774. *The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part XVI.*[1] *Rates and Products of Chlorination of Biphenyl and some t-Butyl-substituted Biphenyls in Acetic Acid.*

By P. B. D. DE LA MARE and E. A. JOHNSON.

The rates of chlorination of 4-t-butyl-, 4,4′-di-t-butyl-, 2-t-butyl-, and 2,2′-di-t-butyl-biphenyl in acetic acid at 25° have been compared, and the products have been examined by vapour-phase chromatography. Products of chlorode-t-butylation accompany those of nuclear substitution for the first three compounds but not for the last. The reactivities at the various nuclear positions in the 4-t-butyl-substituted compounds accord reasonably with predictions based on the additivity of substituent effects; the 2-t-butyl substituent, on the other hand, markedly reduces the reactivity of positions *ortho* and *para* to the aryl group. Weingarten's claim [2] that 3-chlorobiphenyl can be detected by vapour-phase chromatography of the products of chlorination of biphenyl has been confirmed, but evidence is adduced that it is in major part derived from thermal decomposition of the polychloro-adducts which accompany substitution.

IN previous papers [3-5] the rates and products of chlorination of biphenyl and some methyl-substituted biphenyls in acetic acid at 25° have been recorded. Despite the complication that part of the electrophilic reaction has been shown to involve addition rather than substitution, the rates and orientation of substitution in 3- and 4-methyl-substituted biphenyls accord reasonably with predictions based on the additivity principle,[6] specifically that methyl and aryl groups activate the nucleus independently and to an extent that is additive in free energy of activation. Methyl groups in the 2-position, however, reduce the reactivity by interfering with the conjugating power of the aryl group; as expected this effect has a much more pronounced influence on the reactivity of positions *ortho* and *para* to the Ar–Ar link,* no matter which aryl group contains the 2-substituent.

The t-butyl group, like the methyl group, obeys to a reasonable approximation the linear free-energy relationship between the rates of *meta*- and *para*-substitution,[7,8]

$$\log_{10} f_m = \text{Constant.} \log_{10} f_p. \qquad (1)$$

It is likely, therefore, that the additivity principle would apply as well to the t-butyl group as to the methyl group. The former, however, being bulkier, diminishes chlorination in adjacent positions. Furthermore, when introduced into the 2-position in a biphenyl system it should have an even larger effect in reducing the power of each aryl group to release electrons to the other. It seemed of interest, therefore, to examine the rates and products of chlorination of some t-butyl-substituted biphenyls. The occasion has been taken to re-examine the amount of 3-chlorobiphenyl obtained by chlorination of biphenyl, in view of our failure [4] to detect this product, our theoretical [4,9] prediction that very little should be formed by direct electrophilic substitution, Brown and Stock's [10] concordance

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* In this paper, Ar = aryl.

[1] Part XV, de la Mare and Maxwell, *J.*, 1962, 4829.

[2] Weingarten, *J. Org. Chem.*, 1961, **26**, 4347.

[3] de la Mare, Hall, Harris, and Hassan, *Chem. and Ind.*, 1958, 1086.

[4] Beaven, de la Mare, Hassan, Johnson, and Klassen, *J.*, 1961, 2749.

[5] de la Mare, Hall, Harris, Hassan, Johnson, and Klassen, *J.*, 1962, 3784.

[6] Cf. de la Mare and Ridd, "Aromatic Substitution—Nitration and Halogenation," Butterworths Scientific Publns., London, 1958, pp. 88 ff.

[7] Stock and Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 5621.

[8] de la Mare, "Theoretical Organic Chemistry," Kekulé Symposium, Butterworths Scientific Publns., London, 1958, p. 219; *J.*, 1954, 4450.

[9] de la Mare and Hassan, *J.*, 1958, 1519.

[10] Stock and Brown, *J. Amer. Chem. Soc.*, 1962, **84**, 1242.

with this view, and Weingarten's[2] recent report that significant amounts can be detected in the product from chlorination under very similar conditions.

