

585. *The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part V.* Partial Rate Factors for the Acid-catalysed Bromination of Diphenyl by Hypobromous Acid.*

By P. B. D. DE LA MARE and M. HASSAN.

The proportions of isomers produced in the acid-catalysed bromination of diphenyl by hypobromous acid in 50% aqueous dioxan have been determined, by the method of isotopic dilution, as: 2-, 56.8%; 3-, 1.5%; 4-, 41.7%. Under the same conditions, the kinetic form for the bromination is: $-d[\text{BrOH}]/dt = k[\text{ArH}][\text{BrOH}][\text{H}^+]$. Diphenyl reacts 12.6 times faster than benzene. The positions *ortho* and *para* to a phenyl substituent are, therefore, activated, and that *meta* to a phenyl substituent is deactivated for this electrophilic substitution. Some of the theoretical implications of these results are discussed.

Not many quantitative studies are available of the proportions of isomers formed in the substitution reactions of diphenyl. Jenkins, McCullough, and Booth¹ record the isolation, on nitration of diphenyl by mixtures of nitric acid and sulphuric acid, of 71% of 2- and 11% of 4-nitrodiphenyl; and on its chlorination, with iron as catalyst, of 32% of 2- and 26% of 4-chlorodiphenyl. Dewar, Mole, Urch, and Warford,² for nitration in acetic anhydride, record the isolation of a mixture of nitrodiphenyls containing 77% of 2- and 23% of 4-nitrodiphenyl. No observations have been made relating to the amount of 3-substitution with electrophilic reagents, though Cadogan, Hey, and Williams³ measured partial rate factors for a homolytic process, phenylation.

* Part IV, *J.*, 1957, 923.

¹ Jenkins, McCullough, and Booth, *Ind. Eng. Chem.*, 1930, **22**, 31.

² Dewar, Mole, Urch, and Warford, *J.*, 1956, 3572.

³ Cadogan, Hey, and Williams, *J.*, 1954, 794.

[1957] *Mechanisms of Aromatic Halogen Substitution. Part V.* 3005

Similarly, the overall reactivity of diphenyl relative to benzene has been recorded only for nitration in acetic anhydride⁴ ($k_{\text{diphenyl}}/k_{\text{benzene}} = 16 : 1$) and for chlorination in acetic acid⁵ ($k_{\text{diphenyl}}/k_{\text{benzene}} = \text{ca. } 10^3$).

Details of the reactivities and isomer-distributions for substitutions in diphenyl by reagents of known character are of some theoretical interest, since the phenyl group, with its ($-I, \pm T$) effect, is one of those substituents which can either withdraw electrons from, or supply them to, the aromatic nucleus. Which of these effects will predominate in a particular situation will depend, *inter alia*, on the nature of the reaction, the character of the reagent, and the position in the nucleus from which the effect of the substituent is operating. Thus, when attempts are made to classify the phenyl group in terms of Hammett's (σ, ρ) relation,⁶ it is found^{7, 8} that no single value of, or sign for, the substituent (σ) constant successfully describes the electronic character of the group when acting from the *para*-position. It is possible that a value of reasonable general applicability is now available for the *meta*-position.^{9, 10}

Further interest in the substitution reactions involving diphenyl arises because reactivities of the various positions in the nucleus can be calculated. Calculations of the free-valence number¹¹ and of the atom localisation energy¹² indicate qualitatively that the *ortho*- and *para*-positions should be activated, and the *meta*-position slightly deactivated. Theoretically, this type of calculation should be more appropriate in describing homolytic substitution, whereas calculations based on Wheland's model for electrophilic aromatic substitution¹³ should be more appropriate to the cases with which this paper is concerned. For this model, Dewar¹⁴ states that, in the *meta*-position, the phenyl group should have no effect on the rate of electrophilic substitution.

