272. *The Nitration of Phenyl Derivatives of Mercury, Thallium, Lead, Bismuth, Tin, and Iodine.*

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THE diminution in the percentage of *m*-substitution observed in the nitration of quaternary benzyltrimethyl and, to a lesser extent, of phenyltrimethyl derivatives of nitrogen, phosphorus, arsenic, and antimony has been discussed by various investigators (for references, see Challenger and Peters, J., 1929, 2610). A comparison of the (greater) *m*-nitration produced in benzyltrimethylammonium than in benzyldiethylsulphonium picrate has been made by Pollard and Robinson (J., 1930, 1765; 1927, 2772). Baker and Moffitt (J., 1930, 1722) nitrated phenyl- and benzyl-dimethyl-sulphonium and -selenonium salts and found diminished *m*-nitration in the case of the benzylselenonium as compared with the benzylsulphonium ion.

In contradistinction to the work outlined above, no study of the nitration of analogous compounds of metals having consecutive atomic numbers has been made. As regards non-metals, the work of Ingold and Ingold (J., 1926, 1310) and of Holmes and Ingold (*ibid.*, p. 1328) on the nitration of *o*-methoxyacetanilide, *o*-methoxymethylacetanilide, and *o*-fluoroanisole showed that for *op*-substitution the order N>O>F holds good. Le Fèvre (J., 1929, 2771; 1930, 2236; 1932, 1988) found that both 2-phenylbenzopyrylium and 1-methyl-2-phenylquinolinium salts are nitrated exclusively in the *m*-position, so that discrimination between the directive effect of oxygen and nitrogen in compounds of this type was impossible.

The present communication describes the nitration of the phenyl derivatives of several elements occupying consecutive or adjacent positions in the periodic table, as indicated on the next page:

Compound nitrated.	% *m*-Nitration.	No. of Ph groups / Kationic charge.
1. Phenylmercury nitrate	50	1
2. Diphenylthallium oxide	74	2
3. Diphenylthallium nitrate	75	2
4. *Phenylthallium hydroxynitrate*	86	0·5
*5. Diphenyl-lead dinitrate	94	1
*6. Triphenylbismuthine dinitrate	86	1·5
7. Diphenyltin oxide	79	1
*8. Diphenyliodonium nitrate	82·5	2

* These compounds have also been nitrated by Vorländer (*Ber.*, 1925, **58**, 1900), and (6) by one of us and Wilkinson (J., 1924, **125**, 857). Although the former observed *m*-nitration only, small quantities of isomerides may well have been present since his nitration products were often recrystallised or otherwise purified.

The results with (3) and (4) show that the effect of variation in the tabulated ratio in the compounds nitrated needs to be considered. Compounds such as $BiPh_2NO_3$ and $BiPh_2Me(NO_3)_2$, which would therefore appear to be more suitable than (6) for purposes of comparison (the ratios being 2 and 1), are unknown: the first, being a derivative of tervalent bismuth, would be unstable to acid. The mixed thallium compound $TlPhMeNO_3$ (ratio 1) is also unknown (cf. Challenger and Richards, this vol., p. 409).

The nitration of (2) and (3) shows that it is immaterial whether an oxide or the corresponding nitrate is employed, provided excess of acid is present.

In all cases except (8) the whole of the nitrated product (without recrystallisation or any treatment likely to lead to loss or separation of any ingredient) was treated with bromine. This eliminated the metal, giving a mixture of bromonitrobenzenes in which the relative proportions of isomerides were in most cases determined by two independent methods, (*a*) that of Dimroth (*Annalen*, 1925, **446**, 148) and (*b*) by thermal analysis, the results showing satisfactory agreement.

It is surprising, in view of the work of Ingold, Shaw, and Wilson (J., 1928, 1280) and of Baker and Moffitt (*loc. cit.*), that the value for tin should be less than for lead; the reverse relation might have been expected. The compounds nitrated by us are, however, of a different type from those employed by these authors. Preferential decomposition of *op*-derivatives during nitration of diphenyl-lead dinitrate would appear to be excluded by the high yield (93·5—95·5%) of bromonitrobenzenes obtained. The corresponding yield in the case of diphenyltin oxide is 82—84%. The decomposition of small quantities of one or other isomeride is therefore not impossible in this case.

