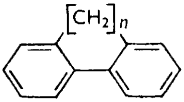
1275. *The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part XXII.*[1] *The Chlorination of 4,5,9,10-Tetrahydropyrene, of some Diphenylalkanes, and of some Related Compounds*

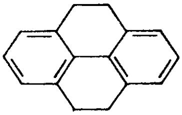
By P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas

The rates and isomer-distributions for chlorination of a series of diphenylalkanes have been examined in acetic acid as solvent. Substitution accounts for about 95—97% of the aromatic compound consumed, but is accompanied by a small proportion of addition, which gives polychlorides and acetoxychlorides. Comparison of partial rate factors for these chlorinations with those for the alkylbenzenes shows that the phenyl group has an appreciable inductive influence on the rate of attack by chlorine on a neighbouring aromatic nucleus. The chlorination of 4,5,9,10-tetrahydropyrene has been shown to occur mainly (60%) in the 2-position; the reactivities of this compound, and of some polyalkylbenzenes and biphenyls, are discussed.

The Ph·CH_2-group in diphenylmethane is known[2] to be *ortho,para*-directing. The phenyl group in this situation would be expected to reduce the activating power of the alkyl group by virtue of its electron-withdrawing inductive effect (—*I*): but there have been no quantitative measurements which allow a satisfactory assessment to be made of the magnitude of this influence, nor of the way in which it diminishes as more methylene groups are interposed between the two phenyl groups. Such a comparison is of interest, in view of our work[3] on bridged biphenyls (I), where part of the influence of one aryl group on the other would be relayed through the saturated bridge.



(I)



(II)

It is also relevant to discussion of the reactivity of 4,5,9,10-tetrahydropyrene (II). This compound is an analogue of 9,10-dihydrophenanthrene (I; *n* = 2), which we have regarded[3] as the most suitable reference compound for comparison of the reactivities of biphenyl systems, especially when these are nearly planar. No previous investigations have been reported, as far as we are aware, of the chlorination of 4,5,9,10-tetrahydropyrene;

---

[1] Part XXI, P. B. D. de la Mare and J. S. Lomas, *J.*, 1965, 5739.

[2] M. J. S. Dewar and D. S. Urch, *J.*, 1958, 3079.

[3] P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas, *J.*, 1964, 5317.

but its nitration has been shown to give more than 50% of the 2-derivative.[4] Accordingly, we have studied the reactivity and orientation in the chlorination of these and of some related hydrocarbons; a preliminary account of part of this work has been reported in summary.[5] The opportunity is taken also to report further on the reactivities of some polymethylbiphenyls.

EXPERIMENTAL

Some of the materials and methods have been described in earlier Papers.[1,3] Diphenylmethane and 1,2-diphenylethane were commercial samples purified by recrystallisation from methanol. 1,3-Diphenylpropane was prepared by the Huang-Minlon reduction of dibenzyl ketone, and had b. p. 294°/754 mm. (lit.,[6] 295°/760 mm.). 1,4-Diphenylbutane was prepared by the condensation of 1,4-dibromobutane with bromobenzene, and after recrystallisation from methanol had m. p. 54·5—55° (lit.,[7] 52°). 4,5,9,10-Tetrahydropyrene was a commercial sample purified by chromatography on alumina in light petroleum (b. p. 40—60°) and after recrystallisation from ethanol had m. p. 139—139·5° (lit.,[8] 138°). Durene and pentamethylbenzene were commercial samples purified by vapour-phase chromatography. Mesitylene was purified by fractional distillation. The following compounds were prepared by the appropriate Ullmann condensations: 2,2′,6,6′-Tetramethylbiphenyl, m. p. 66·5—67·2° (lit.,[9] 66—67°); biduryl (2,2′,3,3′,5,5′,6,6′-octamethylbiphenyl), m. p. 134—135° (lit.,[10] 136—138°); bi-isoduryl (2,2′,3,3′,4,4′,6,6′-octamethylbiphenyl), m. p. 122—123° (lit.,[11] 121—122°); *biprehnityl* (*2,2′,3,3′,4,4′,5,5′-octamethylbiphenyl*), m. p. 140·8—141·2° (Found: C, 90·2; H, 10·0. $C_{20}H_{26}$ requires C, 90·2; H, 9·8%). Bimesityl was prepared by the Grignard condensation of bromomesitylene, and had m. p. 100—101° (lit.,[12] 100·5°).

