

Influence of Substituent Groups on Nuclear Reactivity in the Formation of Substituted Biphenyls by Reaction of Aromatic Diazo and Related Compounds with Aromatic Liquids. VII. p-Nitrophenylation and p-Methoxyphenylation

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(Received May 10, 1963)

In the preceding paper¹⁾, the partial rate factors for the *p*-chlorophenylation of mono-substituted benzenes by the *p*-chlorophenyl radical derived from *N*-nitroso-*p*-chloroacetanilide have been reported. The variation of the reactivity of the meta position with the nature of the substituent has suggested that the attacking *p*-chlorophenyl radical has a somewhat electrophilic nature due to the presence of a chlorine atom. The study has

now been extended to include *p*-nitrophenylation and *p*-methoxyphenylation, the former being expected to be more electrophilic than *p*-chlorophenylation and the latter to be rather nucleophilic because of the electron-releasing nature of the *p*-methoxy group in the radical.

N-Nitroso-*p*-nitroacet(anilide-¹⁴C) and *N*-nitroso-*p*-methoxyacet(anilide-¹⁴C) were used as sources of the *p*-nitrophenyl and the *p*-methoxyphenyl radical, respectively, and the arylated products were analyzed by isotope

1) T. Migita, N. Morikawa and O. Simamura, This Bulletin, 36, 980 (1963).

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

Compound	Exp. No.	Partial rate factors			Relative rate* k_x/k_H
		k_o/k	k_m/k	k_p/k	
$C_6H_5NO_2$	1	0.90	0.347	1.49	0.66
	2	0.95	0.354	1.57	0.69
	Mean	0.93	0.35	1.53	0.68
C_6H_5Cl	1	1.50	0.650	0.99	0.88
	2	1.55	0.645	1.03	0.90
	Mean	1.53	0.65	1.01	0.89
$C_6H_5OCH_3$	3	5.16	0.83	2.45	2.40
	4	5.18	0.85	2.15	2.37
	Mean	5.17	0.84	2.30	2.39
$C_6H_5CH_3$	5	3.27	1.45	1.48	1.82
	6	3.28	1.27	1.53	1.77
	Mean	3.28	1.36	1.51	1.80

$$* \quad k_x = 2k_o + 2k_m + k_p; \quad k_H = 6k$$

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

Compound	Exp. No.	Partial rate factors			Relative rate k_x/k_H
		k_o/k	k_m/k	k_p/k	
$C_6H_5NO_2$	7	6.53	1.26	8.30	3.98
	8	6.37	1.11	8.42	3.90
	Mean	6.45	1.19	8.36	3.94
C_6H_5Cl	7	3.15	1.83	1.78	1.96
	8	3.00	1.80	1.69	1.88
	Mean	3.08	1.82	1.74	1.92
$C_6H_5OCH_3$	9	3.64	1.06	1.32	1.79
	10	3.71	1.00	1.30	1.79
	Mean	3.68	1.03	1.31	1.79
$C_6H_5CH_3$	11	3.10	1.00	1.19	1.56
	12	3.09	0.99	1.17	1.56
	Mean	3.09	1.00	1.18	1.56

dilution analysis. The results are summarized in Tables I and II.

The partial rate factors for the *p*-methoxyphenylation of nitrobenzene had previously been determined to be 7.24, 0, and 8.95 for the *o*-, *m*-, and *p*-position, respectively, the product analysis being done by means of column chromatography²⁾. The more accurate results obtained in the present work have shown that the meta-substituted product is actually formed. Probably the meta isomer could not be separated from the ortho isomer by the chromatographical method used in the previous experiments.

It is apparent from Table I that the relative rate of a monosubstituted benzene in *p*-

nitrophenylation decreases in the order: anisole > toluene > benzene > chlorobenzene > nitrobenzene. This trend, which is parallel to the order of reactivity towards electrophilic reagents, has not been observed in the case of *p*-chlorophenylation¹⁾. This shows that the *p*-nitrophenyl radical is decidedly more electrophilic than the *p*-chlorophenyl radical. It has been shown¹⁾ that in *p*-chlorophenylation the major factor controlling the rate is the stabilization of the transition state due to the delocalization of an odd electron, that is, the conjugative effect, and that the polar character of the attacking radical is of subordinate importance. In the *p*-nitrophenylation, however, it has now turned out that the polar effect of the *p*-nitrophenyl radical is strong enough to compete with the foregoing major