It will be noticed that with diphenylthallium oxide occasional low yields of nitrated product (Expts. 10, 11A, 11B) were obtained, but no regularity in the effect on the proportions of the isomerides is detectable.

Diphenyliodonium nitrate was first nitrated by Vorländer (*loc. cit.*), who, by repeated crystallisation of the product, isolated pure di-*m*-nitrophenyliodonium nitrate. This gave *m*-iodonitrobenzene and *m*-nitrophenol (free from *o*-derivative) with sodium hydroxide. Any *p*- or *o*-compound produced may thus have been separated. We have repeated this work under similar conditions. The nitration product, which was stable to bromine, was decomposed by sodium hydroxide, and the composition of the resulting iodonitrobenzenes determined by thermal analysis. The nitrophenols simultaneously produced were not examined. A method whereby both the nitrated phenyl groups were obtained as halogenonitrobenzenes would have been preferable. The results show *m*-nitration 82·5%, and *p*- 17·5%. The possibility that both in our experiments and in Vorländer's some *o*-nitro-derivative may have resinified during the decomposition with alkali should be borne in mind.

The theoretical discussion of these results is reserved for a later communication, in which it is hoped to deal similarly with the consecutive elements germanium, arsenic, selenium, and tin, antimony, tellurium, iodine. It may be noted, however, that the increase in *m*-nitration in passing from the left to the centre of the periodic table, with a maximum at lead, is probably due to alteration in the nature of the central atom. We believe that this conclusion is not invalidated by the circumstance that it was obviously impossible to keep the ratio (no. of Ph groups)/(kationic charge) constant. In the case of the thallium compounds, in spite of the increase in *m*-nitration on passing from (3) to (4), the amount in the latter case is still appreciably less than that with lead.

EXPERIMENTAL.

(1) *Phenylmercury Nitrate.*—This was obtained in 80% yield by addition of hot aqueous mercuric nitrate (1 mol.) slightly acidified with nitric acid to diphenylmercury (1 mol.) in hot 95% alcohol. On recrystallisation from alcohol, the precipitated solid had m. p. 186·5°.

The nitrate (10 g.) was slowly added during 1 hour to well-stirred nitric acid (*d* 1·52; 45 c.c.) at — 19·5°. The solution darkened, giving a slight odour of nitrobenzene, and was finally poured on ice, neutralised with 10% sodium hydroxide, and stirred with bromine (2 c.c.) till elimination of mercury was complete (Process 1).

The bromonitrobenzenes were extracted with ether, washed with sodium hydroxide, and distilled. The percentage of *o*- and *p*-derivatives in this and the following experiments was determined volumetrically as hydrobromic acid after heating with hydrazine hydrate in a sealed tube at 100°, the value for the *m*-compound being obtained by difference. The toluene-bath employed by Dimroth (*loc. cit.*) is unnecessary. As a check on this method, the content of *o*-, *m*-, and *p*-bromonitrobenzenes in the mixture was determined by thermal analysis :

Expt.	Yield of bromonitrobenzenes, %.	Meta, %.	Thermal analysis.		
			Meta, %.	Ortho, %.	Para, %.
1	85·7	57·6			
3	85·7	54·4			
3a	84·8	48·7	50·5	31·9	17·6
3b	85·7	51·9	49·2	28·8	22·0
		Mean 53·1	49·8		

The yield of bromonitrobenzenes in this and the following experiments is calculated as a percentage of that theoretically obtainable from the phenyl derivative used.

(2) *Diphenylthallium Oxide.*—This was prepared by a slight modification of the method of Goddard and Goddard (J., 1922, **121**, 486), less alkali hydroxide and a shorter time of heating being used. Diphenylthallium bromide (20 g., 2 mols.), potassium hydroxide (8 g., 3 mols.) in alcohol (150 c.c.), and water (150 c.c.) were heated for 2¼ hours and poured into water (80 c.c.). The product (6·2 g., 96%) was completely soluble in hot glacial acetic acid.