EXPERIMENTAL

Some of the materials, and the general methods, were described in early papers.[4,5] We are indebted to Dr. M. S. Lesslie for a sample of 2,2′-di-t-butylbiphenyl, which was purified by chromatography on silica gel and recrystallised from aqueous ethanol. It had m. p. 62—64° (lit.,[11] 63—64°); vapour-phase chromatography gave a single peak. 4,4′-Di-t-butylbiphenyl, m. p. 127—128° (lit.,[12] 122°, 128—129°), and 4-t-butylbiphenyl, m. p. 51·5—52·5° (lit.,[13] 53°), were prepared by direct alkylation of biphenyl with t-butyl alcohol and ferric chloride.[14] The mono- and di-t-butylated products were separated from each other and from unchanged biphenyl by fractional distillation; vapour-phase chromatographic examination of the crude reaction product showed that the other isomers were not formed in significant amount.

2-t-Butylbiphenyl was prepared for us by Dr. M. S. Lesslie by decarboxylation of 2′-t-butylbiphenyl-2-carboxylic acid[11] (0·6 g.) with quinoline and copper bronze. The neutral portion of the product was purified by vapour-phase chromatography in portions of *ca.* 100 mg. There was obtained 2-t-butylbiphenyl (0·25 g.), m. p. 37—38° (lit.,[15] 31—34°). Vapour-phase chromatography did not show the presence of any significant impurity.

The rates of chlorination were determined in acetic acid at 25° in the usual way; 4,4′-di-t-butylbiphenyl, $k_2 = 0{\cdot}42$ l. mole^{-1} min.$^{-1}$; 4-t-butylbiphenyl, $k_2 = 0{\cdot}154$ l. mole^{-1} min.$^{-1}$; 2,2′-di-t-butylbiphenyl, $k_2 = 0{\cdot}0108$ l. mole^{-1} min.$^{-1}$; 2-t-butylbiphenyl, $k_2 = 0{\cdot}006$ l. mole^{-1} min.$^{-1}$.

Vapour-phase chromatographic procedures were essentially as described in an earlier paper.[4] In addition, the high resolution of a capillary column was used to lend additional weight to identifications made on the basis of retention volumes.

The products of chlorination from reactions involving the aromatic compound in excess over the chlorine were recovered in the usual way.

4,4′-Di-t-butylbiphenyl.—This gave a product containing 53% * of the starting material, and 40% of a main peak, which from its retention volume † (V_R 20·5) was substituted in the 2-position and therefore must be *2-chloro-4,4′-di-t-butylbiphenyl*. A small fraction of this material was collected. Its ultraviolet spectrum showed that it had a substituent in the 2-position, thus confirming its structure. The hydrocarbon (0·6 g.) was treated with chlorine (5 ml., 0·5M) in acetic acid. Water was added to the hot solution; the solid which separated on cooling was fractionally crystallised from aqueous methanol, and gave pure 2-chloro-4,4′-di-t-butylbiphenyl, m. p. 88—89° (Found: C, 79·6; H, 8·4; Cl, 12·0. $C_{20}H_{25}Cl$ requires C, 79·9; H, 8·3; Cl, 11·8%). The subsidiary peak which preceded it on the gas chromatogram represented the product of de-t-butylation, 4-chloro-4′-t-butylbiphenyl (cf. below). It had m. p. 152°, and its ultraviolet spectrum and retention volume (9·9) were identical with those of the main product of chlorination of 4-t-butylbiphenyl, thus confirming its structure. Three very minor components were eluted after the 2-chloro-derivative; one of these may be 3-chloro-4,4′-di-t-butylbiphenyl, and the others are probably dichloro-derivatives.

4-t-Butylbiphenyl.—The product from 4-t-butylbiphenyl contained 28% of the starting material, and small amounts (*ca.* 2%) of three minor components of retention volume higher than expected for a chloro-4-t-butylbiphenyl; they were probably dichloro-4-t-butylbiphenyls produced by an addition–elimination sequence. The remainder separated on the gas chromatogram into two major peaks. The first of these was resolved further on a capillary column into two nearly equal peaks with retention volumes (V_R 5·55 and 5·75) expected for the presence

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* Percentages are given on a molar basis.

† Biphenyl, $V_R = 1$; 4,4′-di-t-butylbiphenyl, $V_R = 16{\cdot}5$.

[11] Lesslie and Mayer, *J.*, 1961, 611; 1962, 1401.

[12] Chichibabin, Elgazine, and Lengold, *Bull. Soc. chim. France*, 1928, **43**, 238; Boedtker, *ibid.*, 1929, **45**, 645.

[13] Grosse, Mavity, and Ipatieff, *J. Org. Chem.*, 1938, **3**, 448.

