CCCLI.—*The Nitration of Benzyl Derivatives of Certain Phosphorus, Arsenic, and Antimony Compounds.*

By Frederick Challenger and Arnold Thornton Peters.

This communication contains an account of work on the orienting influence of positive poles and similar groups containing phosphorus, arsenic, or antimony, the term " pole " being used to indicate the seat of the charge in a complex ion. Vorländer concluded (*Ber.*, 1919, **52**, 283) that a positive pole directly attached to the benzene nucleus causes *m*-orientation irrespective of the nature of the charged atom. His fundamental experiments consisted in the bromination of phenyltrimethylammonium bromide and the nitration of the corresponding nitrate, *m*-substitution being exclusively observed. Vorländer's conclusions were amply confirmed by his later work and by that of other investigators (*Ber.*, 1925, **58**, 1900). Ing and Robinson (J., 1926, 1655) showed that predominant *m*-substitution occurred when benzyltrimethylammonium nitrate was nitrated with nitric acid (*d* 1·5) at about 0°, although the positively charged atom is not directly attached to the nucleus (compare Allan, Oxford, Robinson, and Smith, J., 1926, 410). When a positive pole is separated from the benzene nucleus by more than one neutral atom, as in β-phenylethylamine and γ-phenylpropylamine, the *m*-directive effect is very strongly diminished (Goss, Hanhart, and Ingold, J., 1927, 250. Compare also Ing and Robinson, *loc. cit.*). Pollard and Robinson (J., 1927, 2770) observed a progressive fall in the amount of *m*-derivative produced in the nitration of benzylpiperidine, *l*-β-phenylethylpiperidine, and *l*-γ-phenylpropylpiperidine.

Since the positive electricity resides at the nucleus of the charged atom, Ingold, Ingold, and Shaw suggested (J., 1927, 815) that a similar damping action might be expected to arise during the passage of the effect through the successive shells of electrons belonging to the charged atom itself and that phenyl- and benzylphosphonium ions should exhibit a weaker *m*-directive action than the analogous phenyl- and benzyl-ammonium ions. Similarly, aromatic arsonium salts should show weaker *m*-reactivity than the corresponding phosphorus compounds, and phenyl and benzyl sulphoxides should on nitration yield less *m*-derivative than the corresponding aromatic nitro-compounds.

Chatterjee and Robinson (J., 1927, 2782), on the other hand, attribute the smaller *m*-nitration (28%) observed with *m*-nitrophenylbenzylsulphone and with benzylmethylsulphone (30%; Ingold, Ingold, and Shaw, *loc. cit.*) to the smaller degree of polarisation of the oxygen in the two semipolar double bonds of the sulphones as compared with that obtaining in phenylnitromethane. Pollard and Robinson (J., 1927, 2773) state "under comparable conditions we may anticipate diminishing *m*-substitution in ascending a group in the periodic system, *e.g.*, $CH_2Ph{\cdot}NR_3 > CH_2Ph{\cdot}PR_3 > CH_2Ph{\cdot}AsR_3 > CH_2Ph{\cdot}BiR_3$ and $CH_2Ph{\cdot}SR_2 > CH_2Ph{\cdot}SeR_2$."

A recent study by Ingold, Shaw, and Wilson (J., 1928, 1280) of the nitration of phenyltrimethyl-phosphonium, -arsonium and -stibonium picrates and of benzyltrimethyl-phosphonium and -arsonium picrates has furnished results in agreement with some of these predictions. A decrease in the proportion of *m*-substitution in the direction of increasing atomic number is observed.

	$R\overset{+}{N}Me_3$.	$R\overset{+}{P}Me_3$.	$R\overset{+}{As}Me_3$.	$R\overset{+}{Sb}Me_3$.
Phenyl	100	100	98·2	86·3
Benzyl	88	10	3·4	—

Apart from these results, some information already exists regarding the orienting influence of groups containing phosphorus, arsenic, or antimony.

