

### 273. Preparation and Properties of Allyl Phosphines, Arsines, and Stannanes.

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Phosphines, arsines, and stannanes containing allyl and methylallyl groups have been produced by means of the Grignard reaction, their physical properties have been examined, and characteristic derivatives have been prepared.

No phosphine containing either an allyl or a methylallyl group has hitherto been prepared, though Hofmann (*Phil. Trans.*, 1860, **150**, 412) records that he experimented unsuccessfully on the effect of heating phosphorus, zinc, and allyl iodide together in a sealed tube, but phenyl-*p*-tolylmethylallylphosphonium iodide has been obtained by Pope and Gibson (*J.*, 1912, **101**, 737; also Radcliffe and Brindley, *J. Soc. Chem. Ind.*, 1923, **42**, 66) by the combination of phenyl-*p*-tolylmethylphosphine with allyl iodide, and trisdiphenylallylphosphonium bromide by Worrall (*J. Amer. Chem. Soc.*, 1930, **52**, 2936) by the union of trisdiphenylphosphine and allyl bromide. Such phosphines have now been prepared by the Grignard method, *triallylphosphine* and *phenyl*-, *p*-*tolyl*-, *p*-*xylyl*-, *p*-*ethylphenyl*-, *p*-*isopropylphenyl*-, *p*-*methoxyphenyl*-, *p*-*phenoxyphenyl*-, and *p*-*bromophenyl-diallylphosphine* from allylmagnesium bromide, and *tri-β-methylallylphosphine* and *phenyl*-, *p*-*tolyl*-, *p*-*xylyl*-, *p*-*ethylphenyl*-, *p*-*isopropylphenyl*-, *p*-*methoxyphenyl*-, and *p*-*bromophenyl-di-β-methylallylphosphine* from β-methylallylmagnesium bromide.

Triallylarsine has been obtained by Gryszkiewicz-Trochimowski and Zambrzycki (*Rocz. Chem.*, 1926, **6**, 794). *Phenyldiallylarsine* has now been prepared from allylmagnesium bromide, and *tri-β-methylallylarsine* and *phenyldi-β-methylallylarsine* from β-methylallylmagnesium bromide.

Tetra-allyltin has been described by Vijayraghavan (*J. Indian Chem. Soc.*, 1945, **22**, 119), and allylstannonic acid and allylpentachlorostannic acid by Lesbre and Glotz (*Compt. rend.*, 1934, **198**, 1427). *Triethylallyltin*, *diethyldiallyltin*, *tri-n-butylallyltin* and *di-n-butylallyltin* have been prepared in the present work from allylmagnesium bromide.

In order to secure good yields, it has been found necessary to employ the Grignard reagent in excess over the chlorophosphine, chloroarsine, or chlorostannane, to exclude air rigorously during the preparation, and to distil the product under low pressure. In the reaction, diallyl, b. p. 59.5°, or di-β-methylallyl, b. p. 113°, is formed as by-product through the coupling action of the Grignard reagent, but the hydrocarbon is easily separated, after the ether, by distillation from the phosphine, arsine, or stannane.

The allylphosphines rapidly oxidise in contact with air. They combine with mercuric chloride to give mercurichlorides of the general formula  $PR_3 \cdot HgCl_2$ , with benzoquinone to produce pale yellow addition compounds  $PR_3 \cdot C_6H_4O_2$ , with carbon disulphide to yield either intensely red compounds  $PR_3 \cdot CS_2$  or red colorations in solution, and with methyl iodide to give the methylphosphonium iodides. These methiodides combine with mercuric iodide to

form yellow complex mercuri-iodides  $PR_4I_2HgI_2$ , and with cadmium iodide to give cadmi-iodides  $(PR_4I)_2CdI_2$ . The allylarsines closely resemble the phosphines chemically, and the allylstannanes also are rapidly attacked by air.

In the absence of air, the allyl-phosphines, arsines, and -stannanes are thermally stable, being unaffected even on being kept at 25° for an hour. A comparison of the b. p./50 mm. with that of the corresponding *n*-alkyl compound is made in the following table, from which it will be seen that the difference is slight.

