Influence of Substituent Groups on Nuclear Reactivity in the Formation of Substituted Biphenyls by Reaction of Aromatic Diazo and Related Compounds with Aromatic Liquids. VIII. Phenylation and p-Methylphenylation. The Separation of the Polar and the Conjugative Effect

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The results of our study of the influence of some substituent groups, viz., the *p*-methoxy, *p*-chloro, and *p*-nitro group, in the attacking aryl radical on the homolytic arylation of monosubstituted benzenes have been reported in Parts III,[1] VI,[2] and VII[3]. The present paper deals with the phenylation and *p*-methylphenylation, in which *N*-nitrosoacet-(anilide-^{14}C) and *N*-nitroso-(*p*-methyl-^{14}C)-acetanilide have been used as the sources of the phenyl and the *p*-methylphenyl radical, and the arylated products have been analyzed by isotope dilution analysis. The partial rate factors and relative rates are listed in Tables I and II; the values for the phenylation obtained previously[4] by the same method are also included in Table I.

The tables show that all substituents in the aromatic substrate make the aromatic ring more reactive at the ortho and the para than at the meta position or at a nuclear position of benzene itself, and that they consequently direct the phenylation and *p*-methylphenylation preferentially to the ortho and para positions. This observation is in keeping with the already known results[5] concerning the orientation in the homolytic phenylation which were mainly obtained by the study of the decomposition of benzoyl peroxide, and it corroborates the view already adumbrated on the basis of the previous findings[2,3] that the invariable ortho-para orientation is characteristic of the homolytic aromatic arylation, irrespective of the nature of the attacking aryl radical.

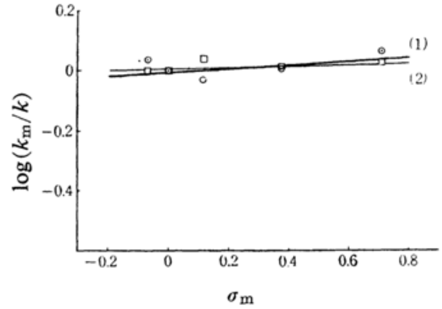

Fig. 1. The Hammett plots for the phenylation (1) and the *p*-methylphenylation (2).

As with the *p*-methoxyphenylation[3], the partial rate factors for the phenylation and *p*-methylphenylation of the meta position of aromatic compounds are all very close to unity. This fact suggests that the *p*-methylphenyl radical has little, if any, measure of polar character. Satisfactory Hammett plots are obtained for both the phenylation and *p*-methylphenylation, as shown in Fig. 1, between the logarithm of the partial rate factor for the meta position and the substituent constant, σ_m. The values for the Hammett reaction constant, ρ, together with those for *p*-nitro-[3], *p*-chloro-[2], and *p*-methoxy-phenylation[3], all obtained by the least squares method, are listed in Table III. The negative ρ values for the *p*-chloro- and *p*-nitro-phenylation indicate the electrophilic character of the *p*-chloro- and the *p*-nitrophenyl radical, as has already been discussed in Parts VI and VII. The polar character of these radicals is obviously attributable to the electron-withdrawing nature of their substituent groups.

The Hammett substituent constants, σ_p, which are shown in Table III for purposes of comparison, may be taken more or less to represent the electronic influence of the substituent groups in the aryl radicals upon the carbon atom on which the odd electron is located. Therefore, it is plausible to suppose that the σ_p value may show some correlation with the polar nature of arylation. In fact, in the *p*-nitro- and *p*-chloro-phenylation and in phenylation

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[1] O. Simamura and T. Migita, This Bulletin, 27, 228 (1954).

[2] T. Migita, N. Morikawa and O. Simamura, ibid., 36, 980, (1963).

[3] R. Itô, T. Migita, N. Morikawa, M. Ōkuni and O. Simamura, ibid., 36, 985 (1963).

[4] T. Inukai, K. Kobayashi and O. Simamura, ibid., 35, 1576 (1962).

[5] G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, Oxford (1960).