Triphenylphosphine and nitric acid (*d* 1·5) yielded the oxide, which, with nitric acid (*d* 1·5) and sulphuric acid, gave trinitrotriphenylphosphine oxide (Michaelis and Soden, *Annalen*, 1885, **229**, 323). This was assumed to be a *p*-derivative, but Challenger and Wilkinson (J., 1924, **125**, 2675) showed that the tri-*m*-nitro-compound was exclusively formed. Nitration of phenylphosphinic acid, $Ph{\cdot}PO(OH)_2$, yields a *m*-nitro-derivative, as does also phenylarsinic acid (Bertheim and Benda, *Ber.*, 1911, **44**, 3297).

Triphenylstibine and nitric acid (*d* 1·5) in glacial acetic acid give triphenylstibine hydroxynitrate, which, on nitration, finally yields tri-*m*-nitrotriphenylstibine dihydroxide (Morgan and Micklethwait, J., 1911, **99**, 2290), which gives *m*-bromonitrobenzene with bromine. Triphenylbismuthine dinitrate gives with nitric acid (*d* 1·5) a *m*-nitro-derivative as determined by two independent methods (Wilkinson and Challenger, J., 1924, **125**, 857; Vorländer and Schroedter, *Ber.*, 1925, **58**, 1900).

Very few nitration experiments on the benzyl derivatives of compounds of the elements of Group V have been recorded. Tribenzylphosphine oxide, $(CH_2Ph)_3PO$, gave a product which was not completely purified but consisted largely of tri-*p*-nitrotribenzylphosphine oxide, since it gave *p*-nitrobenzoic acid on oxidation (Collie, J., 1889, **55**, 223). Dibenzylphosphinic acid gives a dinitro-derivative (Litthauer, *Ber.*, 1889, **22**, 2145) in which the position of the nitro-groups was not determined.

This communication contains an account of the nitration of dibenzylphosphinic and dibenzylarsinic acids, of tribenzylphosphine oxide and tribenzylarsine oxide, and of tribenzylstibine dihydroxide.* Benzyl derivatives of bismuth have not yet been obtained. One of us and Ridgway (J., 1922, **121**, 105, 112) have shown that bismuth chloride and magnesium benzyl chloride yield benzaldehyde and bismuth oxide in presence of air. This oxidation of the benzyl

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* Shortly after the commencement of this research Professor Ingold informed us of his proposed experiments (see p. 2611) and it was decided to confine our studies to compounds of a somewhat different type. See footnote, J., 1928, 1280.

group, so marked in the case of bismuth, can still be detected in the antimony and arsenic compounds, since tribenzylstibine dihydroxide gradually acquires an odour of benzaldehyde, and tribenzylarsine becomes hot and fumes in air, giving benzaldehyde and dibenzylarsinic acid. The corresponding phenyl derivatives are stable.

Magnesium benzyl chloride and arsenic trichloride or tribromide in an atmosphere of nitrogen give a good yield of tribenzylarsine, with smaller amounts of tribenzylarsine oxide and dibenzylarsinic acid, $(CH_2Ph)_2AsO{\cdot}OH$. These compounds had previously been obtained by the use of sodium and benzyl chloride (Michaelis and Paetow, *Annalen*, 1886, **233**, 60). The product $(CH_2Ph)_2As{\cdot}OH,H_2O$, m. p. 215°, described by Sachs and Kantorowicz (*Ber.*, 1908, **41**, 2769) is probably identical with dibenzylarsinic acid, m. p. 211—212°. In one experiment, tetrabenzylarsonium bromide was obtained, and identified by the melting point of its mixtures with the products obtained from potassium bromide and tetrabenzylarsonium chloride and nitrate. Dodonov and Medox (*Ber.*, 1928, **61**, 907) have obtained tetraphenylphosphonium bromide from magnesium phenyl bromide and triphenylphosphine in a current of oxygen, and suggest a mechanism for the reaction.

Morgan and Micklethwait (P., 1912, **28**, 69) obtained tribenzylstibine dichloride from magnesium benzyl chloride and antimony trichloride. Hydrolysis yields tribenzylstibine dihydroxide, but no further details are given. These compounds have now been prepared and analysed.

