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Rate Data and Isomer Distributions in the Reactions of Biphenyl and Fluorene with Mercuric Acetate in Acetic Acid. Partial Rate Factors for the Mercuration Reaction¹⁻³BY HERBERT C. BROWN, M. DUBECK⁴ AND G. GOLDMAN

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The rate constants and isomer distributions for the mercuration of biphenyl with mercuric acetate have been determined at 90, 70 and 50°. The product distribution at 90° is 69.0% *p*-, 23.4% *m*- and 7.6% *o*-; at 70° 72.4% *p*-, 22.6% *m*- and 5.0% *o*-; at 50° 75.1% *p*-, 21.6% *m*- and 3.8% *o*-biphenylmercuric acetate, respectively. Utilizing kinetic data previously obtained for the mercuration of benzene under these conditions leads to the partial rate factors at 25°: $\sigma_{\text{H}}^{\text{Ph}}$ 0.09, m_{H}^{Ph} 0.79 and p_{H}^{Ph} 6.32. As presented in the Discussion, the minor activation in the *para* position of biphenyl is attributed to decreased resonance in the activated complex resulting from the non-coplanar configuration of the phenyl nuclei. This explanation was tested by an examination of the mercuration of fluorene. The partial rate factor, 2-Fl_H is calculated as 122 on the basis of the mercuration rate and 80% substitution in the 2-position of fluorene. The position in the planar fluorene molecule corresponding to the *para* site in biphenyl is strongly activated toward electrophilic substitution.

Introduction

Previous studies in this series have demonstrated that the available data on electrophilic substitution reactions of toluene,⁵ *t*-butylbenzene⁶ and anisole⁷ are correlated with satisfactory precision by the Selectivity Relationship.^{8,9}

The *p*-alkyl and *p*-methoxy substituents are strongly activating in electrophilic substitution reactions. The resonance stabilization of the transition state by these substituents, especially by the *p*-methoxy group, must be considerable. The precision of the correlations obtained was, therefore, most satisfying. The predictions of the σ^+ constants¹⁰ derived from data for the solvolysis of *t*-cumyl chlorides appeared to be fulfilled for the groups considered.

For the phenyl substituent the solvolysis of the *t*-cumyl chloride indicated the *para* substituent should be less activating than a methoxyl group and of the same order of magnitude as methyl, $\sigma_{\text{H}}^+_{\text{p-OMe}} -0.778$, $\sigma_{\text{H}}^+_{\text{p-Me}} -0.311$ and $\sigma_{\text{H}}^+_{\text{p-Ph}} -0.179$.¹⁰ On this basis the conformity of the phenyl group to the Selectivity treatment would be anticipated to be no less satisfactory than for the other activating substituents. There is considerable evidence, however, to indicate the behavior of the phenyl group is anomalous and the conformity to a linear treatment unsatisfactory.¹¹⁻¹³

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(3) Based upon theses submitted by M. Dubeck and G. Goldman in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(4) Monsanto Chemical Co. Fellow, 1956-1957.

(5) (a) F. R. Jensen, G. Marino and H. C. Brown, *J. Am. Chem. Soc.*, **81**, 3303 (1959); (b) H. C. Brown and G. Marino, *ibid.*, **81**, 3308 (1959); (c) H. C. Brown, G. Marino and L. M. Stock, *ibid.*, **81**, 3310 (1959); (d) S. U. Choi and H. C. Brown, *ibid.*, **81**, 3315 (1959); (e) H. C. Brown and B. A. Bolto, *ibid.*, **81**, 3320 (1959); (f) L. M. Stock and H. C. Brown, *ibid.*, **81**, 3323 (1959).

(6) (a) H. C. Brown and M. Dubeck, *ibid.*, **81**, 5608 (1959); (b) H. C. Brown and G. Marino, *ibid.*, **81**, 5611 (1959); (c) L. M. Stock and H. C. Brown, *ibid.*, **81**, 5613 (1959); (d) **81**, 5621 (1959).