We are indebted to Dr. R. Bolton for samples of diphenylmethyl chloride and 2-chloro-4,5,9,10-tetrahydropyrene, and to the British Petroleum Co. Ltd., for pure samples of isodurene and prehnitene.

Rate measurements were carried out in the usual way for the more slowly reacting compounds. The following is an example of a typical kinetic determination, in which 2,2′,6,6′-tetramethylbiphenyl (0·0127M) was allowed to react with chlorine (0·00685M) in acetic acid at 25°; aliquot parts were titrated with 0·005N-sodium thiosulphate after addition to aqueous potassium iodide.

Time (min.)	0	0·72	1·53	2·58	4·00	5·90	8·05	10·30	12·57
Titre(ml.)	5·47	4·47	3·72	3·05	2·32	1·65	1·10	0·72	0·50
k_2 (l. mole^{-1} min.$^{-1}$)	—	23·2	21·8	20·6	20·8	20·9	22·0	23·4	23·3

For the more reactive substances, solutions of chlorine and of the hydrocarbon were placed separately in the compartments of a flask divided by an internal wall, and were mixed by rapid agitation; the reaction was stopped after 5—30 sec. by the injection of a saturated solution of potassium iodide. Blank experiments showed that 1·6% of the chlorine was lost in this process: correction for this loss was made in calculating the rate coefficients.

The following are typical results, for biduryl (0·0035M) with chlorine (0·0022—0·0027M) in acetic acid at 25°.

Time (min.)	0·100	0·167	0·250	0·333	0·333	0·417	0·500
x (% Cl_2 used up)	29·1	42·8	53·5	62·0	61·9	67·2	72·2
k_2 (l. mole^{-1} min.$^{-1}$) ...	1470	1500	1550	1500	1490	1520	1390

The rate coefficients for chlorination in anhydrous acetic acid at 25°, calculated according to the second-order formula, and expressed in l. mole^{-1} min.$^{-1}$, were as follows: diphenylmethane, $k_2 = 0{\cdot}0143$; 1,2-diphenylethane, $k_2 = 0{\cdot}0274$; 1,3-diphenylpropane, $k_2 = 0{\cdot}0427$; 1,4-diphenylbutane, $k_2 = 0{\cdot}0457$; 4,5,9,10-tetrahydropyrene, $k_2 = 14{\cdot}7$; mesitylene, $k_2 = 2564$;

[4] R. Bolton, *J.*, 1964, 4637.

[5] P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas, " Coplanarity and reactivity in some bridged biphenyls," International Symposium on Reaction Mechanisms, Cork, Ireland, July 1964.

[6] D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.*, 1951, **73**, 5691; L. Wolff, *Annalen*, 1912, **394**, 86.

[7] J. van Alphen, *Rec. Trav. chim.*, 1940, **59**, 580.

[8] E. A. Coulson, *J.*, 1937, 1298.

[9] R. B. Carlin, *J. Amer. Chem. Soc.*, 1945, **67**, 928.

[10] E. Marcus, W. M. Lauer, and R. T. Arnold, *J. Amer. Chem. Soc.*, 1958, **80**, 3742.

[11] E. A. Knauf and R. Adams, *J. Amer. Chem. Soc.*, 1933, **55**, 4704.

[12] W. W. Moyer and R. Adams, *J. Amer. Chem. Soc.*, 1929, **51**, 630.

(lit.,[13] 2826); isodurene, k_2 = 5136 (lit.,[13] 5586); prehnitene, k_2 = 176 (lit.,[13] 191); durene, k_2 = 131 (lit.,[13] 150); pentamethylbenzene, k_2 = 12,420 (lit.,[13] 12,540); 2,2′6,6′-tetramethylbiphenyl, k_2 = 22·3; bimesityl, k_2 = 4640; bi-isoduryl, k_2 = 11,380; biprehnityl, k_2 = 2310; biduryl, k_2 = 1510.

