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Relative Rates and Isomer Distributions in the Gallium Bromide-catalyzed Ethylation of Biphenyl and Toluene in Ethylene Dichloride[1]

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The gallium bromide-catalyzed ethylation of biphenyl, toluene and benzene has been examined in ethylene dichloride at 25°. Utilizing a competitive method, the relative rate of ethylation of biphenyl to benzene has been established to be 1.81. The isomer distribution under these conditions is 33.3% *o*-, 25.6% *m*- and 41.1% *p*-ethylbiphenyl. These data provide the partial rate factors for the ethylation of biphenyl, o_f^{Ph} 0.905, m_f^{Ph} 0.695 and p_f^{Ph} 2.23. Under the same conditions toluene reacted 2.34 times faster than benzene. The yield of *o*-ethyltoluene, 38.1%, was identical with that realized in the earlier ethylation of toluene in excess hydrocarbon as solvent. Adopting the isomer distribution observed in the latter case, 38.3% *o*-, 21.1% *m*- and 40.6% *p*-ethyltoluene, provides the partial rate factors, o_f^{Me} 2.69, m_f^{Me} 1.48 and p_f^{Me} 5.70. These data establish the reactivity ratios $m_f^{\mathrm{Me}}/m_f^{\mathrm{Ph}}$ as 2.1 and $p_f^{\mathrm{Me}}/p_f^{\mathrm{Ph}}$ as 2.5. Consequently, the effects of the methyl and phenyl substituents in the ethylation reaction correspond closely to their influence on both the mercuration reaction and the solvolysis of substituted *t*-cumyl chlorides.

Introduction

In order to explore the utility of the Selectivity Relationship[3,4] in correlating the electrophilic substitutions of various monosubstituted benzenes, we undertook to obtain rate and substitution data for a number of typical derivatives. A rigorous test of the applicability of the Selectivity Relationship requires the utilization of data from reactions encompassing a wide range on the Selectivity scale. As minimum requirements, the mercuration (S_f 1.014), nitration (S_f 1.366), acylation (S_f 2.192), chlorination (S_f 2.219) and bromination (S_f 2.644)[5] were to be investigated for each aromatic.

In the course of exploring the applicability of the Selectivity treatment to the substitution reactions of biphenyl, it became important to obtain more data to define the behavior of the Selectivity plot near the origin. For this purpose it was necessary to employ a reaction with a selectivity less than that for mercuration. The gallium bromide-catalyzed ethylation had been shown to exhibit the desired low Selectivity factor (S_f 0.587).[6] An investigation of the rates and isomer distribution for the ethylation of biphenyl was therefore undertaken.

Results

Ethylation of Biphenyl.—The previous study of the ethylation of benzene and toluene had been carried out employing excess aromatic as solvent.[6] The ethylation of biphenyl was first examined in a hydrocarbon solvent. To facilitate direct comparison with the earlier experimental conditions a reaction medium of 70 mole per cent. benzene and 30 mole per cent. biphenyl containing 0.040 *M* gallium bromide and 0.500 *M* ethyl bromide was employed. Unfortunately, the ethylbiphenyls were highly susceptible to isomerization under these conditions. *o*-Ethylbiphenyl was isomerized completely to the *meta* and *para* isomers within 30 min. at 25°. Shorter reaction intervals were attempted, but the isomer distributions were not consistent, indicating isomerization to be an important side-reaction.

The adoption of ethylene dichloride as the reaction medium circumvented these difficulties. Isomerization in this solvent is slow, with significant changes in the isomer distribution observed only after relatively long reaction periods (> 24 hours). Moreover, the alkylation is complete within a few minutes. The observed isomer distribution was found to be constant and readily reproducible.

The relative rate of the ethylation of biphenyl and benzene was determined by competitive reaction. Mixtures of biphenyl and benzene in ethylene dichloride were allowed to react with ethyl bromide under the influence of gallium bromide. After appropriate time intervals, the reactions were quenched and the products analyzed by gas chromatography. Making the reasonable assumption that the reaction is first-order in aromatic allows the calculation of the relative rate, biphenyl to benzene, from the well-known expression

$$\frac{k_{\mathrm{BP}}}{k_{\mathrm{B}}} = \log \frac{C^0_{\mathrm{BP}}}{C_{\mathrm{BP}}} \bigg/ \log \frac{C^0_{\mathrm{B}}}{C_{\mathrm{B}}} \qquad (3)$$

where C^0_{BP} and C^0_{B} are the molar concentrations of biphenyl and benzene initially present in the mixtures, and C_{BP} and C_{B} are the corresponding final concentrations. The results, summarized in Table I, indicate a reactivity ratio, $k_{\mathrm{BP}}/k_{\mathrm{B}}$, of 1.81.