In our nitration experiments tribenzylphosphine oxide and nitric acid (*d* 1·5) at 0° gave tri-*p*-nitrotribenzylphosphine oxide, which was isolated in a pure condition (compare Collie, *loc. cit.*). Oxidation of the crude nitration product with potassium permanganate yielded almost exclusively *p*-nitrobenzoic acid. A trace of *o*-nitrobenzoic acid was detected, but no *m*-compound. Dibenzylphosphinic acid similarly yields *di*-p-*nitrodibenzylphosphinic acid*, the pure compound giving *p*-nitrobenzoic acid on oxidation as before. Oxidation of the crude nitration product gave *p*-nitrobenzoic acid only.

Similar results were obtained with the corresponding arsenic compounds, the nitration products consisting almost wholly of *tri*-p-*nitrotribenzylarsine oxide* (accompanied by some *tri*-p-*nitrotribenzylarsine hydroxynitrate*) in the one case, and of di-*p*-nitrodibenzylarsinic acid in the other. Pure compounds were isolated in each case, and oxidation of the crude nitration products invariably yielded *p*-nitrobenzoic acid, accompanied in some instances by very small amounts of *o*-nitrobenzoic acid. No *m*-nitrobenzoic acid could be detected.

Nitration of tribenzylstibine dihydroxide yielded a product which was rather unstable and was not completely purified. On oxidation, *p*-nitrobenzoic acid and a trace of the *o*-nitro-acid were produced.

The results described in this communication are to some extent analogous to those of Ingold, Shaw, and Wilson on the nitration of compounds of the type $[Me_3M{\cdot}CH_2Ph]X$ inasmuch as they indicate the predominance of *p*-substitution. Whereas, however, these authors observed small quantities of *m*-nitro-derivatives, we have been unable to detect any evidence of *m*-nitration in the case of the compounds of admittedly somewhat different type which are here described.

EXPERIMENTAL.

Nitration of Tribenzylphosphine Oxide.—The oxide (A, 4·6 g.; B, 6·0 g.; C, 6·0 g.) was dissolved in nitric acid (*d* 1·5. A, 15 c.c.; B, C, 25 c.c.) at 0°. The clear yellow solution was left at room temperature for 3 hours and very slowly added to ice-cold water with vigorous stirring; this was necessary in order to obtain a solid product, m. p. 90—130°. Owing to a tendency to occlude nitric acid the solid was shaken with water (500 c.c.) for 17 hours, collected, and dried to constant weight (A, 6·0 g.; B, 8·05 g.; C, 8·0 g.). Calculated for trinitrotribenzylphosphine oxide : A, 92%; B, 95%; C, 94% yield.

The filtrate gave a negligible residue on extraction with ether and chloroform. The crude product now melted from 190—200° and was insoluble in aqueous sodium carbonate or hydroxide. It exploded slightly on heating.

It showed little tendency to crystallise; successive precipitations by water from a glacial acetic acid solution produced no apparent change (compare Collie, *loc. cit.*).

The final method of purification was extraction with boiling alcohol (see later) and crystallisation of the remaining solid (70% of the crude nitration product) repeatedly from dilute acetic acid. Almost colourless needles, m. p. 273°, of tri-*p*-nitrotribenzylphosphine oxide were finally obtained (Found : C, 55·25; H, 3·95; N, 9·15. Calc. for $C_{21}H_{18}O_7N_3P$: C, 55·4; H, 3·95; N, 9·3%).

The pure product, m. p. 273°, is slightly soluble in chloroform, acetone, benzene, ethyl and methyl alcohol, and insoluble in light petroleum. It was pyrophoric and on oxidation with 2% alkaline permanganate gave *p*-nitrobenzoic acid (yield, 80%).

