CLXVIII.—*The Nature of the Alternating Effect in Carbon Chains. Part XXVII. The Nitration of some Aromatic Phosphonium, Arsonium, and Stibonium Salts.*

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This paper records the results which have been obtained in the course of studies on the nitration of phenyltrimethyl-phosphonium, -arsonium, and -stibonium picrates and of benzyltrimethyl-phosphonium and -arsonium picrates. The proportions of meta-derivative are shown in the following table, in which the corresponding data for ammonium salts (Vorländer and Siebert, *Ber.*, 1919, **52**, 283; Goss, Hanhart, and Ingold, J., 1927, 250) are included for comparison.* It will be observed that there is a general decrease in the proportion of *m*-substitution in the direction of an increasing atomic number :

Cation.	$R\cdot\overset{+}{N}Me_3$.	$R\cdot\overset{+}{P}Me_3$.	$R\cdot\overset{+}{As}Me_3$.	$R\cdot\overset{+}{Sb}Me_3$.	
R = Phenyl	100·0	100·0	98·2	86·3	% *m*-substitution
R = Benzyl	88·0	10·1	3·4	—	,,

Ingold, Ingold, and Shaw (J., 1927, 813) discussed the influence of atomic number on the *m*-orienting effect of positive poles and suggested that, since the positive field emanates from the atomic nucleus, the envelopment of the latter by additional electron-

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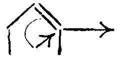
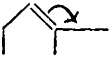
* Contemporaneously with these experiments, others on similar lines have been carried out by Dr. F. Challenger at Manchester, whose studies include the nitration of tribenzyl-phosphine and -arsine oxides and, together with those here described, constitute the first definite comparisons along the lines indicated.

shells in the larger atoms will diminish the field beyond the surface of the atom, and hence diminish *m*-orientation. The *m*-orienting sequence for compounds such as the above was predicted on this basis, and the results, which (excepting those for the ammonium compounds) were unknown at the time, justify the forecast. Pollard and Robinson subsequently suggested (J., 1927, 2772), as the determining circumstance, the principle that the greater the volume of the central charged atom, the greater should be the electrostriction of the organic cations by the anions in a nitration solution. This, however, does not appeal as an adequate cause, in view of Fajans' demonstration (*Naturwiss.*, 1923, **11**, 105) that the smaller a cation the more extensive *ceteris paribus* is the process of co-ordination, and its precursor, electrostriction, with a given anion. Whether we consider the direct influence of atomic size on the field, or the degree of electrostriction by anions, as the essential cause, a comparison of different cases requires the assumption of the approximate equivalence of centrally-acting charges. On various kinds of physical evidence relating to electrovalent compounds, departures from *strict* equivalence are to be expected, but in our view these are not to be regarded as significant in view of the magnitude of the differences under consideration. Chatterjee and Robinson's contention (J., 1927, 2781) that Ingold, Ingold, and Shaw's view is *invalidated* by this cause is entirely devoid of supporting evidence. There is one further consideration, namely, the effect of the stability of the -onium complexes themselves. The stability of an -onium complex may be deduced from the relative extents of the two simultaneous decompositions undergone by suitably constituted quaternary hydroxides, etc. (Hanhart and Ingold, J., 1927, 997), and we intend to institute a comparison between aromatic substitutions and exhaustive methylations on these lines.