TABLE I

BIPHENYL TO BENZENE REACTIVITY RATIO FOR THE GALLIUM BROMIDE-CATALYZED ETHYLATION IN ETHYLENE DICHLORIDE AT 25°

Time, hr.	Init. concn., *M* GaBr$_3$	EtBr	Biphenyl	Benzene	Final concn., *M* Biphenyl	Benzene	Rel. rate $k_{\mathrm{BP}}/k_{\mathrm{B}}$
2.0	0.040	0.400	0.500	0.495	0.394	0.434	1.818
>24	.040	.500	.511	.676	.287	.587	1.758
1.0	.040	.500	.431	.675	.332	.586	1.845
						Mean value	1.81

The isomer distribution for the ethylation of biphenyl was determined by gas chromatographic analysis. A satisfactory separation of the three elution peaks was obtained with either silicone oil or butylene glycol–polyadipate as the liquid phase. The three competitive experiments were examined for the isomer distribution. In addition, an independent experiment was carried out. Biphenyl, 0.5 *M*, was treated with ethyl bromide, 0.5 *M*, and gallium bromide, 0.040 *M*, in ethylene dichloride solution for 1.5 hours (expt. 4).

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(1) Directive Effects in Aromatic Substitution. XLVI.

(2) Post-doctorate research associate, 1959–1960, on project no. AT(11-1)-170 supported by the Atomic Energy Commission.

(3) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953).

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

(5) For a summary of available results for S_f, see L. M. Stock and H. C. Brown, *ibid.*, **81**, 3323 (1959).

(6) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

TABLE II

ISOMER DISTRIBUTIONS IN THE GALLIUM BROMIDE ETHYLATION OF BIPHENYL IN ETHYLENE DICHLORIDE SOLUTION AT 25°

Expt.	Time, hr.	Isomer distribution, %		
		o-	*m*-	*p*-
1	1.0	32.2	26.0	41.8
2[a]	>24	1	45	43
3	2.0	33.4	25.4	41.2
4	1.5	34.0	25.5	40.5
	Mean value[b]	33.3	25.6	41.1

[a] Plus 11% of diethylbiphenyl. [b] Expts. 1, 3, 4.

The results of these four experiments are summarized in Table II.

The constancy of the isomer distributions for reaction periods of 1.0, 1.5 and 2.0 hours suggests that no significant isomerization occurs in this time. The reaction mixture which was permitted to remain overnight revealed an almost complete loss of the *ortho* isomer. Since the reaction mixture contained only 11 mole per cent. diethylbiphenyl, the *o*-ethylbiphenyl presumably disappears by a rapid isomerization into the corresponding *meta* and *para* isomers.

The mean value for expts. 1, 3 and 4, 33.3% *o*-, 25.6% *m*- and 41.1% *p*-ethylbiphenyl, is adopted as the isomer distribution in the ethylation of biphenyl. Combination of this product ratio with the relative rate of ethylation of biphenyl to benzene, 1.81, provides the partial rate factors o_f^{Ph} 0.905, m_f^{Ph} 0.695 and p_f^{Ph} 2.23.

Ethylation of Toluene.—This reaction had been examined in a previous study.[6] However, in the experimental work toluene was employed as the solvent. It was necessary, therefore, to reexamine the relative rate and isomer distribution for ethylation in ethylene dichloride to ascertain the influence of solvent on the partial rate factors. The relative rate, toluene to benzene, was studied by the same competitive procedure as employed to measure the biphenyl to benzene rate ratio. The results are summarized in Table III.

TABLE III

TOLUENE TO BENZENE REACTIVITY RATIO FOR THE GALLIUM BROMIDE-CATALYZED ETHYLATION IN ETHYLENE DICHLORIDE AT 25°

Time, hr.	Init. concn., *M*				Final concn., *M*		Rel. rate k_T/k_B
	$GaBr_3$	EtBr	Toluene	Benzene	Toluene	Benzene	
1.0	0.040	0.500	0.560	0.675	0.415	0.593	2.31
1.0	0.040	0.500	0.532	0.605	0.392	0.532	2.38
						Mean value	2.34

The results indicate a toluene to benzene rate ratio of 2.34. This result is in good agreement with the relative rate obtained by direct kinetic measurement in the aromatic as solvent, 2.47.[6]

In order to determine the isomer distribution, toluene, 0.400 *M*, was ethylated for a relatively brief time, 10 minutes, and the reaction product examined by gas chromatography. A tricresyl phosphate phase gave excellent separation of the *ortho* isomer, but failed to resolve the *m*- and *p*-ethyltoluenes. However, the resulting analysis, 38.1% *o*-, 61.9% *m*- and *p*-ethyltoluene, is consistent with the isomer distribution realized under the earlier conditions, 38.3% *o*-, 21.1% *m*- and 40.6% *p*-. Accordingly, the latter isomer distribution was adopted.