Isomer-proportions were determined by vapour-phase chromatography (cf. refs. 3, 14). The following results are expressed as percentages of the monochloro-derivatives: diphenylmethane, 53·5% *o*, *ca.* 0·5% *m*, 46·0% *p*; 1,2-diphenylethane, 44·0% *o*, *ca.* 0·7% *m*, 55·3% *p*; 1,3-diphenylpropane, 48·5% *o*, *ca.* 0·5% *m*, 51·0% *p*; 1,4-diphenylbutane, 46·0% *o*, *ca.* 0·5% *m*, 53·5% *p*; 4,5,9,10-tetrahydropyrene, 40% 1-, 60% 2-chloro-derivative; 2,2′,6,6′-tetramethylbiphenyl, *ca.* 99% of 3- and 1% of 4-chloro-derivative. It was shown also, by colorimetric estimation in concentrated sulphuric acid of the benzhydrol produced by hydrolysis of the product from diphenylmethane, that not more than 1% (and probably much less) of the chlorine was involved in substitution in the methylene group. Control determinations showed that diphenylmethyl chloride, if it had been present in the reaction mixture, would have been detected by this method. 2-Chloro-4,5,9,10-tetrahydropyrene was identified as the main product of monochlorination of the hydrocarbon by comparison with an authentic sample prepared and identified as has been described by Bolton.[4]

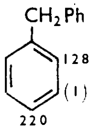
Adduct-formation was detected in some of these chlorinations by determination [15] of (*a*) the ratio of hydrogen chloride liberated to chlorine used up, and (*b*) the ratio of chloride produced by hydrolysis of the total reaction product with 1% sodium hydroxide in 10% aqueous methanol at room temperature for 2—3 days to chlorine used up. Results were as follows: 4,5,9,10-tetrahydropyrene, (*a*) 0·81; (*b*) 0·19; 2,2′,6,6′-tetramethylbiphenyl, (*a*) 0·96; (*b*) 0·10; biduryl, (*a*) 1·02; (*b*) 0·01; biprehnityl (*a*) 1·00; (*b*) 0·07; durene (*a*) 1·01; (*b*) 0·04.

In the case of the diphenylalkanes, adduct-formation was also established by isolation procedures based on column chromatography. The ratio of monochlorides determined by vapour-phase chromatography on a sample of chlorinated diphenylmethane from which the adducts had been removed in this way did not differ significantly from the ratio determined on a sample of the whole reaction product.

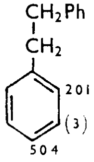
Discussion

Diphenylalkanes. The only previous rate-measurement for the halogenation of diphenylmethane is that recorded by Robertson, de la Mare, and Swedlund,[16] who found it to react with bromine in aqueous acetic acid at 35° some 3½ times more slowly than toluene. The present comparison for chlorination involves a corresponding rate-difference of about two, in tolerable agreement when the different reagent is borne in mind.

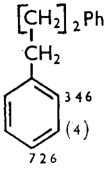
From the rates and isomer-proportions for chlorination of the diphenylalkanes studied in the present work, the partial rate factors shown in formulæ (III)—(VI) can be calculated. For comparison, the corresponding values for toluene and for ethylbenzene, as given by Stock and Brown,[17] are also shown (VII) and (VIII).



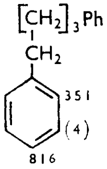
(III)



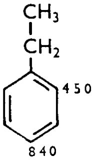
(IV)



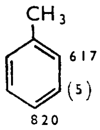
(V)



(VI)



(VII)



(VIII)

The values for *meta*-substitution are given in parentheses since, because the amounts are so small, they are determined with rather less precision than is possible for the other

---

[13] E. Baciocchi and G. Illuminati, *Gazzetta*, 1962, **92**, 89.

[14] P. B. D. de la Mare, D. Muriel Hall, Margaret M. Harris, M. Hassan, E. A. Johnson, and N. V. Klassen, *J.*, 1962, 3784.

[15] Cf. P. B. D. de la Mare, N. V. Klassen, and R. Koenigsberger, *J.*, 1961, 5285; P. B. D. de la Mare and R. Koenigsberger, *J.*, 1964, 5327.

[16] P. B. D. de la Mare, P. W. Robertson, and B. E. Swedlund, *J.*, 1953, 782.

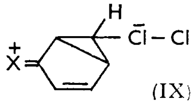
[17] L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 1.

isomers. The values are, however, of the expected magnitudes, the expected inductive influence of the phenyl group being borne in mind. There is no indication from the results that these values are affected by adduct-formation.