Addendum by J. W. BAKER [*Received, April 23rd,* 1928].—The damping action of (1) external electron shells (this paper and cited references) and (2) an intercalated double linkage (Baker and Wilson, J., 1927, 843; Baker and Eccles, *ibid.*, p. 2125) on the meta-orienting action of a positive pole situated in the side chain of a benzene derivative has now been studied, and each condition is found to cause a considerable loss of meta-orienting power. In a recent paper Robinson and Zaki (J., 1927, 2485) stated that Baker and Wilson contested the *op*-directing influence of an ethenoid centre; but this is incorrect, since the investigation of the latter authors was concerned only with the relative amounts of *meta*-nitration produced *by the nitro-group* when the latter is separated from the benzene nucleus by an unsaturated carbon chain, $CHPh{:}CH{\cdot}NO_2$, and by a saturated chain of equal length, $CH_2Ph{\cdot}CH_2{\cdot}NO_2$. This effect, if propagated by conjugated polarisation to the nucleus, should lead to more pronounced meta-substitution in the former case than in the latter. The reverse is true (2% and 13% respectively). Since, on nitration, *p*-nitrobenzylidenephenylnitromethane, $CPh(NO_2){:}CH{\cdot}C_6H_4{\cdot}NO_2$ (in which the double bond is similarly situated with respect to the nucleus but is no longer in the direct path of transmission from the nitro-group) yields 21% of meta-isomeride, it was inferred that the recognised *op*-directive influence of the vinyl double bond is not sufficiently strong completely to annul the meta-directing shift originating in the nitro-group when this effect is not transmitted to the nucleus through the ethenoid centre. These results confirmed the conclusion reached by Baker and Ingold (J., 1927, 832) and Cooper and Ingold (*ibid.*, p. 836) relating to the propagation of meta-directing influences from the side chain to the nucleus by the mechanism  instead of , a view substantiated by independent evidence by Le Fèvre and Turner (this vol., p. 245) and differing in no essential point from that adopted by Robinson and Zaki.

Discussing the meta-nitration of benzaldoxime and its *N*-methyl ether in sulphuric acid, Brady and Miller (this vol., p. 338) remark that this is contrary to the suggestion (Ingold, *Ann. Reports*, 1926, **23**, 131) that the introduction of unsaturated centres between a meta-orienting group and the nucleus causes a very rapid damping of the orienting effect. Baker and Ingold, however, showed that the meta-orienting power of C=O (C=N, etc.) is due to the permanently positively charged carbon atom $\overset{\delta+}{C}=\overset{\delta-}{O}$ just as in $\overset{+}{N}\overset{-}{O}_2$. In $-\overbrace{CH=N}^{+}RR'$ the carbon, not the nitrogen, must be regarded as the effective meta-directing atom, and its positive charge is enhanced as compared with carbon in $-\overset{\delta+}{C}=\overset{\delta-}{N}R$ by distribution (*Ann. Reports*, 1927, **24**, 115) of the ionic charge of the pseudo-basic system of which it forms part. The work of Forsyth, Nimkar, and Pyman (J., 1926, 800) on amidine salts, $-\overbrace{C(NH_2)=N}^{+}RR'$, has already provided evidence illustrating this effect (*Ann. Reports*, 1926, **23**, 140).

EXPERIMENTAL.

Phenyldimethylphosphine has been prepared (Michaelis, *Annalen*, 1876, **181**, 359) with the aid of zinc methyl. We find that it can readily be prepared by the action of magnesium methyl iodide on phosphenyl chloride in an atmosphere of hydrogen. A solution of phosphenyl chloride (25 g.) in an equal volume of ether was added to the Grignard solution prepared from methyl iodide (39·7 g.) and magnesium (6·7 g.). After 2 hours, ice-water was added, and the tertiary phosphine, recovered from the ethereal layer, was distilled (yield, 35%). Treatment with methyl iodide yielded the methiodide; this on addition to saturated aqueous sodium picrate precipitated *phenyltrimethylphosphonium picrate*, which separated from water in yellow needles, m. p. 132—133° (Found: C, 47·2; H, 4·3. $C_{15}H_{16}O_7N_3P$ requires C, 47·1; H, 4·4%).