(7) (a) H. C. Brown and M. Dubeck, *ibid.*, **82**, 1939 (1960); (b) L. M. Stock and H. C. Brown, *ibid.*, **82**, 1942 (1960).

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

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

(10) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

(11) P. B. D. de la Mare, *J. Chem. Soc.*, 4450 (1954).

(12) (a) C. Eaborn, *ibid.*, 4858 (1956); (b) F. B. Deans, C. Eaborn and D. F. Webster, *ibid.*, 3031 (1959); (c) C. Eaborn and R. Taylor, *ibid.*, 1012 (1961).

(13) J. R. Knowles, R. O. C. Norman and G. K. Radda, *ibid.*, 4885 (1960).

Accordingly, it appeared important to extend our examination of electrophilic substitution reactions to biphenyl. The present paper reports a study of the rate constants and the isomer distributions in the mercuration of biphenyl with mercuric acetate in glacial acetic acid. Subsequently, it became desirable to investigate the mercuration of fluorene.

In accompanying papers of this group are reported related substitution data for the ethylation,^{14a} acetylation^{14b} and bromination^{14c} of biphenyl. In the final paper a critical analysis of all available data dealing with electrophilic substitutions in biphenyl and fluorene is presented.^{14d}

Results

Mercuration of Biphenyl.—The rate of mercuration of biphenyl with mercuric acetate in glacial acetic acid was studied at 90, 70 and 50°. The aromatic was employed in large excess, biphenyl approximately 1.00 *M* compared to mercuric acetate, 0.1 *M*, in order to minimize the effects of poly-substitution. The rates of the reaction were followed from the decrease in the concentration of mercuric acetate in aliquots of the reaction mixture determined titrimetrically with standard potassium thiocyanate solution. The pseudo-first-order constants thus obtained were converted into second-order constants by dividing with the average value of the biphenyl concentration over the range of reaction.

The rate constants for the mercuration of biphenyl, together with that for benzene, are presented in Table I.

TABLE I

RATES OF REACTION OF BENZENE AND BIPHENYL WITH MERCURIC ACETATE IN GLACIAL ACETIC ACID

Temp., °C.	—Rate constant, 10 ⁵ k ₂ , l. mole ⁻¹ sec. ⁻¹ —		Relative rate
	Biphenyl	Benzene ^a	
90.0	6.65	3.42	1.94
70.0	1.19	0.565	2.11
50.0	0.174	.075	2.32
25.0	0.0112 ^b	.00413 ^b	2.71

^a Ref. 15. ^b Calculated from data at other temperatures.

In order to determine the isomer distribution in the mercuration of biphenyl, the hydrocarbon was

(14) (a) H. C. Brown and A. Neyens, *J. Am. Chem. Soc.*, **84**, 1233 (1962); (b) H. C. Brown and G. Marino, *ibid.*, **84**, 1236 (1962); (c) H. C. Brown and L. M. Stock, *ibid.*, **84**, 1238 (1962); (d) L. M. Stock and H. C. Brown, **84**, 1242 (1962).

(15) H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2306, 2310 (1955).

mercurated under conditions identical to those utilized for the kinetic experiments. Addition of lithium bromide precipitated the biphenylmercuric bromides. Treatment of the product with the theoretical quantity of bromine produced the corresponding *o*-, *m*- and *p*- bromobiphenyls in virtually quantitative yield.

The isomeric composition of the product was established by infrared analysis. Unfortunately, the relatively complex nature of the infrared spectra for a mixture of the three isomeric bromobiphenyls and weak absorption bands for the *ortho* and *meta* isomers at the only available wave lengths made the analysis somewhat more involved than the problems previously encountered in these studies. However, it proved possible to circumvent these difficulties (see Experimental Part).

The isomer distributions realized at 90, 70 and 50° are summarized in Table II. Combining the isomer distributions at these three temperatures with the second-order rate constants at the same temperatures provided the individual rate constants, k_o , k_m , k_p , for substitution at each of the three positions for each of the three temperatures. Extrapolation of the data to 25° yielded the isomer distribution at this temperature.