The $\frac{1}{2}o:p$-ratios for compounds (III)—(VI) are 0·58, 0·40, 0·48, and 0·43 respectively; all are similar to that (0·54) for ethylbenzene, and substantially lower than that (0·75) for toluene. Clearly the steric effect of groups of the type $R{\cdot}CH_2$ is appreciably greater than that of the methyl group; the $\frac{1}{2}o:p$-ratio for diphenylmethane is, however, appreciably greater than that for the other diphenylalkanes, and especially than that for diphenylethane. The result suggests that for the phenyl group in diphenylmethane there may be a conformation which, in comparison with those which can be adopted by the phenyl groups in the compounds with longer interposed methylene chains, is slightly more favourable for substitution in the *ortho*-position.

The partial rate factors for *para*-substitution, like those for substitution in the other positions, show clearly the operation of the inductive effect of the phenyl group. The rate-reduction from $f_p^{Et} = 840$ to $f_p^{CH_2Ph} = 220$ corresponds with a difference in free energy of activation for substitution in these two positions of 0·8 kcal. mole^{-1}. If a " damping effect " of 0·35 per methylene group in the chain is adopted and applied to this energy difference, the resulting calculated partial rate factors for *para*-substitution are: $f_p^{CH_2{\cdot}CH_2Ph} = 525$; $f_p^{CH_2{\cdot}CH_2{\cdot}CH_2Ph} = 711$; and $f_p^{CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Ph} = 792$. The observed values, 504, 726, and 816 respectively, are thus fitted to a good comparison by this treatment. It will be recalled that a damping factor of 0·36 per methylene group was suggested by Branch and Calvin [18] from studies of the strengths of acids; various other damping factors in the range 0·3—0·5 have been suggested for other systems.[19]

It is of interest to extrapolate these values in order to estimate the influence of the inductive effect on the reactivity of the *para*-position in biphenyl. Such a calculation indicates that the partial rate factor, $f_p^{Ph} = 780$,[14] has been reduced by the inductive effect by a factor of about 46. A similar calculation can be made for the *meta*-position by using the admittedly somewhat less accurate value for this position in diphenylmethane. From this, it can be deduced that the partial rate factor for *meta*-substitution in biphenyl should be about 0·02. No direct estimate of this quantity is available; but indirect estimates give considerably larger values, in the range 0·5—0·7.[14] The divergence indicates that the conjugative effect of the aryl group is reaching the *meta*-position in biphenyl, and increasing by a small rate factor the reactivity in this position. It can, in fact, be estimated that, on the scale in which the conjugative ($+M$, $+E$) effect of the phenyl group increases the rate of *para*-chlorination by a factor of about 36,000, it enhances that of *meta*-chlorination by a factor of about 40; both of these values being reduced (to 780 and *ca.* 0·7, respectively) by the inductive effect ($-I$). The most direct interpretation of the *meta*-activating power of conjugative substituents of this kind is in terms of the relatively unfavourable canonical structures such as (IX).[20]



(IX)

In an earlier Paper,[3] we reported the relative rates of chlorination of some bridged biphenyls, *e.g.*, (I; $n = 1, 2,$ or 3). We did not at that time have the present results to enable a correction to be made for the inductive effect of the aryl group acting through the alkylene bridge. The maximum corrections which could now be suggested are 0·8 ($n = 1$); 0·3 ($n = 2$); and 0·1 kcal. mole^{-1} ($n = 3$). If such a correction were considered appropriate, it would increase the estimated extent to which the reactivity of fluorene could be said to have abnormally great reactivity by comparison with other bridged biphenyls. Previously, this was estimated to involve at least 1·0 kcal. mole^{-1} in free energy of activation, and it is

---

[18] G. E. K. Branch and M. Calvin, " The Theory of Organic Chemistry," Prentice-Hall, New York, 1946, pp. 203—204.

[19] Cf. J. C. McGowan, *J. Appl. Chem.*, 1960, **10**, 312.

[20] Cf. P. B. D. de la Mare and J. H. Ridd, " Aromatic Substitution—Nitration and Halogenation," Butterworths, 1958.

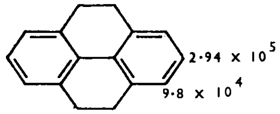
possible on the basis of the present results to suggest an increase by not more than 0·5 kcal. mole^{-1} (*i.e.*, by not more than the difference between the corrections for $n = 1$ and $n = 2$ above).