2) O. Simamura and T. Migita, This Bulletin, 27, 228 (1954).

factor, with the result that the relative rate sequence resembles that observed in electrophilic substitutions. The electrophilic nature of the *p*-nitrophenyl radical becomes even more evident when the reactivity is compared at the meta position, where the conjugative effect of the substituent group in the substrate may be regarded as negligible. Thus, the reactivity of the meta position of monosubstituted benzenes in the *p*-nitrophenylation decreases in the order: toluene > benzene > anisole > chlorobenzene > nitrobenzene. The same trend is observed in the *p*-chlorophenylation¹⁾, but the variation is much more conspicuous in the *p*-nitrophenylation. Figure 1 shows the relation between the partial rate factor for the meta position of a substituted benzene and the Hammett substituent constant for the substituent at the meta position. From the slope of the line, the reaction constant for the *p*-nitrophenylation is found to be -0.81 , while the corresponding value of the *p*-chlorophenylation is -0.27 ¹⁾. It is evident from a comparison of these values that the electrophilic nature of the *p*-nitrophenylation is more pronounced than that of the *p*-chlorophenylation because of the much stronger electron-withdrawing effect of the nitro group.

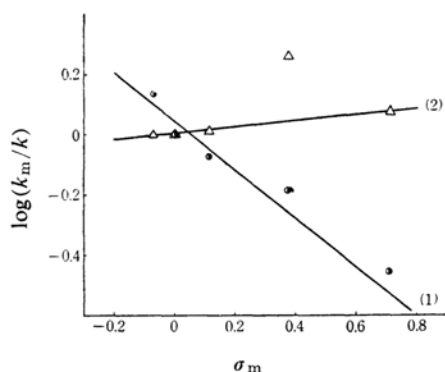


Fig. 1. The Hammett plots for the *p*-nitro-(1) and the *p*-methoxy-(2) phenylation.

In the *p*-methoxyphenylation, on the other hand, Table II shows that all substituents increase the nuclear reactivity of the aromatic nucleus, and that, except for chlorobenzene, the meta position is less reactive than the ortho and the para position, as has been observed in the *p*-chlorophenylation. Except for chlorobenzene, the partial rate factor for the meta position of every compound is approximately unity, so that the reactivity of the meta position of a monosubstituted benzene is close to that of a single position of benzene itself. This finding suggests that the *p*-methoxyphenyl radical has little, if any, polar character.

The reaction constant of the Hammett relation between $\log(k_m/k)$ and σ_m is $+0.09$; this value might indicate a very slight, if any, nucleophilic nature for the *p*-methoxyphenylation. The partial rate factor of 1.82 for the meta position of chlorobenzene seems to be anomalously high; the Hammett plot would predict it to be 1.08. It is not clear whether the value is true or erroneous owing to some unknown experimental difficulty in the analysis of 3-chloro-4'-methoxybiphenyl.

Recently, Hambling, Hey, and Williams³⁾ have observed that the relative reactivity of nitrobenzene towards the arylations by aroyl peroxides increases in the order: *p*-nitrophenylation < *p*-chlorophenylation < *p*-methoxyphenylation < phenylation. On the basis of this tendency, which has also been recognized in the present study, and of its parallelism to the dipole moment values of the compounds corresponding to the aryl radicals which cause these arylations, they have concluded that the *p*-methoxyphenyl radical has rather an electrophilic character compared with the phenyl radical. The disagreement between their view and ours seems to be attributable to the fact that, in their deduction, a comparison has been made between the relative rates of *p*-methoxyphenylation and of phenylation of nitrobenzene, using benzene as the reference substrate in both cases.

Experimental

Melting points are uncorrected.

Solvents.—Nitrobenzene, chlorobenzene, anisole, toluene and benzene were purified as described in Part VI¹⁾.

Substituted Biphenyls Used as Carriers in Isotope Dilution Analysis.—4-Nitrobiphenyl was prepared by nitration of biphenyl according to Maki and Ōbayashi's method⁴⁾, m. p. 112.8~113°C (from methanol).

4-Methoxybiphenyl was prepared by reaction of *N*-nitrosoaceto-*p*-aniside⁵⁾ with benzene and was purified by recrystallization from methanol, m. p. 90°C.