The oxide (10 g.) was slowly added to a well-stirred mixture of nitric acid (*d* 1·52; 16 c.c.) and sulphuric acid (12 c.c.) kept at — 15° to — 10°. The following method (Process 2) was adopted in all subsequent experiments except Nos. 27—30. The mixture was poured on ice, the solid (A_2) separated, and the filtrate neutralised with gaseous ammonia. Evaporation to dryness and extraction with water left a solid (B_2). In the following descriptions, A indicates the solid directly precipitated, and B that obtained from the filtrate.

The combined products $A_2 + B_2$ were decomposed with hot bromine-water in an open vessel, and in Expts. 7—11 under reflux. On distillation of the bromonitrobenzenes in a vacuum, a higher-boiling fraction was obtained in several cases, which on crystallisation from alcohol had m. p. 77° alone and in admixture with authentic 3 : 5-dinitrobromobenzene (Found : C, 29·2; H, 1·4; N, 11·3; Br, 31·5. Calc. : C, 29·1; H, 1·2; N, 11·3; Br, 32·4%). This indicates the occurrence of dinitration in at least one of the phenyl nuclei. Attempts at nitration under other conditions were unsuccessful. In absence of sulphuric acid, and with anhydrous nitric acid at — 18° to — 19°, nitration was incomplete and nitrobenzene was also produced. Hardly any nitration occurred in acetic anhydride at — 18° or at 25°.

Where dinitration occurred, the bromonitrobenzene fraction was analysed completely and shown to be pure, before the percentage of *m*-isomeride was determined.

(3) *Diphenylthallium Nitrate* (cf. Goddard and Goddard, *ibid.*, p. 487).—This was precipitated in 86% yield when nitric acid (*d* 1·53; 4 g.) in glacial acetic acid (10 c.c.) was added to the oxide (19 g.) in the same solvent (190 c.c.). The nitration (Expts. 11c and 11D) was carried out as for the oxide. The bromination product yielded 1—2% of a fraction of high b. p. which was not identified.

Expt.	Yield of bromonitrobenzenes, %.	Meta, %.	C, %.	H, %.	N, %.	Br, %.*	Thermal analysis. m.	o.	p.
4	75	75·1							
5	76	73·5							
6	76	72·0	35·6	2·1	6·7	40·6			
7	80	73·9							
8	78	67·4							
9	78	73·4							
10	53	82·2	35·5	1·9	6·7	40·2			
11	79	72·1							
11A	65	—	34·8	1·9	6·8	40·2	66·0	29·8	4·2
11B	58	—	35·5	2·0	6·6	40·2	72·2	21·7	6·1
11C	82·6	—					74·8	18·2	7·0
11D	85·0	—					76·0	20·0	4·0
	Mean	73·7					72·3		

* Calc.: C, 35·6; H, 1·9; N, 6·9; Br, 39·6%.

(4) *Phenylthallium Hydroxynitrate.*—This was obtained by addition of a slight excess of silver nitrate to the dichloride in hot aqueous solution. The clear filtrate was evaporated at 100° until crystals separated. On cooling, colourless needles, decomposing violently at 268°, were obtained (Found: C, 20·8; H, 1·4; N, 3·6; NO_3, 17·4. $C_6H_6O_4NTl$ requires C, 20·0; H, 1·7; N, 3·9; NO_3, 17·2%). The nitration (Expts. 11E and 11F) was carried out as in the case of (2) and (3).

Expt.	Yield of bromonitrobenzenes %.	Thermal analysis, %. m.	o.	p.
11E	78	86·7	12·3	1·0
11F	87·7	85·8	11·9	2·3
	Mean	86·25		

(5) *Diphenyl-lead Dinitrate.*—The dihydrate of this was prepared by the method of Polis (*Ber.*, 1887, **20**, 720), and analysed according to Gilman and Robinson (*J. Amer. Chem. Soc.*, 1928, **50**, 1715) (Found: Pb, 40·0. Calc.: Pb, 39·8%).