The present results show no indication that, even in diphenylmethane, the chlorinations affected significantly by homolytic processes, since very little, if any diphenylmethyl chloride, which would be expected from side-chain chlorination of this compound, could be detected in the reaction mixture. We found, however, that all the diphenylalkanes gave significant amounts of adducts. These could be isolated by chromatography on silica gel. They comprise some 10% of the chlorine, and hence no more than 3—5% of the aromatic compound, used up in the reaction. Both polychlorides and acetoxypolychlorides were found to be present. It is clear that addition accompanies heterolytic substitution in the chlorination of these compounds, just as it does in derivatives of biphenyl. Energetically, therefore, paths leading to addition and to substitution in aromatic compounds seem to be not so far apart for chlorination as has sometimes been supposed.

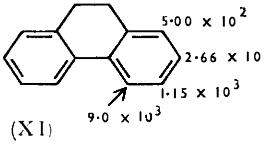
Tetrahydropyrene. The results for this compound are generally similar to those recorded for other substituted biphenyls. As with biphenyl itself and those other bridged biphenyls which we have investigated,[3] 4,5,9,10-tetrahydropyrene gave a little more than 80% of substitution; the remainder of the product is a polychloride, probably a tetrachloride. For this type of compound, little acetoxypolychloride is produced, as judged by the fact that the total amount of chloride produced by chlorination followed by alkaline hydrolysis does not exceed 100% significantly. The polyalkylbenzenes and biphenyls examined in this work, however, give less polychloride and more acetoxychloride, just as we found for a number of methylbiphenyls.[14]

For the purposes of discussion, we ignore the possible effect of adduct-formation on the partial rate factors for chlorination; disturbances from this cause seem usually to be unimportant, at least as far as the major components of the reaction mixture are concerned.[14]

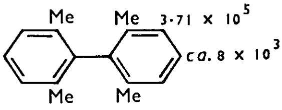
Partial rate factors are given in formulæ (X), (XI), and (XII) for 4,5,9,10-tetrahydropyrene, 9,10-dihydrophenanthrene,[3] and 2,2′,6,6′-tetramethylbiphenyl.



(X)



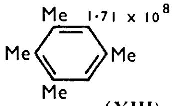
(XI)



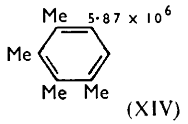
(XII)

The reactivity of the 1-position in 4,5,9,10-tetrahydropyrene is very much what would be expected in terms of the "additivity principle."[20] Thus, this position can be considered to be effected by an *o*-Ar·CH$_2$·CH$_2$ group, by a *p*-Ar·CH$_2$·CH$_2$ group, and by a *m*-Ar group; whence, equating Ar with phenyl, the calculated partial rate factor is (201 × 504 × 0·7) = 7·1 × 10^4. The experimental value is 9·8 × 10^4.

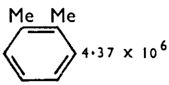
The 2-position in this compound is, however, somewhat more reactive than would be expected on similar grounds, being some 11·1 times more reactive than the 2-position in 9,10-dihydrophenanthrene (XI). If we consider that the extra bridge is like that in bibenzyl (IV), the reactivity is unexpectedly great by a factor of 3·5; if comparison is made instead with toluene, for which the partial rate factor for the *meta*-position, $f_m^{Me} = 5$, is known with somewhat greater certainty,[17] the factor by which the 2-position in 4,5,9,10-tetrahydropyrene exceeds that expected for a compound with the geometry of 9,10-dihydrophenanthrene is 2·2. Although this factor of rate-enhancement is rather small, it is important in that it controls the fact that 2-substitution leads to the major, rather than to the minor, product of reaction. The result suggests, furthermore, that conjugation between the aryl groups in this compound may be greater than that between the aryl groups in 9,10-dihydrophenanthrene. The exact geometry of 4,5,9,10-tetrahydropyrene is not known; but it may be significant that Mislow and co-workers [21] recently concluded, from studies of the ultraviolet spectra of these and of related compounds, that 4,5,9,10-tetrahydropyrene may indeed be flatter than 9,10-dihydrophenanthrene. An increase in reactivity with chlorine by a factor of 2·1 would be consistent with a change in the angle between the planes of the aromatic rings from 16°, as in 9,10-dihydrophenanthrene in the ground state, to 0°.