Benzyl chloride in excess was allowed to react with trimethylphosphine (Renshaw and Greenlaw, *J. Amer. Chem. Soc.*, 1920, **42**, 1472; Renshaw and Bell, *ibid.*, 1921, **43**, 916), and the deliquescent phosphonium chloride was dissolved in water, extracted with ether to remove the excess of benzyl chloride, and converted into *benzyltrimethylphosphonium picrate* by precipitation with aqueous sodium picrate. The salt separated from water in flattened prisms, m. p. 173° (Found: C, 48·7; H, 4·8. $C_{16}H_{18}O_7N_3P$ requires C, 48·6; H, 4·6%).

Phenyldimethylarsine (Burrows and Turner, J., 1920, **117**, 1378) was prepared from dimethyliodoarsine (Roberts, Turner, and Bury, J., 1926, 144), and converted through the methiodide into the quaternary picrate (m. p. 145°; Steinkopf and Schwer, *Ber.*, 1921, **54**, 14), as in the previous examples.

Benzyldimethylarsine was prepared as described by Roberts, Turner, and Bury (*loc. cit.*), excepting that the Grignard reaction was conducted in an atmosphere of hydrogen, and the yield thus increased to 33%. The methiodide yielded *benzyltrimethylarsonium picrate*, which crystallised from water in yellow prisms, m. p. 175—176° (Found: As, 16·9. $C_{16}H_{18}O_7N_3As$ requires As, 17·1%).

Phenyldi-iodostibine was prepared by Schmidt's method (*Annalen*, 1920, **421**, 188) and converted into phenyldimethylstibine by treatment with the requisite amount of magnesium methyl iodide in an atmosphere of hydrogen. The tertiary base (b. p. 110—115°/17 mm.; Grüttner and Wiernik, *Ber.*, 1915, **48**, 1759) was converted into the methiodide and thence into *phenyltrimethylstibonium picrate*, which crystallised from water in needles, m. p. 153° (Found: C, 38·1; H, 3·3. $C_{15}H_{16}O_7N_3Sb$ requires C, 38·2; H, 3·4%).

The conditions used by Vorländer and Siebert (*loc. cit.*) for the nitration of phenyltrimethylammonium nitrate were found to be unsuitable for the corresponding phosphonium picrate, which was therefore nitrated at 60° (7 hours) with a mixture of equal volumes of fuming nitric and sulphuric acids. The product, m-*nitrophenyl-*

trimethylphosphonium picrate, which was for the most part precipitated on addition of ice, the small remainder being obtained by neutralising the filtrate with ammonia, evaporating it, and extracting it with ethyl acetate, consisted of a single substance, m. p. 166—167° (Found : C, 42·15; H, 3·5. $C_{15}H_{15}O_9N_4P$ requires C, 42·25; H, 3·55%), the residues containing no trace of any isomeride. Although we were unable to establish satisfactory conditions for the quantitative application of Francis and Hill's method of orientation, the constitution of the substance follows from analogy with the preparation of the corresponding ammonium and arsonium salts.

The nitration of benzyltrimethylphosphonium picrate occurs much more easily than that of its lower homologue and a low temperature is necessary. The salt (4·0 g.) was added (1 hour) with stirring to nitric acid (30 g., *d* 1·5) at − 17°, and a further hour was allowed for completion of the reaction; ice (60 g.) was then added, and ammonia passed in to neutralise the free acid. The precipitate was collected and washed, the residues obtained on evaporation of the mother-liquors to dryness were extracted with acetone, and the residue from this solvent was washed with water, and so forth, until complete separation from ammonium salts had been effected (yields, 96·5, 97·5%). By crystallisation from water, pure p-*nitrobenzyltrimethylphosphonium picrate* was isolated (yields, 70·1, 72·3%) as needles, m. p. 188—189° (Found : C, 43·9; H, 4·0. $C_{16}H_{17}O_9N_4P$ requires C, 43·6; H, 3·9%), and the proportion of *m*-derivative in the remainder (Found : C, 44·4, 44·3; H, 4·0, 4·1%) estimated as usual by reduction and bromine-titration (Found : meta, 9·5, 10·7% of the total nitration products). The identity of the *p*-compound was proved by oxidation to *p*-nitrobenzoic acid. o-*Nitrobenzyltrimethylphosphonium picrate* was prepared by allowing *o*-nitrobenzyl chloride to react with trimethylphosphine in ethereal solution, and converting the quaternary chloride into the picrate with sodium picrate. It separated from water in small needles, m. p. 152—153° (Found : C, 43·9; H, 4·1%). m-*Nitrobenzyltrimethylphosphonium picrate*, prepared similarly from *m*-nitrobenzyl chloride, formed small needles, m. p. 171—172° (Found : C, 43·4; H, 4·1%), and the *p*-salt obtained in the same manner was identical with the principal nitration product. These salts gave correct results on reduction and bromine-titration by Francis and Wilson's method as used for the nitration product.