[14] Cf. Potts and Dodson, *J. Amer. Chem. Soc.*, 1939, **61**, 2553.

[15] Cadogan, Hey, and Williams, *J.*, 1954, 3352.

of substituents *ortho* to an aryl group; these must therefore be 2- and 2′-chloro-4-t-butylbiphenyl (20% and 18%, respectively). The second represented material identical with the minor product of chlorination of 4,4′-di-t-butylbiphenyl and so can be identified as 4-chloro-4′-t-butylbiphenyl (28%). From the product of chlorination of the hydrocarbon (0·5 g.) with chlorine (5 ml., 0·5M) in acetic acid, there was obtained by preparative vapour-phase chromatography a pure sample of *4-chloro-4′-t-butylbiphenyl*, m. p. 153—154° (Found: C, 78·4; H, 6·9; Cl, 14·2. $C_{16}H_{17}Cl$ requires C, 78·5; H, 7·0; Cl, 14·5%). A minor component was 4-chlorobiphenyl (4%), identified from its retention volume (2·40) and ultraviolet absorption spectrum. About 0·3% of a minor component of retention volume (V_R *ca.* 9·2) expected for 3-chloro-4-t-butylbiphenyl was also detected.

2,2′-*Di-t-butylbiphenyl.*—Vapour-phase chromatography of the product from 2,2′-di-t-butylbiphenyl (V_R 5·05) gave two main peaks very close together (V_R 9·4, 9·65), a small peak before this (V_R 8·9), and two small peaks of higher retention volume. No perceptible amount of 2-chloro-2′-t-butylbiphenyl was formed. This was confirmed by preparing this compound (by mixed Ullmann reaction, without isolating it from the mixture) and observing that the appropriate peak on the gas chromatogram (V_R 3·45) could not be distinguished in the chlorination product. We consider that the two main components are 4- and 5-chloro-2,2′-di-t-butylbiphenyl, for their relative amounts were not altered by carrying out the chlorination with " positive chlorine " (from hypochlorous acid and perchloric acid in the presence of silver perchlorate). For steric reasons [16] this reagent should give a much increased proportion of chlorination adjacent to bulky substituents. Two of the minor components (V_R 8·9 and V_R 10·0) were indeed increased in amount by factors of about two when " positive chlorine " rather than molecular chlorine was used, and these may be the 6- and the 3-chloro-derivative, respectively.

2-*t-Butylbiphenyl.*—The products of chlorination of 2-t-butylbiphenyl were resolved on vapour-phase chromatography into seven components. The first (6%) was 2-chlorobiphenyl, apparently formed by chlorode-t-butylation. The second (2%) had a retention volume (V_R 3·45) identical with that of 2-chloro-2′-t-butylbiphenyl. The fifth (8%; V_R 4·50) was identified as 4′-chloro-2-t-butylbiphenyl (prepared by mixed Ullmann reaction).

The fourth component (20%; V_R 4·15) was shown to be 4-chloro-2-t-butylbiphenyl in the following way. Acetylation of 2-t-butylaniline gave *o*-t-butylacetanilide, m. p. 162° (lit.,[17] 159°). This was treated with one molecular equivalent of chlorine in acetic acid. When all the chlorine had been consumed, water was added and the product was filtered off. Vapour-phase chromatography of the product showed that it contained a single major component (about 90%) together with about 5% of another monochloro-compound and a similar amount of unchanged *o*-t-butylacetanilide. By recrystallisation from aqueous acetic acid there was obtained 4-chloro-2-t-butylacetanilide, m. p. 136° (Found: C, 63·5; H, 6·8; N, 6·2; Cl, 15·7. $C_{12}H_{16}ClNO$ requires C, 63·9; H, 7·1; N, 6·2; Cl, 15·7%). Its infrared spectrum * recorded in Nujol mull on a Grubb-Parsons D.B.1 double-beam spectrophotometer had absorption bands at 668mw, 725mw, 763w, 810ms, 822ms, 842m, 876ms, 884s, 927vw, 976vw, 1010vw, 1024vw, 1042vs, 1095w, 1112s, 1203w, 1247m, 1290s, 1370s, 1399m, 1520s, 1597m, 1661s cm.$^{-1}$. A sample of the 4-chloro-2-t-butylacetanilide was hydrolysed and de-t-butylated by heating it with phosphoric acid at 150° for 2 hr. The product was largely *p*-chloroaniline, m. p. 71—72°, which on acetylation gave *p*-chloroacetanilide, m. p. 181—182°, both identical in m. p. and not depressed in m. p. on admixture with authentic specimens. A second sample of 4-chloro-2-t-butylacetanilide was deacetylated by refluxing it for 12 hr. with sodium n-butoxide in butan-1-ol. The amine was recovered and treated with pentyl nitrite in benzene, Hwang's [18] method being followed. Vapour-phase chromatography of the product gave in low yield in the relevant region a single peak of retention volume V_R 4·15, identical with that of the fourth component from the chlorination of 2-t-butylbiphenyl; it had m. p. 57—58° and an ultraviolet spectrum very similar to that of 2-t-butylbiphenyl. It must, from its mode of formation, be 4-chloro-2-t-butylbiphenyl, as is indicated in the Scheme.