In the present investigation, the bromination of diphenyl by hypobromous acid has been studied in aqueous dioxan with perchloric acid as catalyst. Under these conditions, the electrophilic reagent is a positive ion, either Br^+ or BrOH_2^+ . For substitutions by this reagent, both the inductive and the electromeric effect of substituents seem to play a part in determining the reactivities.¹⁵

EXPERIMENTAL

Materials and Methods.—General methods, including methods of radioactive assay, have been described in previous papers.¹⁵ $^{82}\text{Br}_2$ was prepared by shaking $\text{NH}_4^{82}\text{Br}$ (7 g.) with water (5 ml.) and bromine (5 ml.). The bromine and water were distilled from this mixture under reduced pressure, and were used directly for the preparation of labelled hypobromous acid. After recrystallisation, diphenyl had m. p. 70.0° , and 4-bromodiphenyl had m. p. 89.5° .

2-Bromodiphenyl was prepared as described by Augood, Cadogan, Hey, and Williams,¹⁶ and was recrystallised from pentane at -40° ; it had b. p. $148^\circ/10 \text{ mm.}$, f. p. $1.5-2.0^\circ$, n_D^{25} 1.6248. 3-Bromodiphenyl was prepared by the following route.^{9, 17} 2-Acetamidodiphenyl, m. p. 118° , was brominated with one molecular equivalent of bromine in acetic acid, and the monobromo-derivative was hydrolysed; it gave 2-amino-5-bromodiphenyl, m. p. $53-56^\circ$. This was diazotised, and the diazonium salt was deaminated by hypophosphorous acid, as described by Kornblum.¹⁸ The crude product was dissolved in benzene and was passed through

⁴ Dewar, Mole, and Warford, *J.*, 1956, 3576.

⁵ de la Mare, *J.*, 1954, 4450; Dewar and Mole, *J.*, 1957, 342.

⁶ Hammett, *J. Amer. Chem. Soc.*, 1937, 59, 96; *Trans. Faraday Soc.*, 1938, 34, 156.

⁷ Berliner and Liu, *J. Amer. Chem. Soc.*, 1953, 75, 2417.

⁸ Jaffe, *Chem. Rev.*, 1953, 53, 191.

⁹ Lichtin and Leftin, *J. Amer. Chem. Soc.*, 1952, 74, 4207.

¹⁰ Gould and McCullough, *ibid.*, 1951, 73, 1109.

¹¹ Burkitt, Coulson, and Longuet-Higgins, *Trans. Faraday Soc.*, 1951, 47, 553.

¹² Seel, *Z. Elektrochem.*, 1948, 52, 191; *Z. Naturforsch.*, 1948, 3a, 35.

¹³ Wheland, *J. Amer. Chem. Soc.*, 1942, 64, 900.

¹⁴ Dewar, *J.*, 1952, 3544.

¹⁵ de la Mare and Harvey, *J.*, 1956, 36; 1957, 131.

¹⁶ Augood, Cadogan, Hey, and Williams, *J.*, 1953, 3412.

¹⁷ Huber, Renoll, Rossow, and Mowry, *J. Amer. Chem. Soc.*, 1946, 68, 1111.

¹⁸ Kornblum, in "Organic Reactions," John Wiley and Sons, New York, Vol. II, 1944, p. 294.

a column of alumina, from which the product was then eluted with benzene. The combined benzene solutions were fractionally distilled at reduced pressure; there was recovered slightly impure 3-bromodiphenyl. This was dissolved in light petroleum (b. p. 40—60°) and was washed several times with concentrated sulphuric acid, then successively with water, aqueous sodium hydrogen carbonate, and water again. The solution was dried and fractionally distilled. The colourless product had b. p. 103°/0.2 mm., n_D^{25} 1.6380.

Nitration of 3-bromodiphenyl was carried out as follows. To 3-bromodiphenyl (4 g.) were added concentrated sulphuric acid (16 ml.) and, dropwise, fuming nitric acid (16 ml.). The mixture was heated at the b. p. for 45 min., then poured on ice. The precipitate was filtered off, and, after being washed with water, was dissolved in benzene. This solution was passed through a column of alumina. The material eluted with benzene was recovered by evaporation of the solvent, crude 5-bromo-2:2':4:4'-tetranitrodiphenyl separating as a pasty solid. Repeated crystallisation from acetone-alcohol gave yellow crystals of constant m. p. 160—161° (Found: C, 35.0; H, 1.5; N, 13.6. Calc. for $C_{12}H_5O_8N_4Br$: C, 34.9; H, 1.2; N, 13.7%).