Phosphine.	B. p./50 mm.	Phosphine.	B. p./50 mm.
Triallyl .....	98°	Tri- <i>n</i> -propyl .....	103°
Phenyldiallyl .....	160	Phenyldi- <i>n</i> -propyl .....	159
<i>p</i> -Tolyldiallyl .....	171	<i>p</i> -Tolyldi- <i>n</i> -propyl .....	174
<i>p</i> -Xylyldiallyl .....	179	<i>p</i> -Xylyldi- <i>n</i> -propyl .....	180
<i>p</i> -Ethylphenyldiallyl .....	188	<i>p</i> -Ethylphenyldi- <i>n</i> -propyl .....	181
Tri- $\beta$ -methylallyl .....	142	Tri- <i>n</i> -butyl .....	149
Phenyldi- $\beta$ -methylallyl .....	184	Phenyldi- <i>n</i> -butyl .....	185
<i>p</i> -Tolyldi- $\beta$ -methylallyl .....	190	<i>p</i> -Tolyldi- <i>n</i> -butyl .....	197
<i>p</i> -Xylyldi- $\beta$ -methylallyl .....	200	<i>p</i> -Xylyldi- <i>n</i> -butyl .....	204
<i>p</i> -Ethylphenyldi- $\beta$ -methylallyl ...	205	<i>p</i> -Ethylphenyldi- <i>n</i> -butyl .....	209
Arsine.		Arsine.	
Triallyl .....	111	Tri- <i>n</i> -propyl .....	110
Phenyldiallyl .....	171	Phenyldi- <i>n</i> -propyl .....	165
Tri- $\beta$ -methylallyl .....	143	Tri- <i>n</i> -butyl .....	155
Phenyldi- $\beta$ -methylallyl .....	189	Phenyldi- <i>n</i> -butyl .....	193
Stannane.		Stannane.	
Triethylallyl .....	112	Triethyl- <i>n</i> -propyl .....	112

As is shown in the next table, the average difference between the molecular volumes (in c.c.) of an aryldiallylphosphine and its corresponding aryldi- $\beta$ -methylallylphosphine at 25° is 34.0 c.c., compared with 33.0 c.c. for two  $CH_2$  groups in the higher trialkylphosphines (Jackson, Davies, and Jones, *J.*, 1931, 2109).

Phosphine.	Diallyl.	Di- $\beta$ -methylallyl.	Diff.
Phenyl .....	196.2	230.2	34.0
<i>p</i> -Tolyl .....	211.5	246.5	35.0
<i>p</i> -Xylyl .....	227.6	262.0	34.4
<i>p</i> -Ethylphenyl .....	230.0	263.2	33.2
<i>p</i> - <i>iso</i> Propylphenyl .....	248.0	280.6	32.6
<i>p</i> -Methoxyphenyl .....	216.2	249.6	33.4
<i>p</i> -Bromophenyl .....	210.6	245.8	35.2

The Lorenz-Lorentz molecular refractivities,  $(n^2 - 1)M/(n^2 + 2)d$ , of the allyl phosphines for sodium D light are given in the following table. The calculated values have been obtained by means of the constants given by Eisenlohr (*Z. physikal. Chem.*, 1910, 75, 605), together with those given for phosphorus by Jones, Davies, and Dyke (*J. Physical Chem.*, 1933, 37, 594).

Diallylphosphine.	$[M_L]_D$ .		Di- $\beta$ -methylallylphosphine.	$[M_L]_D$ .	
	Found.	Calc.		Found.	Calc.
Phenyl .....	64.08	63.99	Phenyl .....	73.16	73.23
<i>p</i> -Tolyl .....	68.25	68.99	<i>p</i> -Tolyl .....	78.11	78.24
<i>p</i> -Xylyl .....	72.95	73.35	<i>p</i> -Xylyl .....	82.84	82.58
<i>p</i> -Ethylphenyl .....	73.78	73.82	<i>p</i> -Ethylphenyl .....	83.03	83.05
<i>p</i> - <i>iso</i> Propylphenyl .....	78.24	78.44	<i>p</i> - <i>iso</i> Propylphenyl .....	87.36	87.67
<i>p</i> -Methoxyphenyl .....	70.97	70.83	<i>p</i> -Methoxyphenyl .....	79.65	80.07
<i>p</i> -Phenoxyphenyl .....	89.47	89.76	<i>p</i> -Bromophenyl .....	81.23	80.99

