100. *Mesityldimethylphosphine.*

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THIS *phosphine* has been found by measurements of reaction velocity to be more reactive towards alkyl halides than its arsenic analogue. The corresponding nitrogen compound, dimethylmesidine, gave no quaternary salt with methyl iodide (Hofmann, *Ber.*, 1872, **5**, 718). Thus, the order of reactivity of the *o*-substituted substances, phosphine > arsine > amine, is that which has already been found for the non-substituted bases (Davies and

Lewis, J., 1934, 1599), and is parallel with the dipole moments of the triphenyl bases (Bergmann and Schutz, *Z. physikal. Chem.*, 1932, **19**, 401) (Fig. 3).

The result is of interest in connexion with a suggestion of Lesslie and Turner (J., 1933, 1588) that mesityldimethylarsine (2 : 4 : 6-trimethylphenyldimethylarsine) should be more reactive towards alkyl halides than dimethylmesidine, because the larger arsenic atom is less under the steric influence of the *o*-methyl groups than the smaller nitrogen atom. Extending this view (see Fig. 1, atomic radii), it would appear that the corresponding bismuthine should be the most reactive base, and the phosphine of reactivity intermediate between those of the amine and the arsine. It is known, however, that bismuthines, generally, are non-reactive, and the present work has shown that the phosphine is the most reactive of all the bases of the elements of Group V*b*. Thus, the reactivities of the bases do not follow the order of the atomic radii of the central elements.

It is certain, therefore, that the principal factor determining the reactivity of the bases is one created by the polarisation of the central element. The substitution of *o*-groups diminishes the reactivity in each case, but the author considers that velocity measurements are not suitable, because of the magnitude of the above principal factor, for detecting differences in the effect of the *o*-groups in the various cases.

FIG. 1.

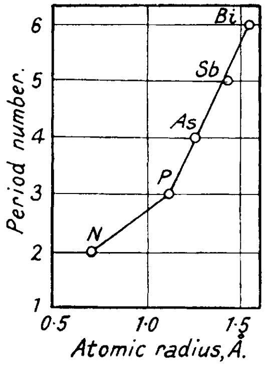


FIG. 2.

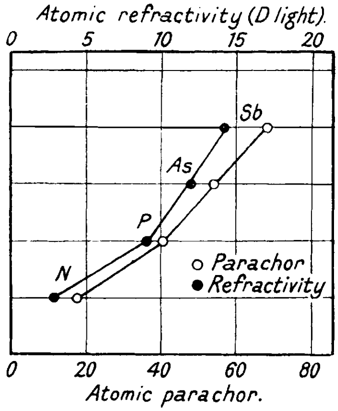
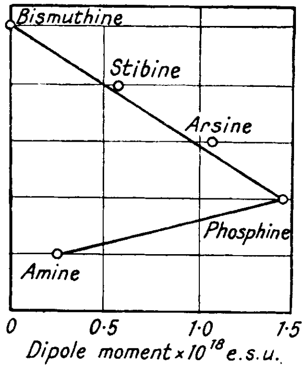


FIG. 3.



The atomic radii of the elements of Group V*b* are shown in Fig. 1. The value for nitrogen is given by Sidgwick ("The Covalent Link in Chemistry," 1933, p. 84), and the values for arsenic, antimony, and bismuth are from Hume-Rothery (*Phil. Mag.*, 1930, **10**, 217). In deriving the mean value for the atomic radius of phosphorus, P- = 1·11 Å., there have been used the results of Wierl (*Ann. Physik*, 1931, **8**, 521) for phosphorus trichloride, of Bergmann and Engel (*Z. physikal. Chem.*, 1931, **13**, 247) for phosphorus trichloride and tribromide, and of Passerini (*Gazzetta*, 1928, **58**, 655) for aluminium phosphide, to which a correction for the triple link has been applied. Values related to the atomic volumes, such as atomic refractivities and parachors, when plotted against the period number of the element, give similar curves (Fig. 2). Such atomic properties of the elements from phosphorus to bismuth fall on a straight line. The anomalous position of nitrogen is related to the fact that in the atoms of all the elements of the Group, except nitrogen, the valency electrons are separated from the helium nucleus by other stable electronic groupings.

EXPERIMENTAL.

(All thermometer readings are corrected.)

Mesityldichlorophosphine.—On account of the low yield in this case, the general method of isolation of a chlorophosphine by distillation at reduced pressure used in these laboratories was replaced by an extraction method, which is a modification of that used by Michaelis (*Annalen*, 1897, **294**, 35) in the preparation of this compound. A mixture of mesitylene (116 c.c.), phosphorus trichloride (73 c.c.), and commercial aluminium chloride (20 g.) was refluxed for 30 hours. The product was extracted with 250 c.c. of light petroleum. The combined extracts from several preparations were distilled through an efficient column up to 165°/760 mm. The residue was fractionally distilled at reduced pressure, giving 15 g. of the dichlorophosphine, b. p. 156—157°/16 mm., from five preparations. The light petroleum, phosphorus trichloride, and mesitylene fraction was treated with excess of water; the hydrocarbon layer was dried over calcium chloride and distilled, light petroleum and mesitylene of sufficient purity for use in the chlorophosphine preparations being recovered.