The alcoholic extracts (see above) on concentration gave an oil which was very soluble in chloroform, acetone, benzene, and methyl alcohol and slightly soluble in light petroleum. It was insoluble in aqueous sodium carbonate and hydroxide and did not completely solidify when kept at 0° for 4 days. Subsequent treatment with acetone and light petroleum yielded a pale yellow mass, melting at about 100°. This with dilute methyl alcohol gave a white solid, m. p. 158°, which when oxidised with 2% alkaline potassium permanganate yielded only *p*-nitrobenzoic acid. The substance, m. p. 158°, was therefore not further examined, being very difficult to purify.

*Attempted Synthesis of Tri-*p*-nitrotribenzylphosphine Oxide.*—*p*-Nitrobenzyl bromide (3 mols.; 15 g.) and phosphorus oxychloride (1 mol.; 3·7 g.) were warmed with "molecular" sodium (7 atoms) in dry benzene (200 c.c.). After 3 days, unchanged *p*-nitrobenzyl bromide was recovered. A similar experiment using dry ether was also unsuccessful.

Oxidation of Crude Nitrated Tribenzylphosphine Oxide.—The solid (5·6 g.) was boiled for 2 hours with 5% potassium permanganate (200 c.c.) and 12% aqueous potassium hydroxide (8 c.c.), the excess of permanganate removed by alcohol, and the liquid filtered. On evaporation and acidification an almost white solid separated, m. p. 235° (mixed with pure *p*-nitrobenzoic acid, m. p. 238°. A, 4·25 g.). Ether-extraction of the acid filtrate gave a further amount of *p*-nitrobenzoic acid (B, 0·12 g.; m. p. 230°). Extraction of the manganese dioxide gave 0·13 g., m. p. 233° (total weight of *p*-nitrobenzoic acid, 4·5 g.).

Similar and concordant results were obtained when 2% alkaline permanganate was used: Crude nitration product, A, 3·0 g.; B, 4·0 g.; 2% alkaline permanganate, A, 350 c.c.; B, 570 c.c. Total yield of nitrobenzoic acid, A, 2·5 g.; B, 3·3 g., or a 76% yield, the crude nitration product being assumed to be trinitrotribenzylphosphine oxide. In the last two experiments the fraction B was viscid. It was treated with aqueous barium hydroxide, and the mixture evaporated until some barium salt separated. This was acidified with dilute hydrochloric acid and extracted with ether, giving a solid, m. p. 110°. The filtrate, containing the more soluble barium salt, was acidified and extracted with ether to give a solid, m. p. 120°, which was crystallised from hot water, yielding white crystals, m. p. 137—138° (mixed with pure *o*-nitrobenzoic acid of m. p. 144°, these had m. p. 143°). The amount of *o*-nitro-acid approximated to 3% of the crude oxidation products.

In each case, 95% of the crude acids could be isolated as *p*-nitrobenzoic acid; the *m*-nitro-acid could not be detected in a chloroform extract of the crude acids. Tests on a mixture of nitrobenzoic acids (2·85 g.; 95% *p*-nitro-acid : 0·15 g.; 5% *m*-nitro-acid) showed that the *m*-acid could be detected in this manner.

The solubility in chloroform (100 g.) at 20° is 1·09, 4·07, and 0·10 for *o*-, *m*-, and *p*-nitrobenzoic acid, respectively.

Oxidation of Tribenzylphosphine Oxide.—The oxide (A, 1·1 g.;

B, 3·0 g.) was boiled with 2% alkaline permanganate (A, 180 c.c.; B, 550 c.c.) for 4 hours, giving unchanged oxide (A, 0·5 g.; B, 1·7 g.) and benzoic acid (A, 0·6 g.; B, 1·06 g.), corresponding to a 73% yield.

The unnitrated oxide is clearly much more resistant to permanganate than its nitro-derivative (compare dibenzylphosphinic acid, below).

Nitration of Dibenzylphosphinic Acid.—The acid (4·0 g.) was dissolved in nitric acid (*d* 1·5; 15 c.c.) at −5° and after 2 hours at room temperature the mixture was poured on well-stirred ice. The solid was shaken with water (300 c.c.) for 15 hours and dried (5·1 g.). The spent acid deposited 0·15 g. of solid on standing overnight; this crystallised in white needles, m. p. 226°. Concentration of the spent acid and of the aqueous washings and extraction with ether and chloroform gave no further solid. Total weight of crude nitration product, m. p. 170°, 5·25 g. Calculated for dinitrodibenzylphosphinic acid, 5·5 g.; yield 96%.