Kinetics of Bromination of Diphenyl.—All results refer to a temperature of 25°, and to 1:1 v/v aqueous dioxan as solvent. The following is an example of a typical kinetic run, for diphenyl (0.0079M), perchloric acid (0.00303M), and hypobromous acid (0.00202M). Samples (25 ml.) were removed at intervals for titration with sodium thiosulphate (0.0041N). A control, with diphenyl omitted, was used to correct for the slight decomposition of hypobromous acid in the solvent.

Reaction			Control		
Time (min.)	Titre (ml.)	10^2k_1 (min. ⁻¹)	Time (min.)	Titre (ml.)	10^2k_1 (min. ⁻¹)
0.0	22.30	—	0.0	22.30	—
5.41	21.10	1.11	5.25	22.20	0.085
10.75	19.90	1.06	10.08	22.20	0.042
14.91	19.10	1.02	14.75	22.20	0.031
19.30	18.50	0.97	19.48	22.20	0.021
25.30	17.50	0.96	31.45	22.00	0.043

Methods of calculation have been described before.¹⁵ Values of k_1 are first-order rate-coefficients calculated on the disappearance of hypobromous acid. The values of k_2 given below are initial second-order rate-coefficients, corrected for decomposition in the control experiments. They show the effects of varying the concentrations of the reactants.

(i) $HClO_4$, 0.0243M; $BrOH$, ca. 0.0015M.

Diphenyl (M)	0.0101	0.0157
k_2 (l. mole ⁻¹ min. ⁻¹)	11.5	11.4

(ii) $HClO_4$, 0.0030M; diphenyl, 0.008M.

$BrOH$ (M)	0.00103	0.00180	0.00202
k_2 (l. mole ⁻¹ min. ⁻¹)	1.43	1.40	1.38

(iii) Diphenyl, 0.008—0.014M; $BrOH$, 0.001—0.002M.

$HClO_4$ (M)	0.00303	0.00972	0.0125	0.0254	0.0486	0.0729
k_2 (l. mole ⁻¹ min. ⁻¹)	1.40	4.37	5.29	11.54	22.56	30.8
$k_2/[H^+]$ (l. ² mole ⁻² min. ⁻¹) ...	462	461	435	469	464	416

The results show that, at 25° in 50% dioxan, the kinetic form of the reaction is in accordance with the equation $-d[BrOH]/dt = k[ArH][BrOH][H^+]$; the mean value of k is, for diphenyl, 451 l.² mole⁻² min.⁻¹; the corresponding value for benzene¹⁵ is 35.9 l.² mole⁻² min.⁻¹.

Proportions of Isomers formed in the Bromination of Diphenyl.—*para-Substitution.* Diphenyl (0.0165M), $^{82}BrOH$ (0.0025M), and perchloric acid (0.243M), all in 50% dioxan, were allowed to react until, as found by titration of an aliquot part, enough hypobromous acid had disappeared to form 0.897 g. of mixed bromodiphenyls, in 1950 ml. of reaction mixture, allowance being made for the small decomposition in a control experiment. To the reaction mixture was added inactive 4-bromodiphenyl (8.822 g.). The bromodiphenyls and unchanged starting material were recovered by extraction with ether, and were oxidised in the following way.¹⁹ To a stirred solution of the diphenyls (5 g.) in hot 75% acetic acid was added dropwise a mixture of

¹⁹ Case, *J. Amer. Chem. Soc.*, 1939, **61**, 3487.

chromic oxide (52 g.), water (30 ml.), and acetic acid (18 ml.). The mixture was refluxed for 2 hr. Excess of acetaldehyde was then added, and the mixture was heated under reflux for a further 15 min. To the cooled mixture was then added a saturated solution of sodium chloride (150 ml.). The organic material was thence recovered by extraction with ether. After evaporation of the ether, the residue was made alkaline with ammonia and filtered. The filtrate was acidified, and the precipitated mixture of acids was recrystallised from water several times. There was obtained *p*-bromobenzoic acid, m. p. 252°, of activity 178 counts per min. (0.0605M, dissolved in dilute alkali), unchanged by further recrystallisation. At the time relevant for comparison, the original hypobromous acid (0.00620M) had an activity of 448 counts per min. Hence 0.374 g. (41.7%) of 4-bromodiphenyl had been produced in the reaction.