Mesityldimethylphosphine.—A solution of 15 g. of the above dichlorophosphine in 50 c.c. of ether was slowly added to a cooled stirred Grignard reagent prepared from 35·5 g. of methyl iodide and 6 g. of magnesium. The mixture was boiled for 2 hours, cooled, and decomposed with aqueous ammonium chloride. The ethereal layer was dried over sodium sulphate, the ether expelled, and the residue fractionally distilled and then redistilled under reduced pressure. The tertiary *phosphine* (11 g.) had b. p. 133°/16 mm.; $d_{4^\circ}^{25^\circ}$ 0·9570; $n_D^{25^\circ}$ 1·5554; $[R_L]_D$ 60·46; $n_F^{25^\circ} - n_C^{25^\circ}$ 0·0187 (Found : C, 73·5; H, 9·8. $C_{11}H_{17}P$ requires C, 73·3; H, 9·5%). The phosphine is not rapidly oxidised in the air.

The value of the atomic refractivity of phosphorus for the D line in the phosphine is 9·96, calculated by deducting the refractivities of two methyl groups and a mesityl group (Eisenlohr, *Z. physikal. Chem.*, 1910, **75**, 585) from the Lorenz–Lorentz molecular refractivity. The optical exaltation due to the attachment of the mesityl group to the phosphorus atom is shown by comparison of the above value with the mean atomic refractivity of phosphorus of 9·14 in the trialkylphosphines (Jones, Davies, and Dyke, *J. Physical Chem.*, 1933, **27**, 583).

Mesityltrimethylphosphonium iodide crystallised from water or alcohol in needles, m. p. 232° (Found : I, 39·4. $C_{12}H_{20}IP$ requires I, 39·4%), and *mesityldimethylethylphosphonium iodide* from alcohol in needles, m. p. 168° (Found : I, 37·6. $C_{13}H_{22}IP$ requires I, 37·8%).

An addition *compound* was obtained as red crystals by mixing the phosphine (1 c.c.) and carbon disulphide (2 c.c.) in benzene (3 c.c.) in the cold. It readily lost carbon disulphide in the air, but could be manipulated and preserved in an atmosphere containing carbon disulphide vapour. The compound dissolved with complete dissociation in the common solvents, but recombination took place when excess of carbon disulphide was added. The addition compound (Found : C, 56·3; H, 7·0. $C_{12}H_{17}S_2P$ requires C, 56·2; H, 6·7%) melted in a sealed tube at 58—59° to a colourless liquid, which solidified to a red crystalline mass on cooling.

Mesityldimethylarsine.—Considerable difficulty was experienced in obtaining the arsine of sufficient purity for quantitative measurements. The method of preparation differed in detail from that given by Lesslie and Turner (*loc. cit.*). An ethereal solution of 35 g. of dimethyliodoarsine was slowly added to a cooled stirred Grignard solution made from 66 g. of bromomesitylene and 10 g. of magnesium. The mixture was boiled for 2 hours, cooled, and cautiously treated with ammonium chloride solution. The ethereal layer was separated and dried, and the ether expelled. The residue was repeatedly fractionally distilled through a long packed column at reduced pressure, until an arsine fraction, b. p. 134—135°/17 mm., was obtained which gave almost a 100% yield of the methiodide when treated with excess of methyl iodide in solution in acetone–water (9 : 1 by vol.).

Velocity Measurements.—The rate of addition of methyl iodide and of ethyl iodide to the bases was measured by a method similar to that described by Davies and Lewis (*loc. cit.*), the following results being obtained.

Temp., 25°. Initial concentrations, 0·1 g.-mol. of the base and of the alkyl iodide/l. *k* (bimolecular), l./g.-mol./min.

Mesityldimethyl-base.	Alkyl iodide.	Solvent.	Mean *k*.	Time, mins., for 25% yield of I^-.
Phosphine	MeI	Alcohol	0·890 *	3·7
,,	EtI	Acetone–water (9 : 1 by vol.)	— †	88
Arsine	MeI	,, ,, ,,	0·104	32
,,	,,	Alcohol	0·00944	353
,,	EtI	Acetone–water	— †	4650

* The -onium salt began to separate from solution when the reaction completed was approximately 70%.

† The bimolecular velocity coefficients drift.

The reaction between the phosphine and methyl iodide in acetone–water was too rapid to be measured by the method employed.

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