2,4'- and 4,4'-Dinitrobiphenyl were prepared by the nitration of *p*-nitrobiphenyl according to Maki and Ōbayashi's method⁴⁾. The 2,4'-isomer was recrystallized from ethanol, m. p. 93.5~94°C, and the 4,4'-isomer from acetone, m. p. 237°C.

3,4'-Dinitrobiphenyl was prepared as follows: To a cooled solution of 3-nitrobiphenyl⁶⁾ (15 g.) in acetic anhydride (20 ml.), a mixture of fuming nitric acid (*d*, 1.54; 6.8 ml.), acetic anhydride

3) J. K. Hambling, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, **1960**, 3782.

4) T. Maki and K. Ōbayashi, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kōgyō Kagaku Zasshi)*, **54**, 375 (1951).

5) J. W. Haworth and D. H. Hey, *J. Chem. Soc.*, **1940**, 361.

6) H. France, I. M. Heilbron and D. H. Hey, *ibid.*, **1940**, 369.

(3.4 ml.) and urea (0.2 g.) was added over a period of 15 min., and the mixture was heated on a steam bath. After being cooled, the mixture was poured into water to give a precipitate (17 g.), which was then collected, washed with water, and dried. The product was purified by chromatography on alumina in benzene-acetone (4 : 1) to give 3,4'-dinitrobiphenyl, m. p. 189°C (from ethanol).

2-Chloro-4'-nitrobiphenyl was prepared by reaction of *N*-nitroso-*p*-nitroacetanilide⁸⁾ with chlorobenzene. The product, which was isolated by removal of chlorobenzene under reduced pressure followed by distillation with superheated steam, was purified by chromatography on alumina in petroleum ether-benzene (4 : 1), m. p. 79~80°C (from methanol).

3-Chloro-4'-nitrobiphenyl was obtained by nitration of 3-chlorobiphenyl⁹⁾. The procedure for the nitration was analogous to that used for preparation of 3,4'-dinitrobiphenyl. The brown oily product was fractionated by distillation under reduced pressure (b. p. 157~158°C/1 mmHg) and then by chromatography on alumina in petroleum ether-benzene (4 : 1), m. p. 93~94°C (from methanol).

The preparation and purification of 4-chloro-4'-nitrobiphenyl were described in Part VI¹⁾.

2-Methoxy-4'-nitrobiphenyl was prepared from *N*-nitroso-*p*-nitroacetanilide and anisole and was purified by chromatography and recrystallization from methanol, m. p. 63~64°C.

3-Methoxy-4'-nitrobiphenyl was prepared from diazotized *m*-anisidine and nitrobenzene by the Gomberg reaction. After removal of the solvent from the reaction mixture, the residue was distilled with superheated steam to afford a crystalline distillate, which was then fractionated by chromatography on alumina in petroleum ether-benzene (1 : 1), m. p. 90~91°C (from methanol).

4-Methoxy-4'-nitrobiphenyl was prepared as described in Part III²⁾.

Methyl-4'-nitrobiphenyls were prepared as follows: *N*-Nitroso-*p*-nitroacetanilide (35 g.) was dissolved in 1 l. of toluene and left to stand for two days. After removal of the toluene, the residue was distilled with superheated steam and the distillate was fractionated by chromatography on alumina in petroleum ether-benzene into three parts: (i) an oily material which contained 3-methyl-4'-nitrobiphenyl (see below), (ii) 2-methyl-4'-nitrobiphenyl (6 g.), m. p. 102.5~103°C, and (iii) 4-methyl-4'-nitrobiphenyl (1.5 g.), m. p. 139~140°C. Fraction (ii) was further purified by similar chromatography, m. p. 102.5~103°C (from methanol). Distillation of fraction (i) under reduced pressure gave nitrobenzene (2 g.) and the residue, which chromatographed on alumina in petroleum ether-benzene (10 : 1) yielded, besides a small amount of 2-methyl-4'-nitrobiphenyl, 3-methyl-4'-nitrobiphenyl (0.5 g.), m. p. 60°C. The structure of this compound was established by the following preparation. Nitrosation of *m*-acetotoluidide (33 g.) by nitrous fumes in a mixture of acetic acid and acetic anhydride yielded oily *N*-nitroso-*m*-acetotoluidide, which was allowed to decompose in

nitrobenzene. The products were isolated as usual and chromatographed on alumina to give the same methyl-4'-nitrobiphenyl (2.5 g.), m. p. 60°C. 3-Methyl-4'-nitrobiphenyl was further purified by chromatography, m. p. 61.5°C (from methanol) (Found: C, 73.10; H, 5.21; N, 6.65. Calcd. for C₁₃H₁₁NO₂: C, 73.22; H, 5.20; N, 6.57%). 4-Methyl-4'-nitrobiphenyl was also prepared by nitration of 4-methylbiphenyl according to Grieve and Hey's method⁸⁾. The product was combined with fraction (iii) obtained above and purified by recrystallization from ethanol, m. p. 141°C.