ortho-Substitution. A similar method was used. The recovered *o*-bromobenzoic acid had m. p. 150°, and the specific activity, constant after several recrystallisations, corresponded with the formation of 56.8% of 2-bromodiphenyl.

meta-Substitution. Very poor yields of pure *m*-bromobenzoic acid were obtained by oxidation of 3-bromodiphenyl. Hence it was found more satisfactory to make radioactive measurements on the tetranitro-derivative of the latter compound. The reactants contained diphenyl (0.01685M), hypobromous acid (0.0040M), and perchloric acid (0.3037M). The uptake of hypobromous acid corresponded with the formation of 1.655 g. of mixed bromodiphenyls for 1925 ml. of reaction mixture. To this was added inactive 3-bromodiphenyl (15.36 g.), and from the diluted mixture was recovered crude 3-bromodiphenyl, b. p. 102—104°/0.2 mm. (12 g.). This material (8 g.) was nitrated as described above. The tetranitro-derivative, m. p. 160—161°, was recrystallised from acetone-alcohol. Successive recrystallisations gave materials of the following activities, expressed in counts per min. for a 0.0129M-solution in acetone: 212, 193, 183. To the final fraction (2 g.) was added 0.2 g. of the material obtained by nitrating, under the experimental conditions used for the 3-isomer, a mixture of inactive 2- and 4-bromodiphenyl. The tetranitro-derivative, m. p. 160—161°, was then again recovered from this mixture; it should by this procedure have been freed from any traces of highly active nitro-derivatives of 2- and 4-bromodiphenyl. Successive fractions now had specific activities, expressed in the same units as before, of 168, 162, and 159 counts per min., and it was considered that the final value gave the limiting specific activity within experimental error. Comparison with the corresponding value for the original hypobromous acid (468 counts per min., 0.000606M) showed that 1.5% of 3-bromodiphenyl had been produced in the reaction.

Kinetics of Bromination of 2- and 4-Bromodiphenyl.—These have been investigated only in the barest outline. The rate-coefficients ($k_2/[H^+]$; units: $l.^2 \text{ mole}^{-2} \text{ min.}^{-1}$) were: 2-, 160; 4-, 98. The kinetic forms were not studied in detail, but the reactions are both slower than the corresponding bromination of diphenyl. This confirms the finding that, in the latter reaction, under the experimental conditions adopted, dibromination is unlikely to be important.

DISCUSSION

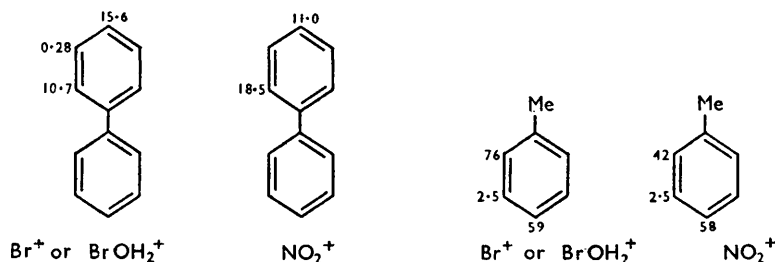
The values given above for *ortho*-, *meta*-, and *para*-substitution are entirely independent, and, fortuitously, together account for all of the disappearance of hypobromous acid. It is thought that the values given for *ortho*- (56.8%) and *para*-substitution (41.7%) are reliable to within about 0.5 unit %, and that for *meta*-substitution (1.5%) within about 0.1 unit %.