TABLE II

ISOMER DISTRIBUTIONS IN THE MERCURATION OF BIPHENYL WITH MERCURIC ACETATE IN GLACIAL ACETIC ACID

Temp., °C.	Biphenylmercuric acetate, %		
	<i>Ortho</i> -	<i>Meta</i> -	<i>Para</i> -
90.0	7.6	23.4	69.0
70.0	5.0	22.6	72.4
50.0	3.8	21.1	75.1
25.0	2.0 ^a	19 ^a	79 ^a

^a Calculated from rate constants and isomer distributions at higher temperatures.

Mercuration of Fluorene.—The high reactivity of fluorene enabled us to measure the rate constant at 25°. However, the low solubility of the hydrocarbon in acetic acid at this temperature made it impossible to employ the reactant at 1.00 *M* as had been adopted in earlier studies. In order to obtain comparable results for fluorene and the other aromatics examined previously, it was decided to utilize a solution 0.80 *M* in benzene and 0.20 *M* in fluorene. Thus the concentration of aromatic material was maintained at 1.00 *M* for facile comparison.

The procedure was tested with diphenyl ether. The original procedure, 1.00 *M* in diphenyl ether, yielded a second-order rate constant of 2.73×10^{-6} l. mole⁻¹ sec.⁻¹. The revised conditions, 0.20 *M* diphenyl ether and 0.80 *M* benzene, indicated the rate constant to be 2.89×10^{-6} l. mole⁻¹ sec.⁻¹ (after a small correction for concurrent mercuration of the benzene). The agreement was considered satisfactory and the correction factor of 2.73/2.89 was applied to the fluorene data to obtain the rate constant of 2.11×10^{-6} l. mole⁻¹ sec.⁻¹.

Fluorene has four different nuclear positions susceptible to attack. Since we were primarily interested in the partial rate factor for substitution in the 2-position, the analytical problem was greatly simplified. The mercurated products were converted to bromofluorenes and this mixture analyzed

only for the 2-isomer. The analysis was accomplished by determination of the cryoscopic constant for 2-bromofluorene, dissolution of the reaction product in pure 2-bromofluorene and measurement of the freezing point depression by a modified Rast procedure. This procedure indicated the reaction product contained $80 \pm 3\%$ 2-bromofluorene.

Discussion

Partial rate constants for the mercuration of biphenyl, fluorene and benzene are summarized in Table III.

An interesting feature of these results has been pointed out previously.^{6a} Mercuration *ortho* (−25.4 e.u.), *meta* (−24.9 e.u.) or *para* (−25.0 e.u.) to the methyl group in toluene exhibits a uniform activation entropy. Similar constancy is evident for substitution *meta* (−24.3 e.u.) and *para* (−24.5 e.u.) to the *t*-butyl substituent and *meta* (−25.4 e.u.) and *para* (−24.9 e.u.) to the phenyl group. The entropies of activation for nitration of the three isomeric ring positions of ethyl benzoate have been established by le Noble and Wheland to be identical within experimental error.¹⁶ Consequently, these data strongly support the usual assumption of the essential constancy of the entropy of activation in aromatic substitution.¹⁷

In the case of the *ortho* position of biphenyl, a significant change in the entropy of activation is detectable (−18.5 e.u.). Of course, it would not be counter to theory to observe a change in the entropy of activation for substitution *ortho* to a group with large steric requirements. Unfortunately, there is a considerable uncertainty in the present instance. The value is based upon the relatively small quantities of the *ortho* isomer formed in the mercuration, Table II, and is quite sensitive to relatively minor errors in the difficult analysis for this component (see Experimental Part).

Partial rate factors for the mercuration of toluene, biphenyl and fluorene are summarized in Table IV.

Clearly, a methyl group activates the *meta* position and the phenyl substituent deactivates that site. The results are in accord with dominant control of substitution in the *meta* position by the +I inductive effect of the methyl group and the −I inductive effect of the phenyl ring.

