788. *The Effect of the Nitro-group on the Reactivity of the Diphenyl Nucleus in Nitration. Competitive Nitration of Nitrodiphenyls and Benzene by Nitric Acid in Acetic Anhydride.*

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Competitive nitration of nitrodiphenyls and benzene has been carried out by nitric acid in acetic anhydride at 0°. The proportions of isomeric dinitrodiphenyls produced and the partial rate factors show that the polar effect of the nitrophenyl groups is similar to that of halogen atoms with mesomeric electron-releasing and inductive electron-attracting effect. The theoretical implication of the change in the *ortho* : *para* ratio of the nitration products of isomeric nitrodiphenyls is discussed.

Nitrodiphenyls undergo electrophilic substitution, such as nitration,[1,2] bromination,[1,3] and acetylation,[4] at the 2- and 4-position of the unsubstituted ring. These facts led many workers [5] to adopt the view that the two nuclei of diphenyl act independently in substitution. Later, evidence from physical measurements including dipole moments,[6] *X*-ray crystal analysis,[7] and absorption spectra [8] showed, however, that the lack of conjugation between the two nuclei in the diphenyl system was not complete. That the effect of substituents is also transmitted through the diphenyl system in chemical reactions was shown by more recent studies of the dissociation constants of 4′-substituted diphenyl-4-carboxylic acids [9] and 4-hydroxy-4′-nitrodiphenyl [10] and of the rates of nucleophilic substitution of 4-bromo-3 : 4′-dinitrodiphenyl by piperidine [11] and of alkaline hydrolysis of substituted ethyl diphenyl-4-carboxylates.[12] In electrophilic substitution, 2- and 4-nitrodiphenyls are chlorinated in aqueous acetic acid at a rate some two-thousand times slower than diphenyl,[13] showing that the deactivating influence of the nitro-group is relayed to the unsubstituted nucleus. To provide further evidence of a quantitative nature, we now report the competitive nitration of each of three isomeric nitrodiphenyls and benzene.

The nitrations were carried out with nitric acid in acetic anhydride at 0°. The experimental conditions and results are summarized in Tables 1, 2, and 3. From the amounts of dinitrodiphenyls and nitrobenzene produced the relative rates of the nitration of nitrodiphenyls with respect to benzene were calculated, according to the method of Ingold and

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[1] Blakey and Scarborough, *J.*, 1927, 3000.

[2] Gull and Turner, *J.*, 1929, 491; Maki and Ohayashi, *J. Chem. Soc. Japan, Chem. Ind. Sect.*, 1951, **54**, 375.

[3] Le Fèvre and Turner, *J.*, 1926, 2041; Case, *J. Amer. Chem. Soc.*, 1938, **60**, 424.

[4] Grieve and Hey, *J.*, 1933, 968.

[5] Le Fèvre and Turner, *J.*, 1928, 245; Burkhardt, Horrex, and Jenkins, *J.*, 1936, 1654; Campbell, Anderson, and Gilmore, *J.*, 1940, 446.

[6] Le Fèvre and Le Fèvre, *J.*, 1936, 1130.

[7] Dhar, *Indian J. Physics*, 1932, **7**, 43.

[8] Pickett, Walter, and France, *J. Amer. Chem. Soc.*, 1936, **58**, 2296; Gillam and Hey, *J.*, 1939, 1170; Jones, *J. Amer. Chem. Soc.*, 1941, **63**, 1658; Williamson and Rodebush, *ibid.*, p. 3018.

[9] Berliner and Blommers, *ibid.*, 1951, **73**, 2479.

[10] Kreiter, Bonner, and Eastman, *ibid.*, 1954, **76**, 5770.

[11] Berliner, Newman, and Riaboff, *ibid.*, 1955, **77**, 478.

[12] Berliner and Liu, *ibid.*, 1953, **75**, 2417.

[13] Hartman and Robertson, *J.*, 1945, 891.

TABLE 1. *Competitive nitration of* 4-*nitrodiphenyl and benzene at* 0°. (*The amounts of compounds taken or formed are expressed in millimoles.*)

Experiment no.:	1	2	3	
Benzene taken	100	25·0	25·0	
4-Nitrodiphenyl taken	25·0	25·0	25·0	
Nitric acid	100	120	120	
Acetic anhydride	1400	1500	1500	
Reaction time (hr.)	72	42	45	
Nitrobenzene formed	20·1	12·2	13·9	
Dinitrodiphenyls formed	1·76	4·95	5·56	
Isomer composition (%)				Mean
2 : 4′-	—	35	34	34·5
3 : 4′-	—	0·5	0	0·3
4 : 4′-	—	64	66	65
Relative rate	0·33	0·33	0·32	0·33