The kinetic form for the reaction is the same as that which has been observed for bromination of other aromatic compounds in the same medium, and indicates clearly that the effective brominating species is a positive entity, either Br^+ or $BrOH_2^+$. The above isomeric proportions, and the observed rate-ratio, $k_{\text{diphenyl}}/k_{\text{benzene}} = 12.6$, determine the partial rate factors in the formulæ. Values are given also for nitration, as far as they are known, using the rate-ratio, $k_{\text{diphenyl}}/k_{\text{benzene}} = 16.1$, recorded by Dewar, Mole, and Warford,⁴ and the proportions² of *ortho*- (77%) and *para*-isomers (23%) produced in the reaction.* For comparison are given also the values which have been recorded for the similar reactions of toluene.¹⁵

* The latter values do not accord with those calculated, using the same experimental data, by Dewar, Mole, and Warford.²⁰

²⁰ Dewar, Mole, and Warford, *J.*, 1956, 3581.

The present experiments show that the *meta*-position in diphenyl is, for bromination by a positive entity, deactivated by a small factor. Whether or not the same is true of nitration is not known, though this would be expected, since in both these reactions the electron-withdrawing ($-I$) inductive effect of the phenyl substituent should be of



considerable importance. It is of interest to compare the effects of substituents on the rate of this type of bromination with the corresponding effects (cf. ref. 8) on the strengths of *meta*-substituted benzoic acids, as shown below :

Substituent group (R)	Bu ^t	Me	H	Ph
Bromination of PhR by Br^+ or BrOH_2^+ ; $\log_{10} f_m^{\text{R}}$	0.41	0.40	0	-0.55
Relative acid strengths* of <i>m</i> -R-C ₆ H ₄ ·CO ₂ H; $\log_{10} K_{\text{R}}/K_{\text{H}}$	-0.12	-0.07	0	0.66

* Otherwise Hammett's substituent (σ_m) constants.⁶ Positive values show electron-withdrawal.

The spread of rates (expressed as logarithms of partial rate factors, $\log_{10} f^{\text{R}}$, so that the values are proportional to the changes in free energy of activation) is rather greater than that of strengths of acids, emphasising that aromatic substitution, even in the *meta*-position, is somewhat sensitive to the effects of substituents. The fact that, as measured by the rate of *meta*-bromination of diphenyl, the phenyl substituent has a marked power of electron-withdrawal from the *meta*-position—greater in magnitude, for example, than the electron-releasing power of *meta*-alkyl groups—accords with the opinion expressed elsewhere¹⁵ that the inductive effect has a considerable influence in reactions involving electrophilic reagents which bear a full positive charge.

Consider now *para*-substitution: the phenyl group, as would be expected, is electron-releasing in character, thereby showing its power of conjugative ($+E$) electron-release at the demand of an electrophilic reagent. In some reactions which are facilitated by electron-release, the phenyl group is more effective than a single methyl group.²¹ The phenyl group is, however, notoriously variable in its power of releasing electrons as measured by its influence compared with that of other substituents,⁷ and it is not surprising that in this reaction, where inductive effects seem also to be rather important, the methyl group should have a greater activating power for the *para*-position by a factor of four or more.

Comparison of the partial rate factors for *para*-bromination with the strengths of the related benzoic acids shows, however, that, for the limited range of groups which have so far been examined, the structural effects in the two series are not closely related, the phenyl group being much less powerfully electron-releasing when its effect is measured with reference to the latter series. This is shown by the following data :

Substituent group (R)	Bu ^t	Me	Ph	H
Bromination of PhR by Br^+ or BrOH_2^+ ; $\log_{10} f_p^{\text{R}}$	1.57	1.77	1.19	0
Relative acid strengths of <i>p</i> -R-C ₆ H ₄ ·CO ₂ H; $\log_{10} K_{\text{R}}/K_{\text{H}}$	-0.20	-0.17	-0.01	0

The $\frac{1}{2}0$: *p*-ratios in bromination by positive bromine (0.68) and in nitration (1.7) show features of considerable interest. The *ortho*-position is, in the first reaction, less activated

²¹ de la Mare, *Quart. Rev.*, 1949, **3**, 126; Vernon, *J.*, 1954, 423.

than the *para*-position. This type of orientation has been discussed by R. D. Brown.²² He showed that molecular-orbital calculations of the reactivities of these positions indicate that the *ortho*-position should, in compounds of this type, be the more reactive, and he ascribed low $\frac{1}{2}o : p$ -ratios in electrophilic substitution in diphenyl to steric hindrance of *ortho*-substitution.