Previously, the relatively small amount of *ortho* mercuration in toluene, $p_i^{Me}/o_i^{Me} = 4.0$, was suggested to be indicative of a large steric requirement in the mercuration reaction. For biphenyl, this ratio is even larger, $p_i^{Ph}/o_i^{Ph} = 79$. The increase presumably arises from the combined influence of the greater steric requirements of the phenyl substituent and its electron-withdrawing inductive effect operating on the neighboring position. A contributing factor may also be the loss of a considerable portion of the resonance stabilization from the phenyl substituent as the conformation required to accommodate the aryl group and the mercuriacetate substituent in the transition state results in non-coplanarity of the phenyl rings.¹⁸

(16) W. J. le Noble and C. W. Wheland, *J. Am. Chem. Soc.*, **80**, 5397 (1958).

(17) I. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 124.

TABLE III
PARTIAL RATE CONSTANTS AND DERIVED KINETIC DATA FOR THE MERCURATION OF BENZENE, BIPHENYL AND FLUORENE WITH MERCURIC ACETATE IN GLACIAL ACETIC ACID

Compound	Partial rate constant 10 ⁴ k ₁ , l. mole ⁻¹ sec. ⁻¹			90.0°	ΔE _{act} , kcal. mole ⁻¹	log A	ΔH‡, kcal. mole ⁻¹	ΔS‡, cal. deg. ⁻¹
	25.0°	50.0°	70.0°					
Benzene ^a	0.00688	0.125	0.943	5.70	22.2	8.12	21.6	-23.6
Biphenyl								
<i>ortho</i> ^a	0.000610	0.0165	0.149	1.25	25.2	9.26	24.5	-18.5
<i>meta</i> ^a	.00533	.0920	0.673	3.89	21.8	7.73	21.2	-25.4
<i>para</i> ^a	.0440	.654	4.32	22.9	20.7	7.84	20.1	-24.9
Fluorene								
2-position ^a	0.84							
Benzene ^b	.0413	0.750	5.65	34.2	22.2	8.91	21.6	-19.6
Biphenyl ^c	.112	1.74	11.9	66.5	21.2	8.60	20.5	-21.5
Fluorene ^c	2.11							

^a 1 Position. ^b For all 6 positions. ^c For all positions—total rate constant.

TABLE IV
PARTIAL RATE FACTORS FOR THE MERCURATION OF TOLUENE, BIPHENYL AND FLUORENE WITH MERCURIC ACETATE IN GLACIAL ACETIC ACID

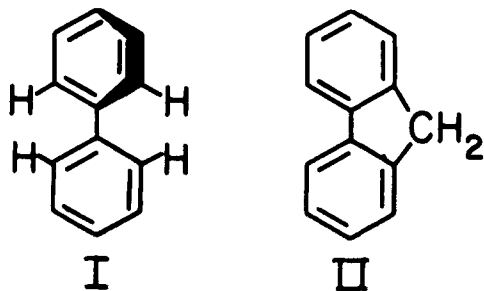
Temp., °C.	Toluene ^a			Biphenyl			Fluorene 2-Fl ₁
	<i>o</i> _T ^{Me}	<i>m</i> _T ^{Me}	<i>p</i> _T ^{Me}	<i>o</i> _T ^{Ph}	<i>m</i> _T ^{Ph}	<i>p</i> _T ^{Ph}	
90.0	3.51	1.70	11.2	0.221	0.681	4.02	
70.0	4.03	1.83	13.5	.158	.715	4.58	
50.0	4.60	1.98	16.8	.132	.735	5.23	
25.0	5.71	2.23	23.0	.0813	.773	6.42	122

^a Ref. 15.

The *para* position is moderately activated by the phenyl substituent. Resonance interactions with the phenyl substituent sufficiently large to overcome the -I inductive effect of that group would account for the observation. However, it is unexpected that the activating effect of the phenyl substituent should be not only not greater than methyl, but should actually be less; $p_T^{\text{Ph}}/m_T^{\text{Ph}} = 8.4$, $p_T^{\text{Me}}/m_T^{\text{Me}} = 10$.