TABLE I. PARTIAL RATE FACTORS AND RELATIVE RATES IN PHENYLATION OF MONOSUBSTITUTED BENZENES AT 20.0°C

Compound	Exp. No.	Partial rate factor			Relative rate k_X/k_H
		k_o/k	k_m/k	k_p/k	
$C_6H_5NO_2$	*	9.38	1.16	9.05	5.02
C_6H_5Cl	1	3.09	1.01	1.48	1.61
$C_6H_5OCH_3$	*	3.56	0.93	1.29	1.71
$C_6H_5CH_3$**	2	3.30	1.09	1.27	1.68

* Results by Inukai, Kobayashi and Simamura[4].

** Simamura and Inukai (This Bulletin, **28**, 445 (1955)) reported the partial rate factors of 3.7, 0.9 and 1.1 for the *o*-, *m*-, and *p*-position, as determined by infrared spectrophotometry.

TABLE II. PARTIAL RATE FACTORS AND RELATIVE RATES IN *p*-METHYLPHENYLATION OF MONOSUBSTITUTED BENZENES AT 20.0°C

Compound	Exp. No.	Partial rate factor			Relative rate k_X/k_H
		k_o/k	k_m/k	k_p/k	
$C_6H_5NO_2$	3	10.73	1.07	8.93	5.50
C_6H_5Cl	3	3.10	1.04	1.16	1.57
$C_6H_5OCH_3$	4	3.69	1.09	1.52	1.85
$C_6H_5CH_3$	5	3.27	1.00	1.33	1.65

TABLE III. POLAR NATURE OF ARYL RADICALS IN ARYLATION

Aryl radical	Hammett's reaction constant, ρ	Substituent constant		
		σ_p	σ_p^n	σ_p^o
p-Nitrophenyl	−0.81	0.778	0.78	0.73
p-Chlorophenyl	−0.27	0.227	0.24	0.27
Phenyl	0.05	0	0	0
p-Methylphenyl	0.03	−0.170	−0.13	−0.15
p-Methoxyphenyl	0.09	−0.268	−0.11	−0.16

the numerical magnitudes of ρ and σ_p approximately coincide with each other. Although no theoretical significance can be attached to this numerical coincidence, if this correlation should hold throughout the entire range of σ_p values, it would predict much larger ρ values for the *p*-methyl- and *p*-methoxy-phenylation than have actually been found. In fact, the values for these arylations are practically indistinguishable from that for the phenylation. If, for purposes of comparison, we take σ_p^n[6] or σ_p^o[7] as a measure of the polar influence of a substituent, the parallelism becomes much better. This fact evidently indicates that the influence on the arylation reaction exerted by a substituent group in the attacking radical is purely inductive in nature, since both σ_p^n and σ_p^o are thought to represent the inductive polar effect for the para-substituted phenyl group, including the conjugative interaction between the substituent and the benzene ring. This view seems quite reasonable in view of the nature of the orbital occupied by the odd electron, for that orbital does not allow the electron to conjugate with the π-elctronic system of the substituted phenyl group.

The value of ρ should be dependent, at least partly, on the reactivity of the attacking radical as well; the more reactive an attacking radical is, the more difficult it is for this radical to discriminate differently substituted substrates, and, consequently, the lower will be the absolute value of ρ. Such an effect ought to be observed in the arylations by substituted phenyl radicals, which simple molecular orbital calculations have shown to be more reactive than the phenyl radical itself. This effect, however, does not seem important in view of the simple correlation between the ρ value and the inductive substituent constant.

No simple correlation can be found of the effect of the polar substituent in the substrate on the partial rate factors of the para and

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6) H. van Bekkum, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959).

7) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960).

TABLE IV. CONJUGATIVE EFFECT OF A SUBSTITUENT GROUP IN THE SUBSTRATE, τ_p

Arylation	Substrate			
	$C_6H_5NO_2$	C_6H_5Cl	C_6H_5OMe	C_6H_5Me
p-Nitrophenylation	0.81	0.19	0.14	0.04
p-Chlorophenylation	1.00	0.19	0.12	0.07
Phenylation	0.92	0.16	0.12	0.11
p-Methylphenylation	0.93	0.06	0.19	0.13
p-Methoxyphenylation	0.85	0.22	0.14	0.09
Mean	0.90	0.16	0.14	0.09