The phosphines, arsines, and stannanes are freely soluble in ether, alcohol, benzene, or carbon tetrachloride, but not in water. The molecular weights, *M*, of the phosphines have been determined by the cryoscopic method in benzene solution, and found to be normal.

#### EXPERIMENTAL.

*Preparation of the Phosphines.*—The necessary dichlorophosphines, phenyl b. p. 221–222°, *p*-tolyl b. p. 100°/12 mm., *p*-xylyl b. p. 133°/16 mm., *p*-ethylphenyl b. p. 133°/18 mm., *p*-*isopropylphenyl* b. p. 132–134°/14 mm., *p*-methoxyphenyl b. p. 153°/21 mm., *p*-phenoxyphenyl b. p. 200°/12 mm., and *p*-bromophenyl b. p. 135–136°/14 mm., were prepared by the method of Michaelis (*Ber.*, 1879, 12, 1009; *Annalen*, 1896, 293, 223) and isolated either by the distillation method of Grüttner and Wiernik (*Ber.*, 1915, 48, 1475) or by the extraction method of Davies (*J.*, 1935, 463). Allyl bromide,

b. p. 70—71°, was prepared as described in *Org. Synth.*, I, 24. To prepare  $\beta$ -methylallyl bromide, phosphorus tribromide (45 c.c.) was added dropwise with exclusion of moisture during 5 hours with periodic shaking to dried (CaO), freshly-distilled  $\beta$ -methylallyl alcohol (118 c.c.) in dried (KOH), freshly-distilled pyridine (32 c.c.) cooled with ice-salt: the reaction mixture was filtered, and the filtrate on distillation gave  $\beta$ -methylallyl bromide, b. p. 94—95° (85 g.). Both bromides after drying ( $P_4O_{10}$  or  $CaCl_2$ ) were used immediately, after a fresh distillation, for the preparation of the phosphines.

To 1½ mols. (36.5 g.) of finely divided magnesium a granule of iodine and 100 c.c. of absolute ether, contained in a dried round-bottom flask fitted with a mechanical stirrer, dropping funnel, reflux condenser, siphon tube, and a gas-inlet tube, through which dry hydrogen was passed, there was added, dropwise in the course of about 2 hours so as to maintain a gentle boiling, ½ mol. of allyl bromide (42 c.c.) or of  $\beta$ -methylallyl bromide (51 c.c.) in 285 c.c. of ether (Gilman and McGlumphy, *Bull. Soc. chim.*, 1928, 43, 1322). After an hour's standing, the Grignard solution was siphoned quickly through a glass-wool filter into a second round-bottom flask provided with similar fittings to the first, and, with continuous stirring, passage of hydrogen and external cooling with ice, thereto was added gradually in ether (100 c.c.) 1/12 mol. of phosphorus trichloride (7.1 c.c.) or 1/8 mol. of the arylidichlorophosphine [phenyl (17 c.c.), *p*-tolyl (19 c.c.), *p*-xylyl (21 c.c.), *p*-ethylphenyl (21 c.c.), *p*-isopropylphenyl (22 c.c.), *p*-methoxyphenyl (20 c.c.), *p*-bromoxyphenyl (24 c.c.), or *p*-bromophenyl (19 c.c.)]. After the addition, the mixture was boiled for ½ hour, again cooled to 0°, and then ammonium chloride (50 g.) in water (250 c.c.) was added gradually through the dropping-funnel until all the precipitated magnesium salts had dissolved. The resulting mixture was siphoned under carbon dioxide into a separating funnel, and the ether layer was dried ( $Na_2SO_4$ ) in a stoppered bottle. The dried solution was distilled in carbon dioxide to remove ether and diallyl or di- $\beta$ -methylallyl, and the residual phosphine was redistilled in carbon dioxide under low pressure and preserved in sealed glass tubes. All subsequent manipulations of the phosphine were carried out under carbon dioxide.