Combination of this product distribution with the relative rate measurement provides the partial rate factors o_f^{Me} 2.69, m_f^{Me} 1.48 and p_f^{Me} 5.70.

Discussion

For the convenience of the following discussion, the observed relative rates and the partial rate factors for the ethylation of toluene and biphenyl are summarized in Table IV.

TABLE IV

PARTIAL RATE FACTORS FOR THE GALLIUM BROMIDE-CATALYZED ETHYLATION OF TOLUENE AND BIPHENYL IN ETHYLENE DICHLORIDE AT 25.0°

Aromatic	Relative rate Aromatic to Benzene	Partial rate factors		
		o_f	m_f	p_f
Toluene	2.34	2.69	1.48	5.70
Biphenyl	1.81	0.905	0.695	2.23

First, attention may be directed to the similarities in the substituent effects in the ethylation and mercuration reactions.[7] In each reaction, the methyl substituent activates the *meta* position of toluene, m_f^{Me} 1.48, whereas the phenyl substituent deactivates the corresponding position in biphenyl, m_f^{Ph} 0.695. This influence upon reactivity is in accord with the generally accepted inductive influences of the methyl (+I) and phenyl (−I) substituents.

The partial rate factors for mercuration, a reaction of apparently large steric requirements, in the *ortho* position of toluene and biphenyl are greatly reduced from the partial rate factors for *para* mercuration. For ethylation of these aromatics, the p_f/o_f ratio is approximately 2. Presumably, this is a result of the reduced steric requirements and enhanced reactivity of the ethylating reagent.

Finally, the relative rate data indicate the phenyl substituent activates the *para* position of biphenyl to a lesser extent than the methyl group activates the *para* position of toluene. Even after correction for the different inductive effects of the two substituents by comparison of the *para* to *meta* partial rate factors, p_f^{Ph}/m_f^{Ph} 3.2 and p_f^{Me}/m_f^{Me} 3.8, it is evident that the electron-rich phenyl group is significantly less effective than methyl in stabilizing the electron deficiency in the transition state. As was discussed in the previous paper, the unusually low activation by the phenyl substituent is reasonably attributed to difficulties involved in achieving the coplanar configuration desirable for maximum electron supply to the electron-deficient center.[7] A detailed discussion of this problem and its implications for the Selectivity Relationship is deferred to the final paper of this group.[8]

Although a specific study of the isomerization of the ethylbiphenyls was not made, the results clearly indicate *o*-ethylbiphenyl undergoes isomerization with remarkable ease. In the >24-hour experiment, Table II, *o*-ethylbiphenyl initially representing 33% of the reaction mixture decreased to only 1%, with a concurrent increase in the quantities of the *meta* and the *para* isomers.

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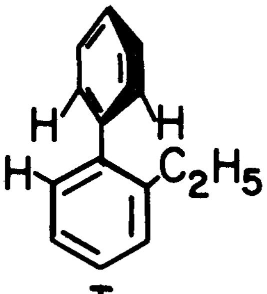
(7) H. C. Brown, M. Dubeck and G. Goldman, *J. Am. Chem. Soc.*, **84**, 1229 (1962).

(8) L. M. Stock and H. C. Brown, *ibid.*, **84**, 1238 (1962).

An explanation for the instability of the *o*-ethylbiphenyl molecule is based upon the problem of coplanarity and resonance stabilization in the biphenyl molecule.[9]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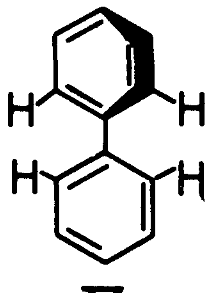
II

The *o*-ethyl substituent should increase the steric interactions and cause an increased deviation from copolanarity, I. The deviation from coplanarity diminishes the strain arising from the conflicting steric requirements of the *ortho* substituents. However, the rotation of the ring is accomplished only at the expense of resonance stabilization maximized by the planar conformation. Transfer of the ethyl substituent to the *meta* or *para* position decreases the deviation from coplanarity with a corresponding increase in the resonance interactions. It is our suggestion that the stabilization achieved in this manner is a powerful driving force for the isomerization of *o*-ethylbiphenyl.