The dinitrate (10 g.) was slowly added to a well-stirred mixture of nitric acid (*d* 1·52; 15 c.c.) and sulphuric acid (12 c.c.) at − 15° to − 10° (Vorlander used acid of *d* 1·51 in a sealed tube at 100°). The mixture was stirred for several hours and left over-night at room temperature. The product was worked up as before, fractions A_3 and B_3 being united [Found: Pb, 32·9. $(C_6H_4{\cdot}NO_2)_2Pb(NO_3)_2,2H_2O$ requires Pb, 33·9%]. It was converted into the bromonitrobenzenes by heating with bromine (6 c.c.) in water (15 c.c.).

Expt.	Yield of bromonitrobenzenes, %.	Meta, %.	Thermal analysis, %. m.	o.	p.
12	95·5	95·5			
13	93·6	93·1	96·6	3·4	—
14	93·6	92·4			
	Mean	93·7			

(6) *Triphenylbismuthine Dinitrate.*—The dinitrate was prepared by the method of Michaelis and Marquardt (*Annalen*, 1889, **251**, 330) and recrystallised from acetone (Found: Bi, 36·8. Calc.: 37·0%). 10 G. were mixed with nitric acid (*d* 1·52; 100 c.c.) cooled to 0°, left for 22 hours, and the clear solution poured on ice. The product ($A_5 + B_5$; 11·55 g.) appeared to contain some unchanged dinitrate [Found: C, 31·7; H, 1·9; N, 7·9; Bi, 30·5. $(NO_2{\cdot}C_6H_4)_3Bi(NO_3)_2$ requires C, 30·9; H, 1·7; N, 10·0; Bi, 29·9%]. 10 G. were heated with bromine (5 c.c.) in water (50 c.c.) under reflux for 2 hours.

Expt.	Yield of bromonitrobenzenes, %.	Meta, %.	Thermal analysis, %. m.	o.	p.
23	97	84·6			
24	100	84·7	84·3	15·7	—
25	96·2	88·5	87·2	11·6	1·2
26	89·7	86·3	85·9	9·7	4·4
	Mean	86·0	85·8		

(7) *Diphenyltin Oxide.*—Tetraphenyltin and stannic chloride (1 : 1 mol.) (Goddard, Ashley, and Evans, J., 1922, **121**, 978) were boiled with xylene for 3 hours, the solvent removed in a

vacuum, and the residue dissolved in light petroleum. Concentration in a vacuum and cooling in ice and salt gave a solid, m. p. 35—40°. Diphenyltin dichloride melts at 42° (Aronheim, *Annalen*, 1878, **194**, 152). The oxide was obtained in nearly theoretical yield by addition of the dichloride in alcohol to ice-cold 15% potassium hydroxide (2 mols.) (*idem, ibid.*, p. 157) (Found : Sn, 41·0. Calc. : Sn, 41·1%).

The oxide (10 g.) was slowly added to nitric acid (*d* 1·52; 25 c.c.) at − 15°, giving a dark mixture and an odour of nitrobenzene. The product ($A_4 + B_4$) was heated under reflux with bromine (5 c.c.) in water (30 c.c.) for 48 hours. The nitration mixture in Expt. 18 included sulphuric acid (20 c.c.); this addition had no effect upon the course of the nitration.

Expt.	Yield of bromonitrobenzenes, %.	Meta, %.	Thermal analysis, %.		
			m.	*o.*	*p.*
15	82	80·8			
16	84	75·3	79·7	13·2	7·1
17	82	78·9	78·8	15·5	5·7
18	82	80·5	79·8	11·1	9·1
		Mean 78·9	79·4		