TABLE V. ESTIMATION OF THE CONJUGATIVE EFFECT IN THE HOMOLYTIC ARYLATION

X	Extra resonance energy[a]			
	C_6H_5X (I)	ArC_6H_5X (II)	Diff.	τ_p[c]
CH_3	0.24[b]	0.26	0.02	0.09
Cl	0.26[b]	0.29	0.03	0.16
OH	0.32[b]	0.37	0.05	0.14 (CH_3O)
NO_2 ($\delta = -0.5$)	0.29	0.48	0.19	0.90
NO_2 ($\delta = -0.2$)	0.35	1.01	0.66	

a) In terms of the usual resonance integral value.
b) See Ref. 11.
c) See Table IV.

ortho position, since the conjugative effect of the substituent is overwhelming at these positions. In fact, the Hammett relation does not hold for the para position. For this position, however, the following equation has now been found to give a very noteworthy correlation with regard to the effect of the substituent:

$$\log (k_p/k) = \rho \sigma_p + \tau_p \qquad (1)$$

where k_p/k is the partial rate factor of the para position of a substituted benzene in an arylation; ρ, the Hammett reaction constant for this arylation as determined from the Hammett plot of the partial rate factors of the meta position; and σ_p, the Hammett substituent constant for the para position. As shown in Table IV, the value for τ_p may be regarded as tolerably constant for each substituted benzene irrespective of the nature of the attacking radical and decreases in the order: $NO_2 \gg Cl$, $MeO > Me$. Since the term $\rho\sigma_p$ obviously represents the polar effect consisting of the inductive and the conjugative or electromeric response in the presence of a polar attacking radical, τ_p may be considered to represent that part of the conjugative effect of the substituent which is independent of the polar nature of the attacking radical. It is therefore natural that τ_p should have been found to be a constant quantity characteristic of the nature of the substituent group, in so far as such a treatment, in which the substituent effect is divided into several independent components, is valid[8]. Thus, τ_p or, expressed in energy term, $2.30 \times \boldsymbol{RT}\tau_p$ may be identified with the difference in extra resonance energy, that is, the additional stabilization due to the conjugation of the substituent group with the π-electronic system, between the transition state and the initial state. The value of 0.90 found for τ_p for the nitro group corresponds to 1.2 kcal./mol. Since the extra resonance energy in nitrobenzene is estimated at 8.5 kcal./mol.[9], that in the transition state will be 9.7 kcal./mol.

Although the exact structure of the transition state is unknown, we may identify it with the structure of the phenylcyclohexadienyl radical[10] (II). The odd electron occupies its non-bonding molecular orbital, and the presence of a substituent group in the radical may be thought to cause the perturbational lowering of the energy of the system. This effect will be greatest for the nitro group, with its comparatively low-lying vacant orbital, resulting in its having the greatest extra resonance energy, in accordance with the observed sequence of the conjugative effect, whereas such an effect becomes much less important for the substituents: chlorine, methoxy and

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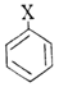
[8] Such division of the electronic effect of a substituent into independent contributions from the inductive and the conjugative effect has first been suggested by Branch and Calvin ("The Theory of Organic Chemistry", Prentice-Hall, Inc., New York (1941), p. 193) for the effect on acid strength and has extensively been applied by Taft ("Steric Effects in Organic Chemistry," Ed. by M. S. Newman, John Wiley & Sons, Inc., New York (1956), p. 577; *J. Am. Chem. Soc.*, **80**, 2436 (1958)) to the consideration of the substituent effect in reaction rates as well.

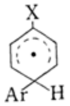
[9] The authors are indebted to Prof. S. Nagakura for this value.

[10] Ref. 5, p. 17.

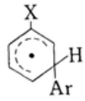
methyl, since these groups are able to contribute only a filled orbital for conjugation. This view is supported by the following consideration based upon the molecular orbital theory. The extra resonance energies in substituted bezenes have been evaluated by Matsen[11] by means of a perturbational treatment with simple molecular orbitals, and those for substituted cyclohexadienyls have now been estimated by the same method as in Matsen's treatment. The results are shown in Table V, which also includes the values similarly calculated for the nitro group, it being assumed that the perturbing vacant molecular orbital of the nitro group has the energy $\alpha+\delta\beta$ ($\delta=-0.5$ or -0.2)[12], and that the coefficient of the atomic orbital of the nitrogen atom constituting the molecular orbital is $1/\sqrt{2}$. The trend seen in the differences in the calculated extra resonance energy between the substrate and the substituted cyclohexadienyl radical shown in the fourth column is in satisfactory agreement with that in the τ_p values, considering the approximate nature of this molecular orbital method.