Experimental Part

Materials.—Biphenyl and gallium bromide were prepared and purified as previously described.[6,7] Benzene, toluene, ethylene dichloride and ethyl bromide were purified by the methods described in earlier papers.[6,10] Pure samples of *o*-, *m*- and *p*-ethylbiphenyl were made available by Professor Ralph Dannley of Western Reserve University. The ethyltoluenes were available from an earlier study.[6]

Relative Rates.—A solution of gallium bromide in ethyl bromide was prepared under strictly anhydrous conditions. An appropriate small quantity of this solution (approximately 1 ml.) was introduced into 50 ml. of ethylene dichloride at 25° containing the two hydrocarbons in known concentrations. After an appropriate time, the reaction mixture was quenched in ice-water. The ethylene dichloride layer was separated, washed with water, dried over magnesium sulfate, and analyzed by gas chromatography using columns packed with silicone or butylene glycol–polyadipate as the liquid phases. The individual peaks were cleanly resolved and the areas were measured with a planimeter. The final concentrations of the two aromatics could be directly determined by comparison with the corresponding peak areas for the initial mixture, obtained under identical operating conditions. The data are summarized in Tables I and II.

Isomer Distribution.—The isomer distribution was established for reactions carried out and treated in the manner described above. In several cases, special experiments were carried out in which biphenyl and toluene were ethylated in the absence of benzene to obtain the isomer distribution. No significant difference in the isomer distribution was observed between the two sets of experiments.

The reaction mixtures were subjected to gas chromatographic analysis. The individual peaks were identified by comparison with authentic samples.

In the case of biphenyl, a variety of columns were investigated in order to obtain a satisfactory resolution of the isomer peaks. The maximum resolution was achieved with either a silicone or a butylene glycol–polyadipate column. The retention times for the ethylbiphenyls, relative to biphenyl, observed for these packings, are: For silicone at 230°: biphenyl, 1.00; *o*- 1.15; *m*- 1.59; *p*- 1.71. For polyadipate at 205°; biphenyl, 1.00; *o*- 0.89; *m*- 1.65; *p*- 1.84. Apiezon separated *m*- and *p*-ethylbiphenyl, but failed to resolve *o*-ethylbiphenyl and biphenyl.

The determination of the relative amounts of *para* and *meta* isomers could be achieved directly because they were well separated from each other as well as from biphenyl and the *ortho* isomer. The estimation of the relative amount of the *ortho* isomer presented a more difficult problem. In the case of the silicone column, the *ortho* isomer appeared as a sharp shoulder on the biphenyl elution peak. The area of this shoulder was assumed to give the percentage of the isomer. In the case of the polyadipate column, analysis was carried out by the measurement of the front-half area of the *ortho* peak. The results provided by the two columns are practically identical, Table V.

TABLE V

ISOMER DISTRIBUTION IN THE GALLIUM BROMIDE-CATALYZED ETHYLATION OF BIPHENYL IN ETHYLENE DICHLORIDE AT 25°

Expt.	$\frac{\%\ (m\text{-} + p\text{-})}{\%\ o\text{-}}$	$\frac{\%\ p\text{-}}{\%\ m\text{-}}$	Liquid phase
1	2.14	1.62	Silicone
	2.05	1.57	Polyadipate
		1.63	Apiezon
3	1.98	1.64	Silicone
	2.00	1.61	Polyadipate
4	2.00	1.62	Silicone
	1.85	1.56	Silicone
	1.99	1.59	Polyadipate
		1.62	Apiezon
Mean	2.00	1.605	

The isomer distributions in the ethylation of biphenyl were calculated from the mean values for the *para/meta* and the (*meta* + *para*)/*ortho* ratios. The results are summarized in Table II.

The percentage of *o*-ethyltoluene formed in the ethylation of toluene was readily determined with a tricresyl phosphate column. However, the *meta* and *para* peaks were not resolved. In view of the excellent agreement realized in the relative rate measurements in the hydrocarbon and halocarbon solvents and the agreement for percentage *ortho* in the same media it appeared safe to adopt the earlier isomer distribution.

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(9) This evidence and literature references relating to this problem are presented in the final paper of this group ref. 8.

(10) F. R. Jensen, G. Marino and H. C. Brown, *J. Am. Chem. Soc.*, **81**, 3303 (1959).