(8) *Diphenyliodonium Nitrate.*—10 G. were added to a mixture of nitric acid (*d* 1·52; 30 c.c.) and sulphuric acid (25 c.c.) at room temperature. [Vorländer (*loc. cit.*, 1899) used 10 g., 30 c.c., and 22 c.c. respectively at 15—20°.] The product was poured on ice, and the separated solid united with that obtained on addition of potassium bromide to the filtrate, and distilled in steam with 10% sodium hydroxide (50 c.c.). The iodonitrobenzenes were extracted with ether, washed with alkali, and fractionated from nitrobenzene derived from un-nitrated material. The yields were calculated from the equation $(NO_2{\cdot}C_6H_4)_2I{\cdot}NO_3 + 2KOH = NO_2{\cdot}C_6H_4I + NO_2{\cdot}C_6H_4{\cdot}OK + KNO_3 + H_2O$. In Expt. 30 the nitro-product was decomposed with 10% sodium hydroxide under reflux at 100°, cooled, and extracted with ether. The mixed iodonitrobenzenes, recrystallised from alcohol and then from glacial acetic acid, gave the pure *p*-compound, m. p. 173°. Evaporation of the alcohol and recrystallisation from the diluted solvent yielded pure *m*-iodonitrobenzene, m. p. 35·3°.

The mixture of isomerides could not be analysed by Dimroth's method as inconsistent results were obtained. Thermal analysis was therefore employed.

Expt.	27	28	29	30
Yield of iodonitrobenzenes, %	27	50	62	70
M. p.	92°	85°	89°	77°
Meta, %	79·8	83·0	81·0	86·0; mean 82·5

The absence of the *o*-compound in Expts. 27 and 28, and therefore presumably in Nos. 29 and 30, was shown by separating about 10% of the *p*-isomeride by repeated crystallisation from alcohol. The mother-liquor was evaporated, the residue distilled in a vacuum, a known amount of *o*-iodonitrobenzene added, and the m. p. again determined.

Determination of o-, m-, *and* p-*Isomerides in Iodonitrobenzenes.*—There appear to be no published data on the m. p.'s of such mixtures, and the following determinations were made :

o- *and* m-*Mixtures.*						p- *and* m-*Mixtures.*			
m, %.	M. p.	*m*, %.	M. p.	*m*, %.	M. p.	*m*, %.	M. p.	*m*, %.	M. p.
0	50·5°	41·2	27·3°	66·0	17·2°	0	173·0°	92·0	60·0°
15·6	42·4	47·1	24·5	72·9	21·8	26·2	158·0	94·9	41·0
25·3	37·1	48·9	24·0	77·2	23·3	46·2	139·5	96·4	35·4
30·9	34·5	52·9	18·3	80·0	25·0	63·6	122·5	97·3	33·6
37·2	31·2	57·6	15·0	88·6	29·0	69·3	110·0	100·0	35·3
38·0	29·4	64·2	16·2	92·8	32·0	84·9	83·5		
				100·0	35·3				

Determination of o-, m-, *and* p-*Isomerides in Bromonitrobenzenes.*—The m. p.'s of mixtures of bromonitrobenzenes as recorded by Jürgens (*Rec. trav. chim.*, 1926, **45**, 61) were not suitable for our determinations, as his samples of the isomerides had somewhat lower m. p.'s than ours. They were therefore re-determined.

o- *and* m-*Mixtures.*

m, %.	M. p.	*m*, %.	M. p.	*m*, %.	M. p.	*m*, %.	M. p.	*m*, %.	M. p.
0	40·90°	17·5	32·20°	32·6	23·60°	71·8	40·43°	86·8	47·58°
7·9	36·80	23·3	29·54	36·8	21·60	73·9	42·18	90·5	50·18
12·9	34·76	24·3	29·96	42·4	22·80	78·7	44·58	93·2	50·59
15·4	33·59	31·4	25·42	54·3	31·00	80·0	45·01	96·0	51·79
16·9	32·98	31·6	25·20	56·6	32·50	84·5	46·40	100·0	53·80

m- *and* p-*Mixtures.*

p, %.	M. p.	*p*, %.	M. p.	*p*, %.	M. p.	*p*, %.	M. p.	*p*, %.	M. p.
0	53·8°	7·76	50·40°	25·77	59·0°	36·30	76·2°	75·70	109·0°
5·17	51·0	16·58	46·60	35·90	77·3	61·50	100·1	82·50	114·4
								100·0	125·1

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