It was wholly soluble in aqueous sodium hydroxide and was reprecipitated by acid. Crystallisation from dilute acetic acid yielded almost colourless needles, m. p. 225—226°, of *di*-p-*nitrodibenzylphosphinic acid* (Found: C, 49·9; H, 4·3; N, 8·3. $C_{14}H_{13}O_6N_2P$ requires C, 50·0; H, 3·9; N, 8·3%) (compare Litthauer, *Ber.*, 1889, **22**, 2145). Oxidation of the pure product with 2% alkaline permanganate gave *p*-nitrobenzoic acid (yield, 83%).

Oxidation of the Crude Nitrated Dibenzylphosphinic Acid.—The crude nitration product, washed and dried (3·6 g.), was boiled for 3 hours with 2% alkaline permanganate (400 c.c.). The mixture, when treated as in the oxidation of trinitrotribenzylphosphine oxide (p. 2615), gave *p*-nitrobenzoic acid (2·9 g.), m. p. and mixed m. p. 238° (Calc. for dinitrodibenzylphosphinic acid, 3·6 g. Yield, 81%).

A similar experiment gave an 82% yield.

These observations are confirmed by the fact that an almost quantitative yield of pure *p*-nitrobenzoic acid was formed on heating dibenzylphosphinic acid in a sealed tube with nitric acid (*d* 1·5).

Dibenzylphosphinic acid is very easily oxidised; 2·1 g. were boiled for 2 hours with 2% alkaline permanganate (270 c.c.), yielding finally 1·7 g. of benzoic acid (81% of the theoretical yield).

Benzoic acid could in no case be detected among the oxidation products of the nitrated phosphine oxide and phosphinic acid, showing that a benzene nucleus had not been split off during nitration.

In a mixture of benzoic acid (0·02 g.) and *p*-nitrobenzoic acid (0·98 g.) benzoic acid was easily detected by its odour on sublimation.

Preparation of Tribenzylarsine.—Arsenic trichloride (1 mol.; 91 g.) in dry ether was slowly added in an atmosphere of nitrogen to a

Grignard solution prepared from benzyl chloride (3·3 mols.; 209 g.) and magnesium (3·4 mols.; 41 g.). The mixture was finally warmed on the steam-bath for 1 hour and left over-night. The ether was then removed, water added, and the separated solid extracted with boiling alcohol. Successive crops, m. p. 104°, consisted almost wholly of tribenzylarsine, which was immediately placed out of contact with air. The final alcoholic mother-liquor was distilled in steam to remove dibenzyl and the residue was extracted with 20% aqueous sodium hydroxide. Addition of acetic acid gave dibenzylarsinic acid, which formed white needles, m. p. 211°, from alcohol (Michaelis and Paetow, *loc. cit.*).

The residue insoluble in alkali, when crystallised from aqueous alcohol, gave tribenzylarsine oxide, m. p. 220° (Michaelis and Paetow, *loc. cit.*).

In a similar experiment with arsenic tribromide, the alcoholic mother-liquor yielded a solid which, after separation from dibenzylarsinic acid, crystallised from aqueous alcohol in white needles, m. p. 175—177°. The product decomposed on heating, giving benzyl bromide, and was tetrabenzylarsonium bromide, which is stated to melt at 173°. It did not depress the m. p.'s (175° and 175—177°) of the products obtained by the action of aqueous potassium bromide on tetrabenzylarsonium chloride and nitrate in aqueous alcohol and in water respectively.