In previous papers,¹⁵ it has been shown that, for bromination by positive bromine, steric hindrance *ortho* to substituent groups is demonstrable for the *tert.*-butyl group, but is probably small, though not necessarily absent, for the methyl group. The phenyl group might well be intermediate in effective size between these two substituents, so that it would not be unreasonable on this basis alone to hold that steric hindrance had, for bromination, reduced the $\frac{1}{2}o : p$ -ratio from slightly greater than 1 (as required, if R. D. Brown's view be adopted) to 0.68.

If this were correct, however, the effect of steric hindrance should be even more marked in nitration. For it has been shown¹⁵ for the crucial examples of toluene and *tert.*-butylbenzene that $\frac{1}{2}o : p$ -ratios are characteristically smaller for nitration than for bromination by positive bromine; and the differences, both qualitatively and quantitatively, fit the view that the entering nitro-group has, because of its triangular shape, a greater effective radius in the direction of the substituent *ortho* to its position of entry than has the more nearly spherical entering bromine atom.*

For the nitration of diphenyl, however, the $\frac{1}{2}o : p$ -ratio (1.7) is very high. There seems to be little doubt that such a high value is satisfactorily experimentally established,† and is determined by a heterolytic process, since it has been confirmed by two groups of workers using widely different nitrating media.^{1,2} Since this difference between nitration and bromination by positive bromine is in the direction opposite to that expected if primary steric hindrance were the determining factor, an alternative explanation is required.

Diphenyl itself, in the gas phase²⁵ and presumably also in solution,²⁶ is non-planar, having an angle of *ca.* 45° between the planes of the benzene rings. This angle is almost certainly maintained by van der Waals forces between the *ortho*-hydrogen atoms. These forces become appreciable in the planar state, in which, for a rigid model, the distances between the 2- and the 2'-hydrogen atom are about 1.85 Å; and they are relieved by rotation of the benzene rings. The energy difference between the planar and the non-planar form cannot, however, be large, since the molecule is planar in the crystal.²⁷ Conjugation between the two rings, at a maximum for the planar configuration, must play a part in reducing the barrier restricting rotation about the inter-nuclear bond.

The electron-releasing properties of the phenyl group are at a maximum for the fully conjugated planar conformation. It is suggested that in the transition state for *ortho*-substitution the entering group forces the adjacent ring towards the coplanar conformation; for nitration, rearrangement (I), indicated in perspective in Fig. 1, is favoured. In this, an *ortho*-hydrogen atom of the directing ring is held between the entering nitro-group and the departing hydrogen substituent. The electronic activation of the aromatic nucleus is thereby kept at, or near, its maximum. The arrangement in which the two ring-planes are at right angles might be slightly preferable if steric factors alone were to be considered; but, electronically, diphenyl in this conformation would be deactivated for electrophilic substitution.

The $\frac{1}{2}o : p$ -ratio is, therefore, higher than it would be for nitration, were it not for the

* Thus steric hindrance is significant for nitration *ortho* to a methyl group. In this respect, the authors disagree with the conclusions implicit in the treatment given by H. C. Brown and Smoot.²³

† An earlier report,²⁴ which sometimes has been taken as showing that *para*-nitration predominates, would probably not have been considered by the experimenters as a demonstration of a low $\frac{1}{2}o : p$ -ratio.

²² R. D. Brown, *J. Amer. Chem. Soc.*, 1953, **75**, 4077.

²³ H. C. Brown and Smoot, *ibid.*, 1956, **78**, 6255.

²⁴ Bell, Kenyon, and Robinson, *J.*, 1926, 1239.