(I)



(II)



(III)

In this connection, it is to be noted that the extra resonance energies of the substituted cyclohexadienyl radicals (III) simulating the transition state of the arylation at the meta position are calculated to be the same as those in the corresponding substrates (Table V, column 2), except for the case of the nitro group. Even in this case, however, the discrepancy is not serious, being 0.01 and 0.02 for $\delta=-0.5$ and -0.2, respectively. This result is very gratifying, since it means that the conjugative effect is nil for every substituent in accordance with the fact that the Hammett relation has been found to hold for the partial rate factors at the meta position.

Since the polar and the conjugative effect are separately taken into account above, the use of a substituent constant, such as σ_I[13], σ_p^o, or σ_p^n, which measures only the inductive effect, instead of σ_p, might seem more appropriate. The substitution of σ_I in Eq. 1, however, gives too large a value of τ_p for the nitrophenylation of chlorobenzene and anisole, and the use of σ_p^o or σ_p^n gives, although very slightly, too large a value of τ_p again for the nitrophenylation of chlorobenzene and anisole. On the other hand, Brown and Okamoto's σ^+ values[14] give negative values of τ_p for the nitrophenylation of anisole and toluene, indicating that in the *p*-nitrophenylation the electromeric electron-demand at the reaction centre is not so strong as to justify the use of σ^+. The fact that Hammett's σ_p gives the best constancy in τ_p values for each substituted benzene undoubtedly shows that the electromeric electron-demand at the reaction centre, even by an electrophilic radical such as *p*-nitrophenyl, is of so small a magnitude that the use of σ_p is suitable.

Experimental

Melting points are uncorrected.

Solvents.—Nitrobenzene, chlorobenzene, anisole, toluene and benzene were purified as described in Part VI[2].

Substituted Biphenyls Used as Carriers in Isotope Dilution Analysis.—2- and 3-Chlorobiphenyl were prepared according to Elks, Haworth and Hey's method[15] and were purified by chromatography on alumina in petroleum ether followed by recrystallization from methanol, m. p. 35°C and 19°C, respectively.

4-Chlorobiphenyl was prepared and purified as described in Part VI[2].

2- and 3-Methylbiphenyl were prepared by reaction of cyclohexanone with *o*- and *m*-tolylmagnesium bromide followed by dehydration and dehydrogenation, analogously to Hey and Jackson's preparation[16] of 3,4′-bitolyl, but with the use of twice the amount of sulphur in the dehydrogenation; they were then purified by repeated fractional distillations under reduced pressure. The boiling points are: 2-CH_3-, 126°C/13 mmHg (Found: C, 93.02; H, 7.12. Calcd. for $C_{13}H_{12}$: C, 92.81; H, 7.19%); 3-CH_3-, 135~136°C/13 mmHg (Found: C, 92.67; H, 7.21. Calcd. for $C_{13}H_{12}$: C, 92.81; H, 7.19%).

4-Methylbiphenyl was prepared by reaction of *N*-nitroso-*p*-acetotoluidide[17] with benzene and was recrystallized from methanol, m. p. 50.5°C.

4-Methyl-2′-nitrobiphenyl was prepared by reaction of *N*-nitroso-*p*-acetotoluidide[17] with nitrobenzene. After removal of the nitrobenzene, the residue was distilled with superheated steam and the distillate was fractionated by chromatography on alumina in petroleum ether-benzene (4 : 1) into an oily material and 4-methyl-4′-nitrobiphenyl, m. p. 140°C. The oil was fractionated under reduced pressure, and the distillate (b. p. 190~195°C/17 mmHg) was further purified by chromatography similar to the above to give 4-methyl-2′-nitrobiphenyl, m. p. 37~37.5°C (from methanol).

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[11] F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5243 (1950).

[12] The energy of the vacant orbital of the nitro group may be estimated to be $\alpha-0.15\beta$ ($\beta=-3$ eV.) from the energy level values quoted by Nagakura and Tanaka (*J. Chem. Phys.*, **22**, 236 (1954)) for the nitro group in nitromethane.

[13] R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).

[14] H. C. Brown and Y. Okamoto, ibid., **79**, 1913 (1957).