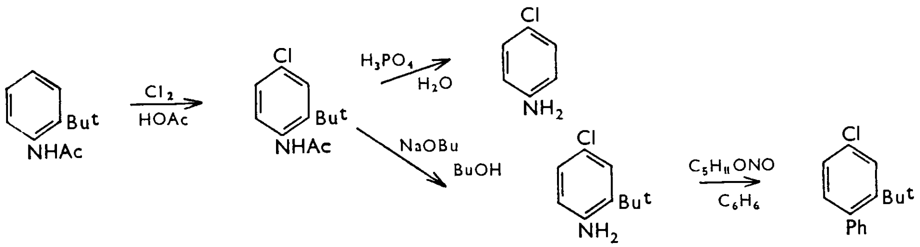
* Early, slightly impure crops seemed to crystallise in what is presumably a polymorphic form of appreciably different spectrum.

[16] de la Mare, Harvey, Hassan, and Varma, *J.*, 1958, 2756.

[17] Seńkowski, *Ber.*, 1890, **23**, 2412.

[18] Hwang, *Acta Chim. Sinica*, 1959, **33**, 171; cf. (*a*) Beaven, de la Mare, Johnson, and Klassen, *J.*, 1962, 988 (erratum, p. 989; for pentyl nitrate read pentyl nitrite); (*b*) ref. 1; (*c*) Cadogan, *J.*, 1962, 4257.

Orientation of major product of chlorination of *o*-t-butylacetanilide, and identification of 4-chloro-2-t-butylbiphenyl.



The orientation of 4-chloro-2-t-butylacetanilide was also indicated by mixed m. p. determinations. On admixture of our 4-chloro-2-t-butylacetanilide with 4-bromo-2-t-butylacetanilide, m. p. 163—164°, there was no depression of m. p., whereas on admixture with 5-bromo-2-t-butylacetanilide the m. p. was depressed to 110—120°. We are indebted to Professor Dr. B. M. Wepster, of the Technische Hogeschool, Delft, Holland, for authentic samples of the bromo-compounds; other cases are known [19] is which bromo- and chloro-acetanilides of corresponding structure and orientation show no depression of melting point.

A concentrate of the other, minor, chlorination product from *o*-t-butylacetanilide was obtained by vapour-phase chromatography of the crystallisation residues, and treated with phosphoric acid in the same way. The recovered base was found by vapour-phase chromatography to be *o*-chloroaniline mixed with some of the *p*-isomer, and this was confirmed by comparing its infrared spectrum with that of an authentic mixture. The minor component was therefore 6-chloro-2-t-butylacetanilide.* The modified Gomberg procedure, when applied to the product of alkaline deacetylation of the concentrate of this, gave a biaryl fraction which on vapour-phase chromatography contained no material of retention volume 3·85, but the yield was so poor that, in view of the presence of the isomeric impurity in the starting material, we think that this result does not exclude the possibility that the peak obtained at this point in the vapour-phase chromatogram of 2-t-butylbiphenyl is due to the 6-isomer.