4-Methoxy-2'-nitrobiphenyl was prepared as described in Part III²⁾, m. p. 62.5~63°C.

4-Methoxy-3'-nitrobiphenyl was prepared by reaction of *N*-nitroso-*m*-nitroacetanilide⁹⁾ with anisole and was purified by distillation and chromatography on alumina in petroleum ether-benzene (4 : 1), m. p. 78~79°C (from methanol).

2-Chloro-4'-methoxybiphenyl was prepared as follows: 2-Nitro-4'-methoxybiphenyl (5 g.) was reduced with activated iron powder and water¹⁰⁾ to 2-amino-4'-methoxybiphenyl, which was then diazotized and allowed to react with cuprous chloride in a manner similar to the preparation of 2,4'-dichlorobiphenyl described in a previous paper¹⁾, giving 2-chloro-4'-methoxybiphenyl (0.5 g.), m. p. 24~24.5°C. In another preparation *N*-nitroso-*p*-acetoanisidide (50 g.) was allowed to decompose in 700 ml. of chlorobenzene. The isolated product was treated with a little stannous chloride and concentrated hydrochloric acid in methanol and then distilled under reduced pressure. The distillate (b. p. 135~141°C/1 mmHg, 3.1 g.) was purified by chromatography on alumina in petroleum ether, yielding 2-chloro-4'-methoxybiphenyl (3.5 g.), m. p. 24~24.5°C. Specimens from both preparations were combined and purified by recrystallization from methanol, m. p. 24~24.5°C (Found: Cl, 16.18. Calcd. for C₁₃H₁₁ClO: Cl, 16.21%).

3-Chloro-4'-methoxybiphenyl was prepared by heating *m*-chloroiodobenzene (25 g.), *p*-iodoanisole (73.3 g.), and copper powder (100 g.) at 250°C for 8 hr. and purified by distillation under reduced pressure (b. p. 130~140°C/1.3 mmHg; yield, 13.1 g.) followed by chromatography on alumina in petroleum ether, m. p. 56~57°C (from methanol) (Found: Cl, 16.08. Calcd. for C₁₃H₁₁ClO: Cl, 16.21%).

4-Chloro-4'-methoxybiphenyl was prepared and purified as described in Part VI¹⁾.

2,4'-Dimethoxybiphenyl was prepared by the method described by Dunstan and Hughes¹¹⁾ and was purified by recrystallization from methanol, m. p. 71.5°C.

3,4'-Dimethoxybiphenyl was prepared by the Ullmann reaction of *p*-iodoanisole (70 g.) and *m*-iodoanisole (25 g.), m. p. 60~61°C (yield, 7 g.) (Found: C, 78.64; H, 6.63. Calcd. for C₁₄H₁₄O₂:

8) W. S. M. Grieve and D. H. Hey, *ibid.*, 1932, 1888.

9) H. France, I. M. Heilbron and D. H. Hey, *ibid.*, 1939, 1288.

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

11) W. J. Dunstan and G. K. Hughes, *J. Proc. Soc. N. S. Wales*, 80, 77 (1947); *Chem. Abstr.*, 42, 4160 (1948).

7) J. Elks, J. W. Haworth and D. H. Hey, *J. Chem. Soc.*, 1940, 1284.