[15] J. Elks, J. W. Haworth and D. H. Hey, *J. Chem. Soc.*, **1940**, 1284.

[16] D. H. Hey and E. R. B. Jackson, ibid., **1934**, 645.

[17] W. S. M. Grieve and D. H. Hey, ibid., **1935**, 689.

TABLE VI. DECOMPOSITION OF *N*-NITROSOACET(ANILIDE-^{14}C) AT 20.0°C AND RESULTS OF ISOTOPE DILUTION ANALYSES OF THE PRODUCTS

Exp. No.	Ratio of the portion taken to the total reaction mixture $f\times10^2$	Carrier added $C_6H_5C_6H_4X$		Specific activity of biaryl μc./mol.	Amount of biaryl formed μmol.
		X	*M*, mmol.		
1	The nitroso compound, 42.1±0.6 mc./mol., 82.5 mg.; the substrate, an equimolar mixture (4.32 g.) of chlorobenzene and benzene; nitrogen evolved 86%				
	7.58	H	4.09	69.8±0.7	89.7
	7.38	2-Cl	3.26	88.0±0.9	92.5
	38.45	3-Cl	7.02	69.2±0.7	30.1
	38.37	4-Cl	3.07	116.3±1.2	22.1
2	The nitroso compound, 42.1±0.6 mc./mol., 82.0 mg; the substrate, an equimolar mixture (3.84 g.) of toluene and benzene				
	8.18	H	2.34	56.2±0.8	38.3
	8.27	2-CH_3	2.47	59.2±0.8	42.1
	23.47	3-CH_3	2.39	57.4±0.8	14.0
	39.97	4-CH_3	1.96	69.2±0.9	8.1

TABLE VII. DECOMPOSITION OF *N*-NITROSO-(*p*-METHYL-^{14}C)-ACETANILIDE AT 20.0°C AND RESULTS OF ISOTOPE DILUTION ANALYSES OF THE PRODUCTS

Exp. No.	Ratio of the portion taken to the total reaction mixture $f\times10^2$	Carrier added 4-$CH_3C_6H_4C_6H_4X$		Specific activity of biaryl μc./mol.	Amount of biaryl formed μmol.
		X	*M*, mmol.		
3	The nitroso compound, 185.8±1.8 mc./mol., 81.2 mg.; the substrate, an equimolar mixture (4.29 g.) of nitrobenzene, chlorobenzene, and benzene; nitrogen evolved, 55%				
	7.96	H	2.01	226±2	30.7
	3.98	2′-NO_2	4.06	200±2	110
	19.82	3′-NO_2	2.00	202±2	11.0
	3.97	4′-NO_2	2.01	168±2	45.8
	7.93	2′-Cl	4.00	117±2	31.8
	19.88	3′-Cl	2.01	196±3	10.7
	16.92	4′-Cl	2.13	104±1	6.0
4	The nitroso compound, 185.8±1.8 mc./mol., 61.0 mg.; the substrate, an equimolar mixture (3.04 g.) of anisole and benzene; nitrogen evolved, 77%				
	29.81	H	5.98	533±4	57.7
	5.90	2′-OCH_3	2.02	384±3	70.9
	19.87	3′-OCH_3	2.01	384±3	20.9
	23.85	4′-OCH_3	1.46	443±4	14.6
5	The nitroso compound, 185.8±1.8 mc./mol., 63.3 mg.; the substrate, an equimolar mixture (2.75 g.) of toluene and benzene; nitrogen evolved, 82%				
	11.07	H	4.64	151±1	34.1
	11.13	2′-CH_3	12.04	64±1	37.3
	33.30	3′-CH_3	6.04	116±1	11.3
	18.50	4′-CH_3	2.01	129±1	8.7

4-Methyl-3′-nitrobiphenyl was prepared according to Hey, Nechvatal and Robinson's method with some modification. Reduction of 4-methyl-4′-nitrobiphenyl (10 g.) with activated iron and water in benzene[18] followed by acetylation with acetic anhydride gave 4-acetamino-4′-methylbiphenyl (7.5 g.), m. p. 221°C. Into a mixture of this compound (1 g.), acetic acid (15 ml.) and concentrated sulphuric acid (1.6 ml.) maintained at 10°C, fuming nitric acid (d, 1.52; 0.25 g.) was gradually stirred. After 15 min., the mixture was poured into water to yield the 3-nitrated product (m. p. 164°C; 0.7 g.). The procedure for hydrolysis and deamination was the same as that described by Hey, Nechvatal and Robinson[19]. The final product was purified by recrystallization from methanol, m. p. 77.7°C.