The nitration of phenyltrimethylarsonium picrate takes place with difficulty, and the best conditions found were as follows. A solution of the salt (4·0 g.) in 30 g. of nitric acid (*d* 1·52) was heated in a closed tube at 100° for 5 hours. During this process the picrate ion is partly oxidised but the aryltrimethylarsonium ions only slightly so (less than 1·5%). The cooled solution was diluted with water (225 c.c.) containing 2·5 g. of picric acid and neutralised with sodium hydroxide solution (50 c.c.). The major portion of the nitration product was precipitated as picrate, and the remainder isolated, as in the foregoing experiments, acetone being used as solvent (yields, close to 98·5%). Preliminary experiments having shown that m-*nitrophenyltrimethylarsonium picrate* was the main product but that the residues contained isomerides, the bulk of the *m*-compound was separated in the pure state by crystallisation from water (94·6, 95·5, 95·5% of the total yield), and oriented by reduction and bromination. It forms orange-yellow needles, m. p. 180° (Found: C, 38·1; H, 3·0; As, 15·6. $C_{15}H_{15}O_9N_4As$ requires C, 38·2; H, 3·2; As, 15·9%). The residual mixtures (equivalent to 5·4, 4·5, 4·5% of the total) were reduced and titrated with bromine to obtain the meta-content (Found: 76, 74, 75%). The final figure for the proportion of *m*-compound is therefore 98·2% (mean). An approximate check was obtained by determining the solubility of the *m*-compound in solutions equivalent, except for the absence of the other isomerides, to those from which it was crystallised, and this gave 98·0%.

The nitration of benzyltrimethylarsonium picrate, the isolation of the products (yield, 100%), the partial separation (64·5%) of the para-compound, and the estimation of the *m*-isomeride in the unseparated mixture (Found: C, 40·1; H, 3·6%) were conducted as in the case of the corresponding phosphonium compound (Found: meta, 3·4, 3·4%). p-*Nitrobenzyltrimethylarsonium picrate* crystallises from acetone in orange-yellow needles, m. p. 166—168° (Found: C, 40·1; H, 3·8; As, 15·1. $C_{16}H_{17}O_9N_4As$ requires C, 39·7; H, 3·5; As, 15·5%).

Phenyltrimethylstibonium picrate is nitrated noticeably more readily than its phosphonium and arsonium analogues, and satisfactory conditions (yields, 99·5, 99·0%) were obtained by using the method for the former, except that the temperature was 0°. The isolation, partial separation of the *m*-isomeride (76·8, 73·0%), and the estimation of the *m*-isomeride (Found: meta, 85·4, 87·2%) were carried out by the method described for the arsonium compounds. m-*Nitrophenyltrimethylstibonium picrate* separates from water in needles, m. p. 203° (Found: C, 34·5; H, 2·9. $C_{15}H_{15}O_9N_4Sb$ requires C, 34·8; H, 2·9%).

In the absence of definitely comparative experiments, reference was not made in the introduction to Ingold and Shaw's suggestion (J., 1927, 2923) that the speed of nitration in *m*-substituting compounds should show a general decrease in a series in which the proportion of *m*-derivative formed increases; nevertheless, the above qualitative observations give considerable support to this deduction.

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