TABLE 2. *Competitive nitration of* 3-*nitrodiphenyl and benzene at* 0°. (*The amounts of compounds taken or formed are expressed in millimoles.*)

Experiment no.:	4	5	6	
Benzene taken	25·0	25·0	0	
3-Nitrodiphenyl taken	25·0	25·0	12·9	
Nitric acid	37·5	25	20	
Acetic anhydride	800	500	250	
Reaction time (hr.)	26	7	7	
Nitrobenzene formed	4·11	5·20	0	
Dinitrodiphenyls formed	3·99	5·64	5·60	
Isomer composition (%)				Mean
2 : 3′-	—	46	44	45
3 : 4′-	—	54	56	55
Relative rate	0·97	1·09	—	1·03

TABLE 3. *Competitive nitration of* 2-*nitrodiphenyl and benzene at* 0°. (*The amounts of compounds taken or formed are expressed in millimoles.*)

Experiment no.:	7	8	9	
Benzene taken	25·0	25·0	25·0	
2-Nitrodiphenyl taken	25·0	25·0	25·0	
Nitric acid	20	23	23	
Acetic anhydride	400	400	400	
Reaction time (hr.)	24	18	18	
Nitrobenzene formed	5·28	6·05	5·12	
Dinitrodiphenyl formed	1·79	2·04	1·79	
Isomer composition (%)				Mean
2 : 2′-	31	29	30	30
2 : 3′-	2	4	4	3
2 : 4′-	67	67	66	67
Relative rate	0·31	0·31	0·32	0·31

TABLE 4. *Partial rate factors for the nitration of nitrodiphenyls and* ortho : *para-ratios of the products.*

	Partial rate factors			
Nuclear position:	2′	3′	4′	*o* : *p*
4-Nitrodiphenyl	0·35	<0·01	1·3	0·54
3-Nitrodiphenyl	1·4	0	3·4	0·82
2-Nitrodiphenyl	0·28	0·03	1·2	0·46
Diphenyl [15]	41	<0·6	38	2·2

Shaw.[14] The relative rates and the proportions of isomeric dinitrodiphenyls formed gave the partial rate factors for nitration of nitrodiphenyls, the rate constants of separate nuclear positions of nitrodiphenyls relative to one nuclear position of benzene being taken

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[14] Ingold and Shaw, *J.*, 1927, 2918.

as unity. The values are shown in Table 4, in which those for nitration of diphenyl[15] itself are included for comparison.

The present results show that, although the substitution takes place at positions 2 and 4 of the nucleus from which the nitro-group is absent, nitrodiphenyls are largely deactivated in comparison with diphenyl, though only slightly deactivated with respect to benzene. This situation is very similar to those observed in the nitrations of compounds with substituents which are classed as type 3 ($-I + T$) by Ingold and Shaw,[16] such as halogenobenzenes, cinnamic acid,[17] benzyl chloride, and ethyl phenylacetate, and the present case offers a further example. The *ortho-para*-orientation is attributed to the electromeric electron-release due to the polarisable π-electrons in the nitrophenyl group. An explanation for this orientation in terms of resonance structures contributing to the transition state has been given by Berliner and Blommers.[9] The deactivation with respect to diphenyl and even to benzene is obviously caused by relay of the electron-attracting effect of the nitro-group through the 1 : 1′-linkage. The orientation in nitrobenzene shows that the deactivating electron-attraction is less from a 3-nitro- than from a 2- or 4-nitro-group, resulting in 3-nitrodiphenyl's being appreciably more reactive than the 2- or the 4-isomer.

The *ortho* : *para* ratio in which the diphenyls are nitrated falls in the order diphenyl > 3- > 4- > 2-nitrodiphenyl, as shown in Table 4. According to the generally accepted view[18] that the *ortho* : *para* ratio decreases with the increasing electron-attracting inductive effect of the orienting substituent, the above order suggests that this effect increases in the order phenyl < 3- < 4- < 2-nitrophenyl. This order is in conformity with the nature of transmission of the polar effects of these groups, except for the 2-nitrophenyl group (upon which result some doubt could be thrown). Ingold[18] has attributed the activation of the *ortho*- with respect to the *para*-position of nitrobenzene towards the electrophilic reagent to the selective deactivation of the latter compared with the former position. If this view is accepted, the 2-nitrophenyl group is to be considered less electron-attracting than the 4-nitrophenyl group. Thus the *ortho* : *para* ratio for 2-nitrodiphenyl would be expected to be larger than that for the 4-nitro-isomer, *viz.*, 0·54. Actually it was found to be 0·46. The discrepancy is probably due to operation on the 2′-position in 2-nitrodiphenyl of steric hindrance due to the presence of the 2-nitro-group.