The preparation of 4-methyl-4′-nitrobiphenyl was described in Part VII[3].

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[18] S. E. Hazlet and C. A. Dornfeld, *J. Am. Chem. Soc.*, **66**, 1781 (1944).

[19] D. H. Hey, A. Nechvatal and T. S. Robinson, *J. Chem. Soc.*, **1951**, 2892.

2-Chloro-4′-methylbiphenyl was prepared as follows: (a) *N*-Nitroso-*p*-acetotoluidide[17] (157 g.) was allowed to decompose in chlorobenzene (3 l.). The product was isolated from the reaction mixture and fractionated by chromatography on alumina in petroleum ether, giving an oily material and a small amount of 4-chloro-4′-methylbiphenyl, m. p. 124°C. The oil was purified by repeating similar chromatography and distillation under reduced pressure to afford 22 g. of 2-chloro-4′-methylbiphenyl, b. p. 120~123°C/2 mmHg. (b) A mixture of *p*-iodotoluene (110 g.), *o*-iodochlorobenzene (40 g.), copper powder (150 g.), and clean sand (150 g.) was heated 6 hr. at 200~210°C. The reaction mixture was extracted with petroleum ether, and on removal of the solvent from the extract, the residue deposited crystals of 4,4′-bitolyl, which were then filtered off. The filtrate was purified in the same way as described under heading (a), b, p. 112~115°C/1 mmHg (yield, 7 g.). The specimens obtained by both method (a) and method (b) showed the same infrared spectrum (Found: Cl, 17.44. Calcd. for $C_{13}H_{11}Cl$: Cl, 17.48%).

Similarly, 3-chloro-4′-methylbiphenyl was prepared by the Ullmann reaction, m. p. 44~45°C (Found: Cl, 17.36. Calcd. for $C_{13}H_{11}Cl$: Cl, 17.48%).

The preparation of 4-chloro-4′-methylbiphenyl was described in Part VI[2].

2- and 3-Methoxy-4′-methylbiphenyl were prepared by the Ullmann reaction of *o*- and *m*-iodoanisole with *p*-iodotoluene. The experimental procedure was analogous to that mentioned above. Recrystallization of the crude products from methanol yielded the 2-isomer, m. p. 83°C (Found: C, 84.84; H, 7.17. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12%) and the 3-isomer, m. p. 80°C. (Found: C, 84.72; H, 7.20. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12 %).

The preparation of 4-methoxy-4′-methylbiphenyl was described in part VII[3].

2,4′- and 3,4′-Bitolyl were prepared from 4-methylcyclohexanone and *o*- and *m*-bromotoluene according to Hey and Jackson's method[16] with some modification. The products were purified by repeated distillation under reduced pressure. The boilng points are: 2,4′-$(CH_3)_2$-, 149°C/20 mmHg (Found: C, 92.22; H, 7.87. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74%); 3,4′-$(CH_3)_2$-, 161~162°C/20 mmHg (Found: C, 92.22; H, 7.80. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74%), and the latter melts at 15°C.

4,4′-Bitolyl was prepared by the Ullmann reaction of *p*-iodotoluene and recrystallized from ethanol, m. p. 125°C.

Preparation of Labelled Compounds.—*N*-Nitrosoacet(anilide-^{14}C) (specific activity, 42.1±0.6 mc./mol.) was prepared by a method described elsewhere[20].

(*p*-Methyl-^{14}C)acetanilide was prepared from labelled toluene by acetylation and oximation followed by the Beckmann rearrangement. The detailed experimental procedure is described elsewhere[21].

N-Nitroso-(*p*-methyl-^{14}C)acetanilide was prepared by nitrosating (*p*-methyl-^{14}C)acetanilide (specific activity, 185.8±1.8 mc./mol.; 238 mg.) with nitrosyl chloride (2.6 ml. of a 10% solution in acetic anhydride) in a mixture of acetic acid (2.4 ml.) and acetic anhydride (0.6 ml.) in the presence of fused potassium acetate (0.67 g.) and a trace of phosphorus pentoxide according to the usual method (yield, 180 mg.).