The phenomena are quite similar to those previously observed in the solvolysis of the phenyl substituted *t*-cumyl chlorides.¹⁹ In the latter case the slow rate for *p*-phenyl-*t*-cumyl chloride solvolysis was attributed to the non-coplanarity of the phenyl rings in the activated complex. The same explanation can account for the observed low activity of the *para* position in biphenyl in the mercuration reaction.²⁰

The observed partial rate factor for mercuration in fluorene, 2-Fl₁ 122, is much larger than for sub-



(18) For a discussion of this point, see P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths Scientific Publications London, 1959, Chap. 12.

(19) H. C. Brown, Y. Okamoto and T. Inukai, *J. Am. Chem. Soc.*, **80**, 4964 (1958).

(20) P. B. D. de la Mare and M. Hassan, *J. Chem. Soc.*, 3004 (1957).

stitution in the *p*-position of biphenyl, p_T^{Ph} 6.4. A small portion of this rate increase is attributable to the inductive influence of the methylene bridge, m_T^{Me} 2.23. However, another more important effect appears to be operative. The coplanarity enforced by the methylene bridge in fluorene (II) is presumably responsible for the greatly enhanced reactivity.²¹

A detailed discussion of the precise nature of the transition state in the electrophilic substitution reactions of biphenyl and literature references to this interesting problem are presented in the final paper of this group.^{14d}

Experimental Part

Materials.—The glacial acetic acid used as solvent in the mercuration experiments was Baker and Adamson reagent grade material, analyzing for 0.1 *M* water by the Karl Fischer procedure. Since it had been established that water in this concentration range did not influence the observed rate constants,^{6a} no attempt was made to render the material more anhydrous. Mercuric acetate was Mallinckrodt analytical reagent grade material.

Biphenyl was recrystallized from glacial acetic acid to a constant melting point of 70°. Fluorene recrystallized in this manner exhibited in mercuration rate studies the presence of 7% of a highly active impurity. Accordingly, the fluorene was subjected to partial mercuration, the mercured material precipitated with lithium bromide, and the residual unattacked fluorene recovered. It was recrystallized from ethanol to a constant melting point of 114° and then exhibited no anomalies in the kinetic studies.

The isomeric bromobiphenyls were synthesized by standard methods. The *para* isomer was recrystallized from ethanol to a constant melting point of 90°. The *ortho* and *meta* isomers were carefully fractionated through a column rated at 60 plates: *o*-bromobiphenyl, b.p. 148° at 11 mm., n_D^{20} 1.6284; *m*-bromobiphenyl, b.p. 173° at 17 mm., n_D^{20} 1.6415. 2-Bromofluorene was recrystallized from ethanol to a constant melting point of 110°. These isomeric bromides possessed purities of greater than 99.5 mole per cent., calculated from cooling curves. The carbon disulfide employed as a solvent in the infrared analysis was dried and distilled from mercuric chloride and then from calcium hydride, center cuts being retained for the spectral measurements.

Rates of Mercuration.—Biphenyl, 11.56 g., was weighed in a reaction flask and 15.00 ml. of acetic acid was added, followed by 50.00 ml. of 0.1498 *M* mercuric acetate solution. The mixture was shaken until the biphenyl had dissolved and allowed to attain thermal equilibrium at 25.0°, after which the mercuric acetate concentration was determined titrimetrically with standard potassium thiocyanate solution. The decrease in mercuric acetate concentration from that of the original 50.00 ml. permitted a precise calculation of the final volume of the solution and of the concentration of the biphenyl. Ten-ml. samples of the reaction mixture

(21) P. B. D. de la Mare, D. M. Hall, M. M. Harris and M. Hassan, *Chemistry & Industry*, 1086 (1958).