TABLE III. DECOMPOSITION OF *N*-NITROSO-*p*-NITROACET(ANILIDE-¹⁴C) 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 $f \times 10^2$	Carrier added $4\text{-NO}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{X}$		Specific activity of biaryl $\mu\text{C.}/\text{mol.}^*$	Amount of biaryl formed $\mu\text{mol.}$
		X	M, mmol		
1 The nitroso compound (61.2 ± 0.5 mc./mol.), 141 mg.; the substrate, an equimolar mixture (6.21 g.) of nitrobenzene, chlorobenzene, and benzene; nitrogen evolved, 82%					
	2.97	H	2.02	115.4 ± 0.9	128
	8.93	2'-NO ₂	2.01	104.6 ± 1.0	38.5
	29.87	3'-NO ₂	2.00	135.1 ± 1.1	14.8
	11.96	4'-NO ₂	2.01	115.9 ± 1.0	31.8
	8.95	2'-Cl	2.01	174.8 ± 1.4	64.1
	8.94	3'-Cl	2.00	75.9 ± 0.7	27.8
	14.92	4'-Cl	2.00	97.0 ± 0.7	21.3
2 The nitroso compound (61.2 ± 0.5 mc./mol.), 140 mg.; the substrate, an equimolar mixture (6.21 g.) of nitrobenzene, chlorobenzene, and benzene; nitrogen evolved, 78%					
	3.01	H	2.05	108.6 ± 1.2	121
	9.97	2'-NO ₂	2.10	110.3 ± 1.1	37.2
	26.79	3'-NO ₂	2.06	113.5 ± 1.1	14.3
	11.87	4'-NO ₂	2.05	112.4 ± 1.1	31.7
	5.96	2'-Cl	2.07	109.9 ± 1.0	62.4
	12.95	3'-Cl	2.05	100.3 ± 1.1	26.0
	17.93	4'-Cl	2.04	111.3 ± 1.1	20.8
3 The nitroso compound (46.6 ± 0.3 mc./mol.), 192 mg.; the substrate, an equimolar mixture (7.69 g.) of anisole and benzene; nitrogen evolved, 73%					
	9.89	H	2.03	377 ± 3	167
	5.91	2'-OCH ₃	2.02	390 ± 3	288
	29.75	3'-OCH ₃	2.03	314 ± 3	46.3
	33.76	4'-OCH ₃	2.02	530 ± 5	68.6
4 The nitroso compound (46.6 ± 0.3 mc./mol.), 192 mg.; the substrate, an equimolar mixture (7.70 g.) of anisole and benzene; nitrogen evolved, 76%					
	9.98	H	2.02	342 ± 3	149
	5.89	2'-OCH ₃	2.01	349 ± 3	257
	19.80	3'-OCH ₃	1.89	205 ± 2	42.2
	23.95	4'-OCH ₃	2.01	294 ± 3	53.4
5 The nitroso compound (61.2 ± 0.5 mc./mol.), 185 mg.; the substrate, an equimolar mixture (6.73 g.) of toluene and benzene; nitrogen evolved, 39%					
	5.88	H	1.98	218 ± 2	120
	6.10	2'-CH ₃	2.02	243 ± 2	132
	17.98	3'-CH ₃	2.02	317 ± 3	58.2
	29.91	4'-CH ₃	2.02	270 ± 2	29.8
6 The nitroso compound (46.6 ± 0.3 mc./mol.), 193 mg.; the substrate, an equimolar mixture (7.04 g.) of toluene and benzene; nitrogen evolved, 50%					
	8.00	H	2.02	172 ± 2	93.5
	7.99	2'-CH ₃	2.17	174 ± 2	102
	15.95	3'-CH ₃	3.10	93.8 ± 0.9	39.3
	31.96	4'-CH ₃	2.17	162 ± 2	23.7

* Indicated deviations are probable errors.

C, 78.48; H, 6.59%). The structure of this compound was established by the fact that it was different from the possible isomeric products, the 3,3'- (m. p. 35°C)¹² and the 4,4'- (m. p. 173°C)¹³ isomer.

12) J. van Alphen, *Rec. trav. chim.*, **50**, 1111 (1931).13) F. Ullmann, G. M. Meyer, O. Loewenthal and E. Gilli, *Ann.*, **332**, 38 (1904).

4,4'-Dimethoxybiphenyl was prepared by the Ullmann reaction from *p*-iodoanisole and was purified by recrystallization from ethanol, m. p. 173~173.5°C.