Decomposition of Labelled *N*-Nitroso Compounds and Isotope Dilution Analyses. — The reactions were carried out in an equimolar binary or ternary mixture of aromatic solvents at 20.0°C (see Tables VI and VII); the general procedure for the analysis of the products was analogous to that described in previous papers, but the original reaction mixtures were diluted with acetone instead of benzene. The results of the isotope dilution analyses are summarized in Tables VI and VII.

Labelled biaryls recovered from the reaction mixtures were purified normally by recrystallization from methanol or ethanol until a constant specific activity was reached. The carbon-14 assay is described in Part V[4]. Biphenyl was recrystallized from methanol and finally sublimed. Since the following biaryls were difficult to purify enough for a correct carbon-14 assay, they were converted into suitable derivatives, which can be readily purified to afford specimens pure enough for the radioactivity measurement.

3-Chlorobiphenyl was nitrated by the method described in Part VII[3] to give 3-chloro-4′-nitrobiphenyl, which was purified by repeated recrystallization from methanol.

2- and 3-Methylbiphenyl and 2-chloro- and 2-nitro-4′-methylbiphenyl were converted, by oxidation with potassium permanganate in pyridine by a method similar to Dauben and Tanabe's method[22], into biphenyl-2-carboxylic acid, m. p. 110~111°C, biphenyl-3-carboxylic acid[23], m. p. 160°C, 2-chlorobiphenyl-4′-carboxylic acid, m. p. 247°C (Found: C, 66.95; H, 4.04; Cl, 15.44. Calcd. for $C_{13}H_9ClO_2$: C, 67.11; H, 3.90; Cl, 15.24%), and 2-nitrobiphenyl-4′-carboxylic acid, m. p. 251°C (Found: C, 64.30; H, 3.88; N, 5.92. Calcd. for $C_{13}H_9NO_4$: C, 64.20; H, 3.73; N, 5.76%), respectively. These acids were purified by recrystallizations from ethanol.

In experiments 4 and 5, the 4-methylbiphenyl recovered was nitrated by Grieve and Hey's method[24] to give 4-methyl-4′-nitrobiphenyl, which was then purified by recrystallization from methanol.

Similar nitration of the 2,4′-bitolyl recovered followed by reduction with hydrogen and a Raney nickel catalyst (W-7)[25] in ethanol and acetylation of the resulting amine with acetic anhydride gave monoacetamino-2,4′-bitolyl (Found: N, 6.02. Calcd. for $C_{16}H_{17}NO$: N, 5.85%), m. p. 166°C (from methanol). Similarly, the 3,4′-bitolyl recovered was converted into 4-acetamino-3,4′-bitolyl, m. p. 221°C (from ethanol).

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Summary

N-Nitrosoacet(anilide-^{14}C) and *N*-nitroso-(*p*-methyl-^{14}C)acetanilide have been decomposed at 20.0°C in mixtures of benzene and monosubstituted benzenes, and the reaction products have been analyzed for biphenyl and substituted biphenyls by the isotope dilution method. From the results of these competitive experiments, the partial rate factors for the phenylation and *p*-methylphenylation have been calculated (Tables I and II).

The values of the partial rate factor for the meta position give a satisfactory Hammett plot with a slope of +0.05 for the phenylation and one with a slope of +0.03 for the *p*-methylphenylation, suggesting that the *p*-methylphenyl radical has little, if any, measure of polar character.

The correlation of the ρ values for various arylations with the inductive constant for the substituent group on the arylating radical indicates that the effect of the substituent group in the radical is purely inductive in nature.

The partial rate factor for the para position, k_p/k, is found to be related to Hammett's substituent constant by the following equation:

$$\log(k_p/k)=\rho\sigma_p+\tau_p$$

where ρ is the Hammett reaction constant for this arylation as determined from the Hammett plot of the partial rate factors of the meta position. τ_p is found to be tolerably constant for each substituted benzene, irrespective of the nature of the attacking aryl radical, and represents that part of the conjugative effect of the substituent which is independent of the polar nature of the attacking radical.

Molecular orbital calculations have given results which rationalize the trend found in the τ_p values.

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