*Triallylphosphine*.—This compound was prepared from allylmagnesium bromide and phosphorus trichloride; the liquid (4 g.) had b. p. 69°/13 mm. (Found: C, 70.1; H, 10.0; P, 19.7.  $C_9H_{15}P$  requires C, 70.1; H, 9.8; P, 20.1%). Mercuric chloride added to the phosphine in alcohol precipitated the *mercurichloride*, rhomboids, m. p. 135° (Found: Cl, 16.9; P, 7.2.  $C_9H_{15}P, HgCl_2$  requires Cl, 16.7; P, 7.3%). This and all the succeeding mercurichlorides, mercuri-iodides and cadmi-iodides were repeatedly recrystallised to constant m. p. from alcohol, except where another solvent is stated.

The phosphine (1 c.c.) in alcohol (20 c.c.) mixed with *p*-benzoquinone (0.4 g.) in alcohol (20 c.c.) produced a red coloration, and after standing, the addition of ether precipitated pale-yellow stellate crystals of *triallylphosphine-p-benzoquinone*, which darkened at 100° and became black at 130° (Found: C, 69.1; H, 7.5.  $C_{15}H_{19}O_3P$  requires C, 68.7; H, 7.3%). Excess of carbon disulphide added to the phosphine (2 c.c.) in alcohol (5 c.c.) gave a dark red coloration, and on cooling to 0° *triallylphosphine-carbondisulphide* separated as red needles, m. p. 32.5°, unstable in the air (Found: C, 51.7; H, 6.9.  $C_{10}H_{15}PS_2$  requires C, 52.1; H, 6.6%). Mixed in the absence of air, the phosphine and methyl iodide in ether immediately gave a precipitate of *methyltriallylphosphonium iodide*, pearly flakes from alcohol-ether (Found: I, 42.7.  $C_{10}H_{15}PI$  requires I, 42.9%).

*Phenyltriallylphosphine*.—This compound (8 g.) was obtained by the interaction of allylmagnesium bromide and phenylidichlorophosphine and had b. p. 127°/14 mm.,  $d_4^{25}$  0.9693,  $n_D^{25}$  1.5670 (Found: C, 75.5; H, 8.1.  $C_{12}H_{16}P$  requires C, 75.7; H, 8.0%). It formed the *mercurichloride*, needles, m. p. 123° (Found: Cl, 15.6.  $C_{12}H_{16}P, HgCl_2$  requires Cl, 15.4%).

*p-Tolyldiallylphosphine*.—The phosphine (7 g.) was produced from allylmagnesium bromide and *p*-tolylidichlorophosphine and had b. p. 138°/14 mm.,  $d_4^{25}$  0.9651,  $n_D^{25}$  1.5545 (Found: C, 75.9; H, 8.9.  $C_{13}H_{17}P$  requires C, 76.4; H, 8.4%). It yielded the *mercurichloride*, elongated prisms, m. p. 110.5° (Found: Cl, 14.9.  $C_{13}H_{17}P, HgCl_2$  requires Cl, 14.9%).

*p-Xylyldiallylphosphine*.—The interaction of the allyl Grignard reagent and *p*-xylyldichlorophosphine gave the phosphine (16 g.), which had b. p. 144°/13 mm.,  $d_4^{25}$  0.9584,  $n_D^{25}$  1.5540 (Found: C, 76.6; H, 8.8; P, 14.0; M, 223.  $C_{14}H_{18}P$  requires C, 77.0; H, 8.8; P, 14.2%; M, 218). The *mercurichloride* crystallised in rhomboids, m. p. 170° (Found: Cl, 14.9; P, 6.3.  $C_{14}H_{18}P, HgCl_2$  requires Cl, 14.5; P, 6.3%).