The sixth (V_R 4·60) and seventh (V_R 4·70) components from the chlorination of 2-t-butylbiphenyl were not clearly resolved in the chromatogram of the products from reaction with molecular chlorine, where the component of retention volume 4·60 predominates. This must be the 5-isomer, in view of its amount, and the expected activation of this position by the t-butyl group. The best estimate that we can make of its amount is *ca.* 40%; the upper limit (48%) must be reduced by the amount of the seventh component. The presence of the latter was revealed with certainty when chlorination was repeated in aqueous dioxan, by using hypochlorous acid and perchloric acid in the presence of silver perchlorate. The reaction was slow, and some chlorination of the dioxan occurred. The chromatogram showed the presence of all the isomers previously detected, together with the seventh component, V_R 4·70, which now was the major product of chlorination. Since the ½*o* : *p*-ratio for chlorination directed by the t-butyl and other alkyl groups is much greater for " positive chlorine " than for molecular chlorine,[16] this result makes it probable that the component of retention volume 4·70 is 3-chloro-2-t-butylbiphenyl, which is present in the reactions of 2-t-butylbiphenyl with " positive chlorine " to the extent of *ca.* 40%, and is probably also present in the product from molecular chlorine to the extent of up to about 8%.

The third component (16%; V_R 3·85) still remains to be identified. We think that it must be 2-chloro-6-t-butylbiphenyl. Like the seventh component, its proportion is much increased in the product of chlorination by " positive chlorine," a result consistent with expectations for chlorination in a position where substitution is occurring in a hindered position, in this case adjacent to the bulky aryl group.

Biphenyl.—The products of chlorination of biphenyl (0·069M) with chlorine (0·042M) in

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* There was no vapour-phase chromatographic evidence for the presence of 5-chloro-2-t-butylacetanilide in the product of chlorination of *o*-t-butylacetanilide. This is consistent with an approximate estimate of the ratio of chlorination of the latter compound; the reactivity is obviously much reduced by steric inhibition of resonance (cf. ref. 9), but not enough to make 5-chlorination significant.

[19] Wepster, personal communication. Cf. Larsson, *Acta Chem. Scand.*, 1962, **16**, 1751.

acetic acid at 25° were examined in order to reinvestigate the amount of *m*-substitution. Some specimens which had been examined earlier [4] were re-examined also. The results are discussed below.

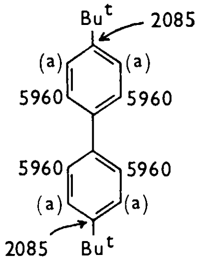
DISCUSSION

The partial rate factors set out below are calculated on the assumption that the additions which probably accompany the substitutions do not modify the proportions of isomeric derivatives produced in the reactions. No obvious difficulties seemed to result from this assumption when applied to the methyl-substituted biphenyls,[3] but it will appear that especially 2,2′-di-t-butylbiphenyl gives an orientation which is unusual.

4,4′-Di-t-butylbiphenyl.—The partial rate factors for chlorination of 4,4′-di-t-butylbiphenyl are as shown below (I); corresponding values for 4,4′-dimethylbiphenyl [5] (II), and for various reference compounds,[6,7] are also given.

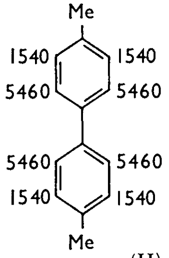
The overall reactivity of 4,4′-di-t-butylbiphenyl is, as would be expected, much the same as that of 4,4′-dimethylbiphenyl. This would be expected on the basis that the t-butyl group is more activating than the methyl group for *meta*-substitution, as is shown by the partial rate factors (see III, IV) for *meta*-chlorination of t-butylbenzene (6·0) and toluene (5·0).

Substitution *ortho* to the t-butyl group is sterically hindered; the partial rate factor for *o*-chlorination of t-butylbenzene (56·6) is less by a factor of *ca.* 11 than that for *ortho*-chlorination of toluene. It is not surprising, therefore, that substitution in the 3-position of 4,4′-di-t-butylbiphenyl was not detected; if the corresponding partial rate factor for substitution in 4,4′-dimethylbiphenyl had been reduced in the same ratio, the expected value would be 140, representing 1·5% of the product, and this is about the limit at which we could hope to detect with certainty the presence of any component of the reaction mixture by our chromatographic techniques.



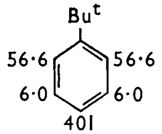
(I)

Rel. rate (PhH = 1) 4670



(II)

4670



(III)

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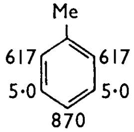

(IV)

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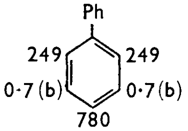

(V)

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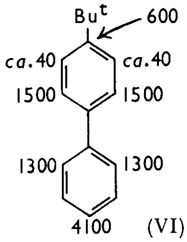
(*a*) Not detected; probably less than 2% ($f < ca.$ 200).
(*b*) Indirect estimate, discussed below.