It reacted readily with silver nitrate to give silver bromide. Aqueous sodium picrate was added to an aqueous-alcoholic solution of the compound, yellow needles, m. p. 173°, being obtained which contained no halogen and were probably the *picrate* of the above product (Found: C, 61·2; H, 4·1. $C_{34}H_{30}O_7N_3As$ requires C, 61·2; H, 4·5%). The formation of dibenzylarsinic acid and tribenzylarsine oxide is due to the oxidation of the tertiary arsine. This was clearly demonstrated when pure tribenzylarsine, m. p. 106°, was boiled with alcohol, and the solution fractionated. Crops 1 and 2 consisted of tribenzylarsine, and crop 3 melted at 207°. Treatment with aqueous sodium hydroxide and addition of acetic acid gave dibenzylarsinic acid, m. p. 211°.

The residue insoluble in alkali was tribenzylarsine oxide, m. p. 220—222° on crystallisation from aqueous alcohol. The final mother-liquor contained benzaldehyde. The dry arsine decomposes when exposed to air, giving white fumes and a strong odour of benzaldehyde and leaving dibenzylarsinic acid (compare Michaelis and Paetow, *Annalen*, 1886, **233**, 62).

Interaction of Tribenzylarsine and Bromine.—The arsine (3·5 g.) was mixed with bromine (1·6 g.) in dry chloroform (16 c.c.) at 0°, kept in ice for ½ hour, and added to excess of light petroleum

(150 c.c.). The white crystalline precipitate was immediately collected, dried, and analysed by silver nitrate–thiocyanate titration in aqueous alcoholic solution [Found : Br, 26·7. Calc. for $(C_7H_7)_3AsBr_2$: Br, 31·5%]. The product, m. p. 110—115°, was therefore the crude dibromide, which is very sensitive to moisture and has never been prepared in a pure condition. It was converted into tribenzylarsine hydroxybromide, m. p. 165°, by addition of water (compare Michaelis and Paetow, *loc. cit.*). This was shaken with aqueous sodium hydroxide, giving white needles of tribenzylarsine oxide, m. p. 220°.

Nitration of Dibenzylarsinic Acid.—The acid, m. p. 211° (A, 4·0 g.; B, 2·9 g.) was dissolved in nitric acid (*d* 1·5 : A, 13 c.c.; B, 10 c.c.) at $-5°$. The clear yellow liquid was left at room temperature for 3 hours and then added to well-stirred ice-water. The resulting viscid solid was separated, shaken for 3 hours with water (300 c.c.), collected, washed, and dried to constant weight (m. p. 120—130°. A, 4·85 g.; B, 3·6 g.). Calculated for dinitrodibenzylarsinic acid, A, 5·2 g.; 93% : B, 3·8 g.; 95% of the theoretical yield. It was completely soluble in aqueous sodium hydroxide.

The aqueous filtrate (see above) was extracted with chloroform, but the extract left no residue. The spent acid from the nitration contained no organic matter.

The crude nitration product was extracted with alcohol (A, 25 c.c.; B, 20 c.c.), fractionation of the extract yielding white needles, m. p. 211°, and a small amount of oil which on oxidation with 2% alkaline permanganate gave only *p*-nitrobenzoic acid.

About 80% of the crude nitration product was insoluble in the alcohol and was crystallised six times from dilute acetic acid, giving almost colourless needles of *di*-p-*nitrodibenzylarsinic acid*, m. p. 210—211°, identical with the product obtained from the alcoholic extract (Found : C, 44·3; H, 3·4; N, 7·45. $C_{14}H_{13}O_6N_2As$ requires C, 44·2; H, 3·45; N, 7·4%).

Oxidation of the pure product, m. p. 211°, with 2% alkaline permanganate gave *p*-nitrobenzoic acid in 80—83% yield. Di-*p*-nitrodibenzylarsinic acid is soluble in chloroform and glacial acetic acid, slightly soluble in methyl and ethyl alcohol, and is reprecipitated from an alkaline solution by acidification with acetic acid. It explodes slightly when heated to 300°.