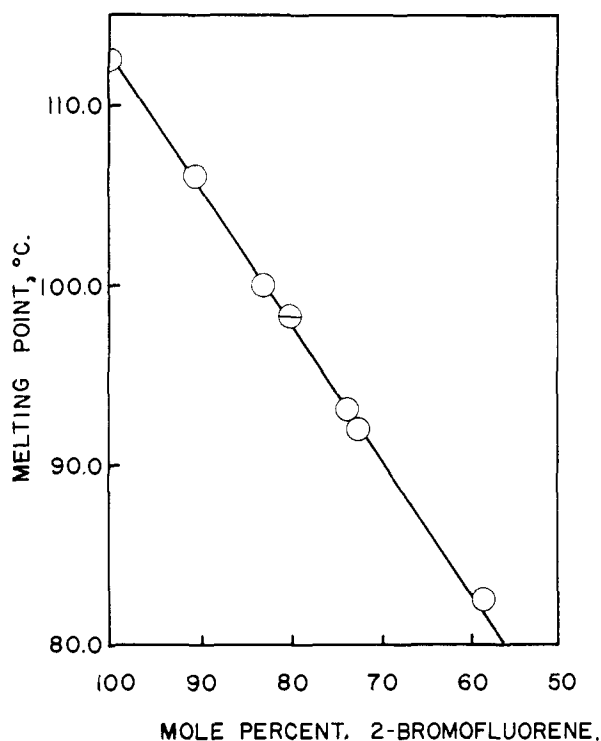


Fig. 1.—Relationship between the mole per cent. of 2-bromofluorene and 4-bromobiphenyl and the melting point of the mixture. The lined circle indicates the unknown mixture.

were pipetted into thin-walled bulbs and sealed. These were then placed in a constant temperature bath maintained at the desired temperature. After 5 min., one of the bulbs was removed, crushed in ice-water, and analyzed titrimetrically for mercuric acetate. This value was taken as the initial concentration at time zero. The remaining bulbs were removed at appropriate time intervals and the decrease in concentration of mercuric acetate determined. The concentrations at the reaction temperature were calculated from the known expansion of acetic acid with temperature. The data were also corrected for the slight side-reaction of mercuric acetate with the solvent.^{5a}

During the titration of mercury salts in the presence of precipitated biphenyl, it proved desirable to add benzene as the end-point was approached. Benzene dissolves the biphenyl and liberates occluded mercuric acetate and the biphenylmercuric acetates, promoting sharper end-points.

The rate constants are reported in Table I.

In the case of fluorene the hydrocarbon was sufficiently reactive so that the reaction could be followed at room temperature. These rate measurements were made by mixing 50.00 ml. of a 0.150 *M* mercuric acetate solution with 25.00 ml. of a 3.00 *M* solution of the aromatic (2.40 *M* in benzene and 0.600 *M* in fluorene) in glacial acetic acid. The resulting solution was maintained at 25.0° and aliquots removed at appropriate time intervals for titrimetric analysis of the residual mercuric acetate. The data were corrected for the slow side-reaction involving mercuration of the benzene.

Isomer Distributions.—A preheated solution of mercuric acetate in acetic acid, 350 ml., 0.15 *M*, was mixed with a preheated solution of biphenyl in the same solvent, 175 ml., 3.0 *M*, and the mixture was maintained at the desired temperature until approximately 30% of the mercuric acetate had reacted. The reaction mixture was then quickly cooled to room temperature and 9.0 g. of lithium bromide dissolved in 50 ml. of acetic acid was added, followed by about 600 to 800 ml. of water. The precipitated solid containing the isomeric biphenylmercuric bromides and unreacted biphenyl was collected on a filter, transferred to a 1-l. flask, and the biphenyl removed by steam distillation. The biphenylmercuric bromides, containing small amounts of residual biphenyl, were dried, ground to a fine powder, and maintained under vacuum at 50° to remove the last traces of

the hydrocarbon. The yields of the isomeric arylmercuric bromides were nearly quantitative.