EXPERIMENTAL

Reagents.—4-Nitrodiphenyl was prepared by nitration of diphenyl with nitric acid in acetic acid as described by Bell, Kenyon, and Robinson.[19] Recrystallization from ethanol gave pure 4-nitrodiphenyl, m. p. 113·5°. 3-Nitrodiphenyl, m. p. 61° (from methanol), was synthesized according to the method of France, Heilbron, and Hey[20] by decomposing *m*-nitro-*N*-nitrosoacetanilide in benzene. 2-Nitrodiphenyl, m. p. 37° (from methanol), was obtained by Elks, Haworth, and Hey's method,[21] the action of sodium acetate on a stirred mixture of diazotized *o*-nitroaniline and benzene. Benzene was purified by shaking with concentrated sulphuric acid, fractionally distilling it through a Vigreux column, and finally freezing it. Nitric acid was prepared by distilling commercial fuming nitric acid from concentrated sulphuric acid at ordinary pressure, and then twice at 20 mm. The faintly yellow distillate was stored in a refrigerator. Acetic anhydride was purified by fractional distillation (b. p. 140°).

Competitive Nitration of 4-Nitrodiphenyl and Benzene.—A typical experiment (No. 2 in Table 1) was carried out as follows: Nitric acid (5 ml.) in acetic anhydride (10 ml.) was added dropwise at 0° to a stirred solution of 4-nitrodiphenyl (4·981 g.) and benzene (1·985 g.) in acetic anhydride (140 ml.). The reaction was allowed to proceed for 42 hr. at 0°. The mixture was

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[15] Simamura and Mizuno, *Bull. Chem. Soc. Japan*, 1957, **30**, 196.

[16] Ingold and Shaw, *J.*, 1949, 575.

[17] Bordwell and Rohde, *J. Amer. Chem. Soc.*, 1948, **70**, 1191.

[18] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N.Y., 1953, p. 261.

[19] Bell, Kenyon, and Robinson, *J.*, 1926, 1239.

[20] France, Heilbron, and Hey, *J.*, 1939, 1288.

[21] Elks, Haworth, and Hey, *J.*, 1940, 1284.

then poured into ice-water (400 ml.) and left overnight. The crystalline precipitate was filtered off, dried, and weighed (5·145 g.). About one-third (1·681 g.) of this solid was chromatographed in 100 ml. of 1 : 1 light petroleum–benzene on alumina (2·5 × 30 cm.). Elution with the same solvent gave unchanged 4-nitrodiphenyl and then 2 : 4′-dinitrodiphenyl (0·124 g.), m. p. and mixed m. p. 92—93°. Subsequent elution with benzene afforded 4 : 4′-dinitrodiphenyl (0·252 g.), m. p. and mixed m. p. 232—233°. The filtrate from the crystalline precipitate was neutralized with sodium hydrogen carbonate, and extracted with ether (800 ml.). The ethereal extract was washed with dilute sodium hydroxide solution and then with water and dried ($CaCl_2$), and the ether was distilled off through a Vigreux column. When concentrated to about 50 ml., the solution was shaken with an aqueous solution (25 ml.) of sodium sulphite (3 g.) and sodium hydrogen carbonate (0·7 g.) in order to remove tetranitromethane.[22] The ethereal solution was further concentrated to about 5 ml. The residue was dissolved in ethanol, and the solution made up to 25 ml. and analyzed for nitro-groups by titrating aliquot parts (1·00 ml.) with standard titanium trichloride and ferric alum solution.[23] The remainder of the ethanolic solution was distilled at 20 mm., with occasional additions, into the distilling flask, of a little aniline as carrier for nitrobenzene, until nitrobenzene was completely removed, giving an oily mixture of aniline, 4-nitrodiphenyl, and dinitrodiphenyls. The mixture was dissolved in ether and the solution was extracted with dilute hydrochloric acid. The ether was removed, the residue dissolved in ethanol, and the solution made up to 25 ml. and analyzed for nitro-groups on aliquot portions (1·00 ml.). The difference between the two values for the nitro-group determination, before and after the removal of nitrobenzene, represents the amount of the nitrobenzene formed. The remaining solution was evaporated and the residue comprising eight-tenth parts of the dinitrodiphenyls contained in the original filtrate was chromatographed in light petroleum–benzene on alumina. Elution with the same solvent mixture gave 4-nitrodiphenyl, 2 : 4′- (41 mg.), 3 : 4′- (4 mg.), and 4 : 4′-dinitrodiphenyl (7 mg.) in succession. The 3 : 4′-dinitrodiphenyl was identified by means of its m. p. and ultraviolet absorption spectrum in ethanolic solution (cf. Table 5). Thus the total amount of dinitrodiphenyls produced was found to be 1·210 g., consisting of 64% of 4 : 4′-, 35% of 2 : 4′-, and 0·5% of 3 : 4′-isomer. The above procedure for estimating the various products was checked by using an artificial mixture of known quantities of these compounds, with the following results:

	Taken	Found		Taken	Found
Acetic anhydride	150 ml.	—	2 : 4′-Dinitrodiphenyl	0·361 g.	0·352 g.
Benzene	0·805 g.	—	3 : 4′-Dinitrodiphenyl	0·011 g.	0·010 g.
4-Nitrodiphenyl	3·752 g.	3·747 g.	4 : 4′-Dinitrodiphenyl	0·683 g.	0·680 g.
Nitrobenzene	1·225 g.	1·211 g.			

Competitive Nitration of 3-*Nitrodiphenyl and Benzene.*—The nitration and the determination of the products were carried out as described above for the competitive nitration of 4-nitrodiphenyl and benzene. Chromatography yielded 2 : 3′-dinitrodiphenyl, m. p. 120°, and 3 : 4′-dinitrodiphenyl, m. p. 187—189°, both undepressed on admixture with authentic specimens. 3 : 3′-Dinitrodiphenyl could not be detected.

TABLE 5. *Absorption spectra* ($10^{-3}\varepsilon$) *of* 4 : x′-*dinitrodiphenyls in* 96% *ethanol.*

λ (mμ)	$x' = 2'$	$x' = 3'$	$x' = 4'$	λ (mμ)	$x' = 2'$	$x' = 3'$	$x' = 4'$	λ (mμ)	$x' = 2'$	$x' = 3'$	$x' = 4'$
220	17·39	19·25	11·30	270	14·35	17·55	9·90	308	7·47	14·45	25·90
230	9·89	15·00	6·75	285	12·67	19·50	19·00	315	5·68	11·03	25·20
245	9·03	9·14	3·82	300	9·57	17·58	25·20	330	2·52	4·69	15·82
260	12·89	13·60	5·29								

Competitive Nitration of 2-*Nitrodiphenyl and Benzene.*—A mixture of 2-nitrodiphenyl and benzene was nitrated under the conditions shown in Table 3. The mixture was added to ice-water (400 ml.) and left overnight. The oily precipitate was extracted with ether after the mixture had been neutralized with sodium hydrogen carbonate. The ethereal extract was concentrated and any tetranitromethane removed. Nitrobenzene was distilled from the mixture as described above and estimated titanometrically. Chromatography of the remaining mixture gave a mixture of dinitrodiphenyls, which was weighed and analyzed for nitrogen (correct value for $C_{12}H_8O_4N_2$). The isomer composition in which the three dinitrodiphenyls

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[22] Ingold and Smith, *J.*, 1938, 905.

[23] Cumming, Hopper, and Wheeler, " Systematic Organic Chemistry," Constable & Co., Ltd., London, 4th edn., 1950, p. 494.

were produced was estimated spectrophotometrically, absorptions in ethanolic solution at 225, 227·5, 280, and 285 mμ being used (cf. Table 6). Lambert–Beer's law was obeyed and tests with artificial mixtures of known compositions showed that this analytical procedure was satisfactory; analysis of a mixture of, *e.g.*, 2 : 2'- (26·5%), 2 : 3'- (5·0%), and 2 : 4'-dinitrodiphenyl (68·5%) gave values of 26·8%, 6·1%, and 67·1% respectively.

TABLE 6. *Absorption spectra* ($10^{-3}\varepsilon$) *of* 2 : x'-*dinitrodiphenyls in* 96% *ethanol.*

λ (mμ)	$x' = 2'$	$x' = 3'$	$x' = 4'$
222·5	18·60	23·50	15·48
225	16·48	23·40	13·57
227·5	14·28	22·95	11·28
235	10·03	19·79	8·14
245	9·77	12·88	9·03
255	11·25	12·50	11·80
260	11·50	12·45	12·89
270	9·85	10·03	14·35
280	6·84	6·79	13·58
285	5·50	5·35	12·67
290	4·63	4·49	11·60
295	4·05	3·92	10·62
300	3·56	3·48	9·57
310	2·72	2·56	7·13

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