Oxidation of the Crude Nitration Product of Dibenzylarsinic Acid.—The crude nitration product, washed and dried (3·9 g.), was boiled with 2% potassium permanganate (450 c.c.) and 12% aqueous sodium hydroxide (15 c.c.) for 2 hours, and the excess of permanganate removed by alcohol. The filtrate was then combined with the washings of the manganese dioxide and evaporated to a small bulk. Acidification with dilute hydrochloric acid gave *p*-nitrobenzoic acid (2·7 g., m. p. and mixed m. p. 238°). An ethereal extract of the acid filtrate gave a small amount of a nitrobenzoic acid (0·15 g., m. p. 125—130°); when mixed with pure *m*-nitrobenzoic acid (m. p. 141°), it melted at 110°; mixed with pure *o*-nitrobenzoic acid (m. p. 144°), it melted at 138—140°. The total weight of nitrobenzoic acids obtained was 2·85 g. [Calc. for the oxidation of $(NO_2{\cdot}C_6H_4{\cdot}CH_2)_2AsO{\cdot}OH$: 3·45 g. Yield, 83%]. A chloroform extract of the crude acids yielded no indication of the presence of any *m*-nitrobenzoic acid, which is very soluble in this reagent.

Nitration of Tribenzylarsine Oxide.—The oxide (A, 1·5 g.; B, 4·8 g.) was dissolved in nitric acid (*d* 1·5 : A, 5 c.c.; B, 16 c.c.) at − 5°. After 2 hours, addition of ice precipitated an almost white solid, which was repeatedly washed with water and dried; m. p. 170° (decomp.) (A, 2·0 g.; B, 6·4 g.). Calculated for $(NO_2{\cdot}C_6H_4{\cdot}CH_2)_3AsO$: A, 98%, and B, 97% of the theoretical yield. Calculated for $(NO_2{\cdot}C_6H_4{\cdot}CH_2)_3As(OH)(NO_3)$: A, 91%, and B, 90%.

The crude nitration product was fractionally crystallised from glacial acetic acid. Two pure products were isolated, (1) almost white needles, m. p. 230°, and (2) similar needles, melting very sharply at 189° and evolving gas. This behaviour is unlike that of the nitrated arsine oxide and analysis showed the product of m. p. 189° to be *tri*-p-*nitrotribenzylarsine hydroxynitrate* (Found : C, 44·9; H, 3·4; N, 10·3. $C_{21}H_{19}O_{10}N_4As$ requires C, 44·8; H, 3·4; N, 10·0%).

Product (1) was present in larger amounts than (2) and was more soluble in glacial acetic acid. It was *tri*-p-*nitrotribenzylarsine oxide* (Found : C, 50·7; H, 3·6; N, 8·4. $C_{21}H_{18}O_7N_3As$ requires C, 50·4; H, 3·6; N, 8·4%). Both products of nitration gave *p*-nitrobenzoic acid on oxidation with 2% alkaline permanganate.

Oxidation of the Crude Nitration Product of Tribenzylarsine Oxide.—The oxide (4·0 g.) was boiled for 3 hours with 2% alkaline potassium permanganate (450 c.c.), giving almost exclusively *p*-nitrobenzoic acid. Extraction with chloroform and fractional crystallisation failed to detect *m*-nitrobenzoic acid. A trace of *o*-nitrobenzoic acid was obtained. Total weight of nitrobenzoic acids, 3·1 g. [Calc. for $(NO_2{\cdot}C_6H_4{\cdot}CH_2)_3AsO$: 4·0 g. Yield, 77%].

Interaction of Magnesium Benzyl Chloride and Antimony Trichloride.—Antimony trichloride (1 mol.; 147 g.) in dry ether was added to a solution prepared from benzyl chloride (3·3 mols.; 264 g.) and magnesium (3·5 atoms; 53 g.). The mixture was warmed on the steam-bath, the ether removed, water added, and the resulting viscous mass separated and extracted with 12% aqueous sodium hydroxide (600 c.c.). The alkaline solution gave a negligible precipitate on acidification. The solid insoluble in alkali was shaken with ether (500 c.c.) or distilled with steam to remove dibenzyl, and the residue dissolved in boiling alcohol. Dilution with water gave white glistening plates, m. p. 120°, which on repeated crystallisation from aqueous alcohol yielded a product which melted at 161°, then solidified, and remained unchanged to 250°. It contained no halogen and on heating or leaving in air for a few days gave benzaldehyde and dibenzyl. Benzaldehyde was identified as its 2 : 4-dinitrophenylhydrazone, m. p. 227°, mixed m. p. 231°.

