N. N. Lebedev, *J. Gen. Chem.* (*U. S. S. R.*), **24**, 664 (1954).

(10) H. C. Brown and H. L. Young, *J. Org. Chem.*, **22**, 724 (1957).

(11) G. Baddeley, G. Holt and D. Voss, *J. Chem. Soc.*, 100 (1952).

(12) H. C. Brown and H. Jungk, THIS JOURNAL, **77**, 5579, 5583 (1955); H. C. Brown and C. R. Smoot, *ibid.*, **78**, 2176 (1956).

(13) See Fig. 1 in H. C. Brown and G. Marino, *ibid.*, **81**, 3308 (1959).

tion. However, it should be pointed out that the marked tendency of the benzyl groups to undergo isomerization and disproportionation, together with the much greater analytical difficulties encountered in this system, introduce much larger uncertainties in these benzylation results than in our earlier alkylation data. It is not possible to say whether the lower precision of the fit to the Selectivity Relation is inherent in the reaction or is the result of these experimental difficulties. Finally, it is apparent that the difficulties experienced in the present study suggest that this reaction is not a truly satisfactory one for observing the effect of substituents in the benzyl halide on the partial rate factors.

Experimental Part

Materials.—Benzene and toluene were purified by the standard methods described in previous papers in this series. Benzyl bromide (Eastman Kodak Co.) was fractionated at reduced pressure through a column, packed with glass helices, rated at 50 theoretical plates. The constant boiling center cut, b.p. 64° at 4 mm., was distilled directly into ampoules which were sealed under dry nitrogen. Similarly, diphenylmethane was distilled and the constant boiling center fraction, b.p. 115° at 4 mm., was collected.

The gallium bromide was freshly sublimed material made available by Dr. Sang Up Choi.[4]

The three isomeric methylbenzophenones were prepared in 50–70% yield by converting the tolylmagnesium bromides to the cadmium derivatives, followed by treatment of the organometallic compounds with benzoyl chloride.[14] The three ketones were reduced to the corresponding isomeric methyldiphenylmethanes in 65–70% yield by the Huang-Minlon modification of the Wolff–Kishner reaction.[15] The products exhibited the constants: 2-methyldiphenylmethane, b.p. 137° at 17 mm., $n^{20}\mathrm{D}$ 1.5762; 3-methyldiphenylmethane, b.p. 121° at 4 mm., $n^{20}\mathrm{D}$ 1.5711; 4-methylbenzophenone, b.p. 137° at 9.5 mm., $n^{20}\mathrm{D}$ 1.5691.[16]

Kinetic Studies.—The techniques were identical with those previously utilized by Dr. Smoot.[3] The effect of the nitrobenzene on the rate is indicated by the data in Table II.

In attempting to apply these conditions to benzylation, complete reaction was observed in the first sample, taken within a few seconds after introduction of the catalyst. Likewise, in applying the procedure developed by Dr. Choi[4] to the benzylation of toluene, the reaction was complete in a matter of seconds at −78.5°.

TABLE II

RATE CONSTANTS FOR THE REACTION OF ETHYL BROMIDE WITH BENZENE UNDER THE INFLUENCE OF GALLIUM BROMIDE IN EXCESS BENZENE AS SOLVENT AT 25.0°

Reactants, M			Rate constant	
$[C_2H_5Br]$	$[GaBr_3]$	$[C_6H_5NO_2]$	$k_0 \times 10^4$, mole l.$^{-1}$ sec.$^{-1}$	$k_2 \times 10^2$, l. mole^{-1} sec.$^{-1}$
0.402	0.0374		1.61	15.5[a]
.402	.0241		0.90	15.0
.402	.0241	0.040	0.0045	

[a] Rate constant, $k_2 \times 10^2$ l. mole^{-1} sec.$^{-1}$ 15.9 (ref. 3).

Determination of the Relative Rate.—In view of the rapid isomerization and disproportionation exhibited by the present system, the flow reactor previously utilized in the study of reactions catalyzed by aluminum bromide[12] was used. In one tube of the reactor was placed the gallium bromide catalyst (0.0408 M), dissolved in an equimolar mixture of toluene and benzene, and in the other, a solution of benzyl bromide (0.98 M) also in a 1:1 mixture of the two hydrocarbons. The two solutions were rapidly mixed in the capillary at 25° and quenched, with an estimated reaction time of 0.01 second. The organic layer was separated, washed with aqueous pyridine to remove any unreacted benzyl bromide, and then washed with water until the aqueous layer was neutral. The product was dried over calcium hydride and the excess benzene and toluene removed by fractionation.

Attempts to utilize fractional distillation to separate the methyldiphenylmethanes from diphenylmethane were unsatisfactory. The similarity in the infrared spectra of diphenylmethane and *o*-methyldiphenylmethane rendered this analytical procedure inapplicable. Analysis proved to be moderately satisfactory with a Perkin-Elmer Vapor Fractometer with a silicone column at 220°. Under these conditions diphenylmethane exhibited a retention time of 2.9 minutes, while each of the methyldiphenylmethanes had a retention time of 3.7 minutes. A calibration graph was constructed utilizing synthetic mixtures of diphenylmethane and the methyldiphenylmethanes. The mole per cent. of these materials in the product was then used to calculate the reactivity ratio in the usual manner.[4]

Determination of Isomer Distribution.—Isomer distribution runs were carried out in the flow reactor, using toluene as the solvent, the reaction time being varied by variation in the pressure of nitrogen applied to the reaction reservoirs. The quenched reaction product was worked up as described above for the competition runs. It was analyzed by means of standard infrared procedures, utilizing the base line technique. The *o*- and *p*-isomers were analyzed directly, using the characteristic bands at 13.5 and 12.4 μ, respectively. The results were used to make up a reference solution to blank out these isomers in the infrared spectrum of the sample solutions, obtaining in this way the spectrum of the *m*-isomer. The latter was estimated utilizing the band at 13.2 μ.

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LAFAYETTE, IND.

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[14] H. C. Brown and H. L. Young, *J. Org. Chem.*, **22**, 719 (1957).

[15] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

[16] In each case the refractive index is 0.0001 below that reported: J. H. Lamneck, H. F. Hipsher and V. O. Fenn., Natl. Advisory Comm. Aeronaut., Tech. Note No. 3154 (1954); moreover, the infrared spectra were identical with those reported by Lamneck, *et al.*, who estimated the purity of their compounds to be greater than 99 mole per cent.