4-Methoxy-2'- and -4'-methylbiphenyl were prepared as follows: *N*-Nitroso-*p*-acetoanisidide was allowed to decompose in toluene, and the product was fractionally distilled under reduced pressure to

TABLE IV. DECOMPOSITION OF *N*-NITROSO-*p*-METHOXYACET(ANILIDE-¹⁴C) 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 $f \times 10^2$	Carrier added 4-CH ₃ OC ₆ H ₄ C ₆ H ₄ X		Specific activity of biaryl μ c./mol.	Amount of biaryl formed μ mol.
		X	M, mmol.		
7	The nitroso compound (27.4 ± 0.2 mc./mol.), 496 mg.; the substrate, an equimolar mixture (24.04 g.) of nitrobenzene, chlorobenzene, and benzene; nitrogen evolved, 85%				
	6.98	H	2.01	154 \pm 2	163
	3.98	2'-NO ₂	2.00	191 \pm 2	354
	24.98	3'-NO ₂	2.00	232 \pm 2	69
	5.97	4'-NO ₂	2.00	182 \pm 2	225
	6.98	2'-Cl	2.01	162 \pm 2	171
	19.91	3'-Cl	2.01	267 \pm 3	99
	24.93	4'-Cl	1.99	164 \pm 2	48
8	The nitroso compound (27.4 ± 0.2 mc./mol.), 495 mg.; the substrate, an equimolar mixture (24.01 g.) of nitrobenzene, chlorobenzene, and benzene; nitrogen evolved, 84%				
	8.96	H	2.00	213 \pm 2	176
	3.99	2'-NO ₂	2.00	202 \pm 2	373
	19.95	3'-NO ₂	2.01	176 \pm 2	65
	5.96	4'-NO ₂	2.00	200 \pm 2	247
	7.95	2'-Cl	2.01	190 \pm 2	176
	15.98	3'-Cl	2.01	228 \pm 2	105
	29.94	4'-Cl	2.00	201 \pm 2	50
9	The nitroso compound (31.4 ± 0.4 mc./mol.), 145 mg.; the substrate, an equimolar mixture (6.25 g.) of anisole and benzene; nitrogen evolved, 52%				
	7.91	H	2.00	130 \pm 1	105
	6.98	2'-OCH ₃	2.00	139 \pm 1	128
	19.97	3'-OCH ₃	2.00	116 \pm 1	37.1
	39.94	4'-OCH ₃	2.00	144 \pm 1	23.1
10	The nitroso compound (31.4 ± 0.4 mc./mol.), 145 mg.; the substrate, an equimolar mixture (6.28 g.) of anisole and benzene; nitrogen evolved, 54%				
	7.95	H	2.00	132 \pm 1	107
	5.96	2'-OCH ₃	2.00	123 \pm 1	132
	23.98	3'-OCH ₃	2.00	133 \pm 1	35.6
	39.94	4'-OCH ₃	2.01	144 \pm 1	23.1
11	The nitroso compound (31.4 ± 0.4 mc./mol.), 145 mg.; the substrate, an equimolar mixture (5.70 g.) of toluene and benzene; nitrogen evolved, 46%				
	6.00	H	2.01	47.7 \pm 0.7	51.1
	11.93	2'-CH ₃	4.07	48.4 \pm 0.6	52.7
	29.97	3'-CH ₃	2.03	78.5 \pm 1.0	17.0
	19.98	4'-CH ₃	1.80	35.3 \pm 0.5	10.1
12	The nitroso compound (31.4 ± 0.4 mc./mol.), 145 mg.; the substrate, an equimolar mixture (5.74 g.) of toluene and benzene; nitrogen evolved, 50%				
	7.95	H	2.00	75.9 \pm 1.0	60.9
	14.99	2'-CH ₃	4.00	73.6 \pm 1.0	62.7
	19.98	3'-CH ₃	2.00	63.0 \pm 0.9	20.2
	39.89	4'-CH ₃	2.00	74.2 \pm 0.7	11.9

give two main distillates, b. p. 118~128°C/1 mmHg and b. p. 153°C/1 mmHg. The latter solidified to give 4-methoxy-4'-methylbiphenyl, m. p. 111°C (from methanol). The former was chromatographed on alumina in petroleum ether and distilled under reduced pressure to yield an oily material (b. p. 136~138°C/5 mmHg). The oil was heated with picoline hydrochloride at 220~230°C for 8 hr. After being cooled, the reaction mixture was

poured into water, and the phenolic product was isolated and purified by chromatography on alumina in benzene to give 4-hydroxy-2'-methylbiphenyl (m. p. 80~81°C). The structure of this compound was evident from its preparation by the Ullmann reaction of *p*-iodoanisole and *o*-iodotoluene in the presence of copper powder at 200~220°C, followed by demethylation with picoline hydrochloride at 220~230°C for 8 hr. 4-Hydroxy-2'-methylbiphenyl

was methylated with dimethyl sulphate in aqueous alkali to afford 4-methoxy-2'-methylbiphenyl, b.p. 140~141.5°C/13 mmHg (Found: C, 85.06; H, 7.28. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12%).