The white crystals, m. p. 161°, were *tribenzylstibine dihydroxide* [Found: C, 58·8; H, 5·3. $(C_7H_7)_3Sb(OH)_2$ requires C, 58·7; H, 5·3%].

The product was slightly alkaline to litmus and was readily oxidised by 2% alkaline permanganate, yielding benzoic acid. Benzyl chloride was formed on warming with dilute hydrochloric acid. Tribenzylstibine dihydroxide in chloroform was warmed with concentrated hydrochloric acid, giving white needles, m. p. 108°, which readily evolved benzyl chloride on heating and consisted of *tribenzylstibine dichloride* (Found: C, 54·1; H, 4·8; Cl, 14·9. $C_{21}H_{21}Cl_2Sb$ requires C, 54·2; H, 4·5; Cl, 15·0%).

Nitration of Tribenzylstibine Dihydroxide.—The dihydroxide, m. p. 161° (2·3 g.) was dissolved in nitric acid (*d* 1·5; 10 c.c.) at $-5°$ to 0°. The clear solution was left at room temperature for 2 hours and added to ice-water; a yellow solid (2·7 g.) then separated, which was washed and dried. The spent acid yielded nothing on extraction with chloroform. The yellow solid was probably trinitrotribenzylstibine hydroxynitrate and melted at 115° with much frothing (compare Goddard and Yarsley, J., 1928, 722) [Found: N, 9·3, 9·3. Calc. for $(NO_2{\cdot}C_7H_6)_3Sb(OH)(NO_3)$: N, 9·2%].

The product was difficult to purify and was decomposed by boiling water, giving the odour of a nitrotoluene.

Oxidation of the above Crude Nitration Product.—The crude solid (1·8 g.) was boiled for 4 hours with 4% alkaline potassium permanganate (250 c.c.). Treatment as in previous cases yielded a white crystalline precipitate of *p*-nitrobenzoic acid, m. p. 237° (mixed with pure *p*-nitrobenzoic acid, m. p. 239°). The acid filtrate on extraction with ether gave a few white needles, m. p. 130° [mixed with pure *m*-nitrobenzoic acid (m. p. 140°), these melted at 110—115°; and in admixture with *o*-nitrobenzoic acid (m. p. 144°), at 142—143°. Equal amounts of pure *m*- and *o*-acids when mixed melted at 114°]. The product was therefore *o*-nitrobenzoic acid.

A chloroform extract of the crude acids yielded no trace of *m*-nitrobenzoic acid. The total weight of crude nitrobenzoic acids obtained was 0·95 g. (yield, 70% approx.).

Decomposition of p-*Nitrobenzyl Derivatives of Compounds of Quinquevalent Phosphorus, Arsenic, and Antimony.*—The nitration product of tribenzylstibine dihydroxide gives a yellow colour with cold alkali and a very strong odour of nitrotoluene is developed on slight warming. Tri-*p*-nitrotribenzylphosphine oxide is much more stable : no colour was developed with cold alkali and boiling was necessary before the odour of nitrotoluene was apparent. The stability of the corresponding arsine derivative is intermediate between those of the phosphorus and antimony compounds. Di-*p*-nitrodibenzyl-phosphinic and -arsinic acids were similarly decomposed, the arsenic derivative the more readily. The order of stability of the corresponding nitrobenzyl derivatives could thus be represented : $P > As > Sb$.

Ing and Robinson (J., 1926, 1668) observed a similar decomposition when *p*-nitrobenzyltrimethylammonium nitrate was boiled with 20% aqueous sodium hydroxide, an orange liquid and the odour of *p*-nitrotoluene being produced (see also Pollard and Robinson, J., 1927, 2779).

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