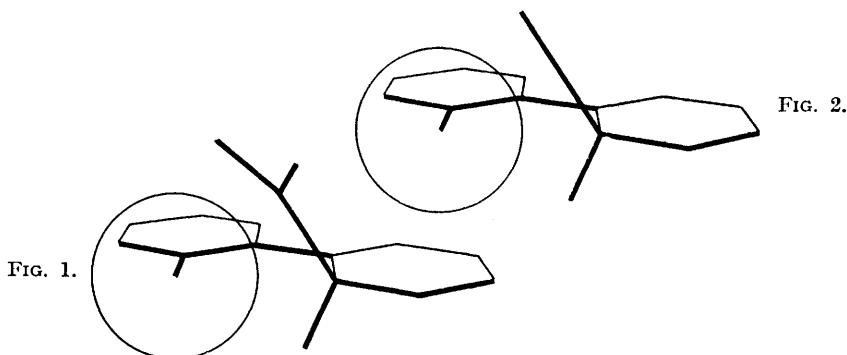
²⁵ Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408; 1950, **4**, 926.

²⁶ Merkel and Wiegand, *Z. Naturforsch.*, 1948, **3b**, 93.

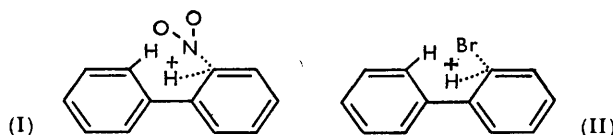
²⁷ Dhar, *Indian J. Phys.*, 1932, **7**, 43.

3010 *Mechanisms of Aromatic Halogen Substitution. Part V.*

fact that the entering and leaving groups hold the directing substituent in a conformation particularly favourable for electronic activation of the nucleus.* This effect must operate also, though apparently to a smaller degree, for bromination (II; Fig. 2); here also the $\frac{1}{2}o$: p -ratio is probably higher than would otherwise have been expected.



Rotation of the activating phenyl group about the inter-nuclear bond towards the position in which the *ortho*- and the leaving hydrogen substituent are at their closest (about 2.07 Å apart, assuming a rigid model with normal C-H bond-lengths) would introduce, in any transition state analogous to (I) or (II), approximately the same amount



of steric hindrance, so to a first approximation one might have expected any electrophilic displacement of hydrogen from diphenyl to show a $\frac{1}{2}o$: p -ratio which was abnormally high to approximately the same extent. It is possible that the observed differences between bromination and nitration are the results of differences in entropy, rather than in energy of activation, the attainment of a favourable conformation being made more probable in the latter *ortho*-substitution by the shape of the entering nitro-group. It is possible alternatively that electrostatic forces between the entering nitro-group and the directing ring may be more favourable than the corresponding interactions involving entering bromine. Again, it is possible that there is a different degree of weakening of the C-H bond which eventually is to be displaced [so that formulæ (I) and (II) do not satisfactorily represent the rate-controlling transition state]. If in bromination the C-H bond were even less displaced than in nitration, the planar structure would be less favoured for the transition state of the former reaction. Considerations of these types have been discussed, more particularly for nucleophilic aromatic displacements, by various workers.^{28,29}

These considerations do not support, but also do not definitely exclude, R. D. Brown's contention²² that the *ortho*-position in diphenyl may, by conjugation, be more activated than the *para*-position, since, on the view developed above that the inductive effect is also of importance in determining reactivity in these compounds, the *ortho*-position would in this

* The idea that increase in resonance energy on going to the transition state may be greater in an *ortho*-displacement if the activating substituent is constrained in the transition state between the entering and the leaving group has been expressed by other workers, e.g., by Hammond,²⁸ for nucleophilic substitutions *ortho* to an activating nitro-group.

²⁸ Hammond, in "Steric Effects in Organic Chemistry," ed. Newman, Chapman and Hall, London, 1956, p. 187.

²⁹ Bunnett and Morath, *J. Amer. Chem. Soc.*, 1955, **77**, 5051; Chapman, Parker, and Soanes, *J.*, 1954, 2109; Corey and Sauers, *J. Amer. Chem. Soc.*, 1957, **79**, 248.

[1957]

A New Synthesis of 1-Alkylfluorenes.

3011

reaction be specifically and preferentially deactivated by the overall inductive effect of the phenyl substituent. The orientational characteristics for molecular chlorination may throw light on this point, since in this reaction it seems, from the incomplete data already in the literature,⁵ that the conjugative effect of the phenyl substituent is greater than the corresponding effect of the methyl group.

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