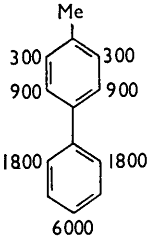
Chlorode-t-butylation, however, accounts for a substantial component of the reaction mixture. The structure of this product is established by its identity, in melting point, ultraviolet absorption spectrum, and retention volume, with the major product of chlorination of 4-t-butylbiphenyl. Relative rates of chlorode-t-butylation are discussed below.

4-t-Butylbiphenyl.—The partial rate factors for chlorination of 4-t-butylbiphenyl, as far as we have determined them, and of 4-methylbiphenyl [5] are shown below (VI, VII).

There is no doubt (cf. V, VI, and VII) that the 4-t-butyl group, like the 4-methyl group, substantially increases the reactivity of the 4′-position—in fact, by a factor of more than 5. Comparison with the 4-methylbiphenyl shows that the activation is in the " Baker–Nathan " (hyperconjugation) order, Me > Bu^t > H; the distance from the substituent is such that the inductive effect would not be expected to be transmitted very effectively in this situation. The $\frac{1}{2}o : p$ ratio for the unsubstituted ring is within experimental error the same as for 4-methylbiphenyl.



(VI)



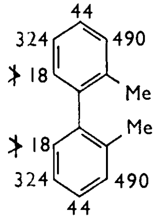
(VII)

	(VI)	(VII)
Rel. rate (PhH = 1)	1710	2000

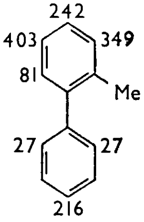
For substitution within the ring containing the t-butyl group, the orientation is much as would be expected. The 2-position is rather more activated by the t-butyl group than by the methyl group; here the inductive order, $Bu^t > Me$, is clearly dominant for positions *meta* to these alkyl groups. Substitution in the 3-position is attributed a partial rate factor of 40, agreeing with that expected for a position activated by an *ortho*-t-butyl group ($f_o^{\text{t-Bu}} = 56{\cdot}6$)[7] and deactivated by a *meta*-phenyl group ($f_m^{\text{Ph}} = 0{\cdot}7$)[9]; the experimental basis for this assignment is the presence of a small peak in the place on the vapour-phase chromatogram expected for 3- or 3′-chloro-4-t-butylbiphenyl; the latter is unlikely to be present in significant amount, because its partial rate factor should not be greater than 0·7; but the discussion below relating to 3-chlorobiphenyl makes this conclusion subject to confirmation.

Chlorode-t-butylation was again detected and qualitatively estimated. The partial rate factor is indicated, and is discussed below.

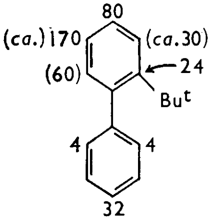
2-t-Butylbiphenyl.—Our analysis of the product from chlorination of 2-t-butylbiphenyl gives the partial rate factors shown in formula (X); values in parentheses refer to orientations of substitution which are not established rigorously. The pattern of orientation is on the whole sensible, as far as it has been determined, when comparison is made with 2-methylbiphenyl (IX). Substitution in the phenyl group is still more decreased in rate by the 2-t-butyl than by the 2-methyl group, as also is substitution in the 4-position, activated by the phenyl group. Substitution in the 5-position is also less, and this would be expected; the partial rate factor for chlorination *para* to a methyl group is more than twice that for chlorination *para* to a t-butyl group, not only in this system (IX, X), but also for the simple hydrocarbons (III, IV), where the " Baker–Nathan " order, $Me > Bu^t > H$, has been attributed [6,8,10,20] to hyperconjugative electron-release in the transition state. The amount of substitution in the 6-position, if we have identified this component correctly, is rather higher than would be expected by comparison with 2-methylbiphenyl.



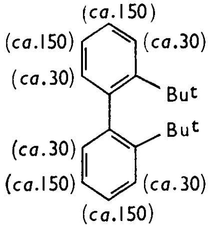
(VIII)



(IX)



(X)



(XI)

	(VIII)	(IX)	(X)	(XI)
Rel. rate (PhH = 1)	292	224	67	120

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[20] Cf. de la Mare and Robertson, *J.*, 1943, 279.