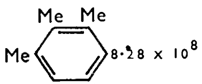
(XIII)



(XIV)



(XV)

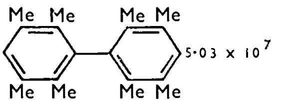


(XVI)

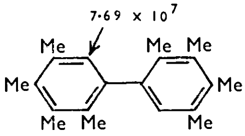
Comparison with 2,2′,6,6′-tetramethylbiphenyl (XII) shows in spectacular fashion the influence of steric inhibition of resonance on orientation. The 3-position in this compound has normal reactivity, slightly greater than that in the corresponding position in 4,5,9,10-tetrahydropyrene (X), no doubt because the inductive effect of the aryl group can in the latter compound in part be transmitted through the bridge. Substitution in the 4-position in (XII), however, *para* to the Ar–Ar bond, accounted for no more than 1% of the product of chlorination; the rate of reaction in this position is very seriously diminished by steric inhibition of resonance.

The polyalkylbenzene and polyalkylbiphenyls. Despite the very considerable reactivity of some of the polyalkylbenzenes, our rate-coefficients for their chlorination are generally in good agreement with the values recorded by Baciocchi and Illuminati.[13] Partial rate factors are shown in formulæ (XIII)—(XVI). As has been noted,[13] the values for the most heavily substituted compounds fall short of what would be predicted by application of the additivity principle. Thus, by comparing durene (XV) with pentamethylbenzene (XVI), it would be concluded that the effect of a single methyl group on the *para*-position involves activation by a factor of 190; for toluene, however, the value of f_p^{Me} is 820. The discrepancy may be the result of steric hindrance, by way of the so-called " buttressing effect " of contiguous groups.[22]

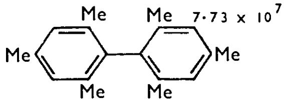
Despite the possible incidence of such effects, the *p*-aryl group in biduryl (XVII) is, by direct comparison with durene (XV), found to be activating for the *p*-position. Models of biduryl show that the blocking methyl groups must hold the aryl group at an angle of about 85° to each other, unless these groups are themselves considerably distorted from planarity. Resonance must be considerably sterically inhibited here, as indeed is witnessed by the fact that the *para*-aryl group is having an activating power much less than that exerted by the *para*-phenyl group ($f_p^{\text{Ph}} = 780$). It may be significant, however, that the activation is not reduced to zero in biduryl; so some conjugation must still be contributing to the reactivity of the *para*-position. The origin of the " residual conjugation " in compounds of this type, however, as we discussed earlier,[3] is obscure.



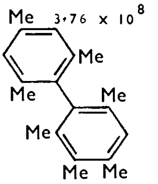
(XVII)



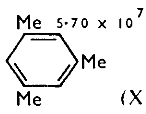
(XVIII)



(XIX)



(XX)



(XXI)

---

[21] K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, *J. Amer. Chem. Soc.*, 1964, **86**, 1710.

[22] M. Rieger and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1950, **72**, 19.

The effect of the aryl group in biprehnityl (XVIII) is, by comparison with prehnitene (XIV), that of a small activation; as would be expected, since it involves an *ortho*-aryl group subject to steric inhibition of resonance, which must be considerable, though not as great as in biduryl. The effects of the aryl groups in bimesityl (XIX) and bi-isoduryl (XX) are, however, by comparison with mesitylene (XXI) and isodurene (XIII) somewhat anomalous, since the *meta*-position is activated by the aryl group by small factors (1·4 and 2·2 respectively). This result contrasts with the small factors of deactivation reported for *meta*-aryl groups in other systems (0·7; 0·5).[14] It seems that there is a slight breakdown of the additivity principle in this example, or that the accumulation of alkyl groups produces an enhancement of their inductive effects, perhaps by direct relay through space.

We are indebted to the D.S.I.R. for a Research Assistantship (to P. B. D. de la M., held by J. S. L.); and to Imperial Chemical Industries Limited, for a grant for equipment on loan.

CHEMISTRY DEPARTMENT, BEDFORD COLLEGE, REGENT'S PARK, LONDON N.W.1.
MEDICAL RESEARCH COUNCIL LABORATORIES,
HOLLY HILL, LONDON N.W.3.

[*Received, March 29th*, 1965.]