4-Methoxy-3'-methylbiphenyl was prepared by the Ullmann reaction from *p*-iodoanisole (110 g.) and *m*-iodotoluene (40 g.) and was purified by chromatography on alumina in petroleum ether (yield, 12 g.), m.p. 53~54°C (from methanol) (Found: C, 84.84; H, 7.21. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12%).

Preparation of Labelled Compounds.—The preparations of *p*-nitroacet(anilide- ^{14}C) and *p*-methoxyacet(anilide- ^{14}C) from benzene- ^{14}C have been described elsewhere^{14,15}. The detailed procedure for nitrosation of these substituted acetanilide- ^{14}C was analogous to that of *p*-chloro(^{36}Cl)acetanilide described in a previous paper¹⁵. Nitrosation of *p*-nitroacet(anilide- ^{14}C) (specific activity, 61.2 ± 0.5 mc./mol., 0.506 g.) with 7 ml. of a 10% solution of nitrosyl chloride in acetic anhydride in a mixture of acetic acid (5.2 ml.) and acetic anhydride (1.3 ml.) in the presence of fused potassium acetate (1.7 g.) and a trace of phosphorus pentoxide yielded 0.475 g. of *N*-nitroso-*p*-nitroacet(anilide- ^{14}C). A mixture of *p*-methoxyacet(anilide- ^{14}C) (specific activity, 27.4 ± 0.2 mc./mol., 0.941 g.), fused potassium acetate (1.2 g.), acetic acid (4.5 ml.), acetic anhydride (1.1 ml.) and a trace of phosphorus pentoxide, treated with 4.5 g. of a similar solution of nitrosyl chloride, gave 0.992 g. of *N*-nitroso-*p*-methoxyacet(anilide- ^{14}C).

Decomposition of Labelled *N*-Nitroso Compounds and Isotope Dilution Analysis.—The reaction was carried out in an equimolar binary or ternary mixture of aromatic solvents at 20.0°C in a manner similar to the *p*-chlorophenylation¹⁵ (see Table III). The general procedure for the analysis of the products was analogous to that described in a previous paper¹⁵. The 4-methoxy-2'-methylbiphenyl recovered from the reaction mixture in the *p*-methoxyphenylation was demethylated by heating it with picoline hydrochloride to crystalline 4-hydroxy-2'-methylbiphenyl, which was then chromatographed on alumina in

benzene, recrystallized from a mixture of benzene and petroleum ether, and assayed for carbon-14. 4,4'-Dinitrobiphenyl was purified by chromatography in acetone and by recrystallization from a mixture of ethanol and acetone. 3,4'-Dinitrobiphenyl, 4-methoxy-4'-nitrobiphenyl, and 4-methyl-4'-nitrobiphenyl were purified by chromatography in benzene and by recrystallization from ethanol. The other biaryls recovered were normally purified by chromatography on alumina in a mixture of benzene and petroleum ether and by recrystallization from methanol or ethanol. Carbon-14 determination was carried out as described in Part V¹⁶. The numerical results are summarized in Tables III and IV.

Summary

N-Nitroso-*p*-nitroacet(anilide- ^{14}C) and *N*-nitroso-*p*-methoxyacet(anilide- ^{14}C) have been decomposed at 20.0°C in mixtures of benzene and monosubstituted benzenes C_6H_5X ($X=NO_2$, Cl , OCH_3 , and CH_3), and the reaction products have been analyzed for 4-nitro- and 4-methoxybiphenyl and isomeric 4- $NO_2C_6H_4C_6H_4X$ and 4- $CH_3OC_6H_4C_6H_4X$ by the isotope dilution method.

From the results of these competitive experiments, the partial rate factors for the *p*-nitrophenylation and *p*-methoxyphenylation 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 -0.81 for the *p*-nitrophenylation and one with a slope of $+0.09$ for the *p*-methoxyphenylation, showing that the *p*-nitrophenyl radical has a pronounced electrophilic character while the *p*-methoxyphenyl radical has little, if any, nucleophilic character.

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