2,2-Di-t-butylbiphenyl.—The products of chlorination of this compound have not been identified positively; but, for the reasons given in the Experimental section, we tentatively assign the partial rate factors indicated above (XI). The value for 4-chlorination seems high in comparison with 2-t-butyl- or 2,2′-dimethyl-biphenyl. We think that in this compound addition may be followed by decomposition, and that this affects the observed orientation to a greater extent than in the other cases studied in this work.

Chlorode-t-butylation.—The present work, together with that of a previous paper[16] and the work of Stock and Brown,[7] enables us to compare partial rate factors for de-t-butylation activated by a number of *para*-substituents, as follows:

Substituent:	p-H	p-Bu^t	p-Me	p-Ph	p(p-Bu ·C$_6$H$_4$)
Partial rate factor for chlorination...............	1·0	401	870	780	4110
Partial rate factor for chlorode-t-butylation...	1·2	456	730	615	2085

It is clear that chlorode-t-butylation resembles chlorination (chlorodeprotonation) in being of similar sensitivity to substituent effects. Since in no case was this reaction the main reaction path, we have no independent evidence that it follows the same kinetic form as the chlorination, but the response to change in the substituent makes it very probable that that transition state is generally similar. The congestion between the entering chlorine and the leaving t-butyl group might be expected to have the result that in the transition state the bond to the aromatic ring would be less strongly developed. This may account for the fact that the response of chlorode-t-butylation to conjugative effects is if anything rather less (though to inductive effects perhaps a little greater) than for chlorination. The difference is not very large, however; it is to be noted that the aryl groups are highly activating for chlorode-t-butylation, and that the " Baker–Nathan " order of electron release, Me $>$ Bu^t $>$ H, is very prominent.

No chlorode-t-butylation was observed for 2,2′-di-t-butylbiphenyl; but 2-chlorobiphenyl was identified on the vapour-phase chromatogram as a component of the product of chlorination of 2-t-butylbiphenyl. Since after several weeks the crude reaction mixture gave still more 2-chlorobiphenyl, it is probable that at least part of this material is obtained by a reaction of an adduct, rather than by a direct electrophilic displacement of the t-butyl group by chlorine.

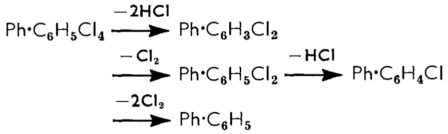
Search for meta-*Chlorination in Biphenyl.*—In an earlier paper[4] we concluded that chlorination of biphenyl in acetic acid gives very little 3-chlorobiphenyl, but were unable to estimate the amount directly. Three independent indirect estimates[5,9] of the partial rate factor for 3-chlorination give values of 0·7, 0·5, and 0·5; if the largest of these is taken, which accords with Stock and Brown's preferred value (0·74),[10] the amount of 3-substitution should be 0·11%.

Recently, however, Weingarten[2] has reported that chlorination of biphenyl in acetic acid gives 0·6% of 3-chlorobiphenyl. He, like Stock and Brown,[10] uses the ratio of 3- to 4-substitution for theoretical arguments. Although his experiments were not made under exactly the same conditions as ours, they are so similar as to render it desirable to establish whether or not his value is correct; for in conjunction with our estimate of the rate of substitution in biphenyl as compared with benzene, it leads to a partial rate factor of *ca.* 8 for 3-chlorination. It seems unlikely, though not impossible, that the phenyl group activates the *meta*-position for chlorination; and the exact value is clearly relevant to Stock and Brown's treatment in terms of equation (1), or the other forms (*e.g.*, equation 2) into which this equation can be transformed.[8]

$$\log_{10}(f_p/f_m) = \text{Constant.}\ \log_{10} f_p \qquad (2)$$

Accordingly, we have re-examined the products of chlorination of biphenyl, using more sensitive gas–liquid chromatographic methods for estimation of the isomeric proportions. The results have not been consistent; in various samples the percentage of 3-chlorobiphenyl in the monochloro-fraction has varied from less than 0·2% to *ca.* 1%. Since a possible explanation for this is that thermal decomposition of the adducts might give 3-chlorobiphenyl, we examined the behaviour of the tetrachloride obtained earlier,[4] and of fresh samples obtained similarly. Vapour-phase chromatography at about 200° gave a complex mixture of mono- and di-chlorobiphenyls, together with a little biphenyl and traces of other unidentified products. In this mixture all three monochlorobiphenyls are present, and the relative proportion of 3-chlorobiphenyl is much higher than appears in the total chlorination product. Attempts to free completely, by liquid-phase chromatography, the products of substitutive chlorination from the products of addition (of which no doubt there are several), before gas–liquid chromatography, have not been completely successful.