Approximately 6.0 g. of the mercury derivatives were converted into the isomeric bromobiphenyls by treating a slurry in carbon disulfide with bromine until a slight red color persisted, indicating the presence of excess bromine. The mixture was permitted to remain for 12 hours to ensure complete conversion of the mercury derivatives. The supernatant liquid was separated from the solid and the latter was thoroughly washed with carbon disulfide. The solution was washed with aqueous bisulfide (to remove residual bromine), dried over calcium hydride, and carefully concentrated to a final volume of 10.00 ml.

The concentration of the *m*-bromobiphenyl in this solution was established by infrared analysis, utilizing the absorption band at 12.70 μ . Next *p*-bromobiphenyl was determined by diluting a 2.0-ml. aliquot to 20 ml. and utilizing the stronger band at 12.10 μ . The *ortho* isomer could not be detected spectroscopically in these solutions.

In order to determine the *ortho* isomer it was necessary to concentrate it by removing most of the *para* derivative. Fortunately, *p*-biphenylmercuric acetate proved to be far less soluble than the other isomers in 50% aqueous acetic acid and could be selectively removed. A reaction mixture identical with that described above containing biphenyl and the three isomeric biphenylmercuric acetates was rapidly cooled from reaction temperature to room temperature and an equal volume of water was added to precipitate most of the *p*-biphenylmercuric acetate and unreacted biphenyl. The solids were filtered off and washed with about 200 ml. of 50% aqueous acetic acid. The soluble isomeric arylmercuric acetates were converted into the insoluble bromides with lithium bromide. After standing for several hours, the solid was removed, washed with 50 ml. of aqueous acetic acid, and dried over phosphorus pentoxide. The yields of the biphenylmercuric bromides always corresponded very closely to the quantity of *ortho* and *meta* isomers estimated to be present on the basis of the analysis for *para*. The solid derivatives were converted into the bromobiphenyls as before, and the carbon disulfide solution of the bromobiphenyls, 0.3 *M*, was subjected to infrared analysis. The concentration of the *meta* isomer was established by means of the 12.70 μ band. Small quantities of the *para* isomer were indicated. To analyze for the *ortho* isomer, the absorption due to the *meta* isomer and the small amounts of the *para* were differentially blanked out by using appropriate solutions in the reference cell, and the *ortho* determined utilizing the 13.45 μ band.

Combining the *para/meta* ratio obtained in the first analysis with the *meta/ortho* ratios obtained in the second analysis yields the isomeric ratios reported in Table II.

Following the same procedure, 100 ml. of a solution of 0.2040 *M* mercuric acetate in acetic acid was added to 100 ml. of a solution which was 0.4075 *M* in fluorene and 0.585 *M* in benzene. The mixture was maintained at 25.0° and then quenched by the addition of lithium bromide in 50% aqueous acetic acid, followed by an amount of water equal to the total volume of the solution. After standing overnight, the solid material was separated and steam distilled to remove fluorene. The solid was washed with anhydrous ether to ensure removal of fluorene. The dried product weighed 97% of the calculated quantity; the fluorene recovered was 95% of theory.

An aliquot of the product, 0.500 g., was converted into the isomeric bromofluorenes in carbon disulfide as previously described. Removal of the carbon disulfide under vacuum yielded the bromofluorenes in yield of 92%.

The cryoscopic constant for 2-bromofluorene was determined to be 29 by adding known amounts of other components to 2-bromofluorene and observing the melting point depression by the Rast procedure. Addition of the reaction product to 2-bromofluorene produced a lowering of the freezing point which corresponded to the presence of 16.5 mole per cent. impurities, indicating the formation of 83.5% 2-bromofluorene.

As a second check on the isomer distribution, a series of mixtures of 4-bromobiphenyl in 2-bromofluorene were prepared and fused, and the melting points of the mixtures were determined. The data were used to construct a plot of m.p. versus mole per cent. 2-bromofluorene, Fig. 1. The melting point of the reaction product, 99°, indicated the presence of 78 mole per cent. 2-fluorene, Fig. 1.

It was concluded that mercuration proceeds to give approximately 80% of the 2-fluorene derivative.