No doubt this is to be interpreted as indicating that the original chlorine addition can be in part reversed under conditions of the vapour-phase chromatography:



$$\mathrm{Ph{\cdot}C_6H_5Cl_4} \xrightarrow{-2\mathrm{HCl}} \mathrm{Ph{\cdot}C_6H_3Cl_2}$$

$$\xrightarrow{-\mathrm{Cl_2}} \mathrm{Ph{\cdot}C_6H_5Cl_2} \xrightarrow{-\mathrm{HCl}} \mathrm{Ph{\cdot}C_6H_4Cl}$$

$$\xrightarrow{-2\mathrm{Cl_2}} \mathrm{Ph{\cdot}C_6H_5}$$

The variability in our results probably arises because the adduct isolated is only part of, and perhaps has not the same composition as, the adduct first formed; as we discussed earlier,[4] the isolated material is a relatively stable material thermodynamically, and could have come in part from a tetrachloride which subsequently underwent rearrangement.

We regard these results as indicating that the amount of 3-chlorobiphenyl produced by direct electrophilic chlorination does not necessarily exceed that estimated from equation (1), or expected by analogy with the rates of chlorination of substituted biphenyls;[5,9] and that the unexpectedly large amount found in our new experiments and in those of Weingarten[2] is at least in part to be attributed to addition–elimination sequences not appropriately discussed in terms of partial rate factors for electrophilic substitution.

[*Added, May* 15*th*, 1963]. Baker, Bott, and Eaborn (*J.*, 1963, 2136) have recently commented on the differences in the $\frac{1}{2}o : p$-ratios for the chlorination of biphenyl recorded by Weingarten[2] and by some of us;[3] and Professor Eaborn has kindly pointed out that one of us[1] recently in another context quoted quite incorrectly the partial rate factors for chlorination of biphenyl. It should here be observed, therefore,[cf. 4] that our preliminary[3,8] values have been superseded[4,5] as the result of measurements carried out after we established the previously unrecognised facts that (i) addition can accompany substitution even under conditions conducive to heterolytic chlorination; and (ii) this can affect the experimental determination of $\frac{1}{2}o : p$-ratios if appropriate precautions are not taken in the experimental procedure, whether this involves measurements by isotopic dilution or by vapour-phase chromatography. Furthermore, our still more recent experience of determinations of isomer-ratios for chlorination by vapour-phase chromatographic analysis is that small differences can result from use of different methods of working up the reaction mixtures. In our view the best experimental value to adopt for discussion of the $\frac{1}{2}o : p$-ratio for the chlorination of biphenyl by a deficiency of chlorine in dilute solution in acetic acid is our quoted[4,5] value of 0·3, since it is confirmed by determinations by two independent methods; but we think that the limits of possible error are ±0·02, and in view of this we would not ascribe any significance to the difference between this value and that determined by Weingarten (0·27) under somewhat different experimental conditions. The adduct as isolated by us gives on pyrolysis some monochlorobiphenyls with a low and variable $\frac{1}{2}o : p$-ratio, usually *ca.* 0·15.

As far as the theoretical interpretation of these experimental values is concerned, our view is[5] that, since reaction of biphenyls with molecular chlorine is now known not to be a clean aromatic substitution, assumptions have to be made in deriving partial rate factors.

In our discussions we have tried to draw only such conclusions as are qualitatively independent of the resulting uncertainties. These uncertainties should not be allowed to obscure the clear generalisation that the pattern of chlorination of alkyl biphenyls on the whole appears to be determined by the additive effects of substituents on the free energy of activation, modified to a major extent by steric inhibition of conjugation when alkyl groups are situated *ortho*- to the biaryl linkage, and to a minor extent by transmission of substituent effects from one aromatic ring to the other. Although, therefore, for molecular chlorination of biphenyl and many other related compounds in acetic acid, the absence of a particular isomer from a chlorination mixture or its formation in amount less than expected can satisfactorily be discussed theoretically, one must be cautious in drawing definite conclusions from small differences in isomer ratios, or from proportions of minor reaction products in excess of the expected amount, except when the role of the adducts has been investigated independently with reference to the particular matter under consideration.

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