*p-Ethylphenyldiallylphosphine*.—Obtained from allylmagnesium bromide and *p*-ethylphenyldichlorophosphine, the phosphine (16 g.) had b. p. 145°/10 mm.,  $d_4^{25}$  0.9484,  $n_D^{25}$  1.5545 (Found: C, 76.7; H, 9.0.  $C_{14}H_{18}P$  requires C, 77.0; H, 8.8%).

*p-isoPropylphenyldiallylphosphine*.—This compound (16 g.) was prepared from allylmagnesium bromide and *p*-isopropylphenyldichlorophosphine and had b. p. 153°/11 mm.,  $d_4^{25}$  0.9361,  $n_D^{25}$  1.5435 (Found: C, 77.5; H, 9.1; M, 242.  $C_{15}H_{21}P$  requires C, 77.5; H, 9.1%; M, 232). It yielded the *mercurichloride*, m. p. 47°, from glacial acetic acid (Found: Cl, 14.6.  $C_{15}H_{21}P, HgCl_2$  requires Cl, 14.1%).

*p-Methoxyphenyldiallylphosphine*.—This phosphine (12 g.), produced from allylmagnesium bromide and *p*-methoxyphenyldichlorophosphine, had b. p. 162°/15 mm.,  $d_4^{25}$  1.0189,  $n_D^{25}$  1.5705 (Found: C, 70.6; H, 8.1.  $C_{13}H_{17}OP$  requires C, 70.9; H, 7.8%). Its *mercurichloride* separated in prisms, m. p. 131° (Found: Cl, 14.8.  $C_{13}H_{17}OP, HgCl_2$  requires Cl, 14.4%).

*p-Phenoxyphenyldiallylphosphine*.—Obtained by the action of the allyl Grignard reagent on *p*-phenoxyphenyldichlorophosphine, this phosphine (12 g.) had b. p. 238°/15 mm.,  $d_4^{25}$  1.0847,  $n_D^{25}$  1.6040 (Found: C, 76.2; H, 7.1; P, 10.9; M, 278.  $C_{18}H_{19}OP$  requires C, 76.6; H, 6.8; P, 11.0%; M, 282). The *mercurichloride*, difficultly soluble in alcohol and ether, became black at 210° (Found: Cl, 13.2.  $C_{18}H_{19}OP, HgCl_2$  requires Cl, 12.8%).

*p-Bromophenyldiallylphosphine*.—The allyl Grignard reagent and *p*-bromophenyldichlorophosphine gave the phosphine (15 g.), b. p. 186°/37 mm.,  $d_4^{25}$  1.2783 (Found: C, 53.1; H, 5.5; P, 11.4; M, 272.  $C_{12}H_{14}BrP$  requires C, 53.5; H, 5.2; P, 11.5%; M, 269). The *mercurichloride* crystallised in needles, m. p. 108° (Found: P, 5.7.  $C_{12}H_{14}BrP, HgCl_2$  requires P, 5.7%).

*Tri- $\beta$ -methylallylphosphine*.—This tertiary phosphine (5 g.) was prepared through the interaction of  $\beta$ -methylallylmagnesium bromide and phosphorus trichloride and had b. p. 112°/15 mm. (Found:

C, 73.1; H, 11.0; P, 15.4; *M*, 196.  $C_{12}H_{21}P$  requires C, 73.4; H, 10.8; P, 15.8%; *M*, 196). It immediately oxidised in the air to form the *oxide*, needles, m. p. 132°, from ether (Found: C, 67.6; H, 10.2.  $C_{12}H_{21}OP$  requires C, 67.9; H, 10.0%); the same compound was also produced from  $\beta$ -methylallylmagnesium bromide and phosphorus oxychloride. In the absence of air the phosphine and mercuric chloride in alcohol gave *tri- $\beta$ -methylallylphosphine mercurichloride*, rhombic plates, m. p. 162° (Found: Cl, 15.2.  $C_{12}H_{21}P, HgCl_2$  requires Cl, 15.2%). *Methyltri- $\beta$ -methylallylphosphonium iodide*, from its components in ether, formed needles, m. p. 151°, from alcohol-ether (Found: I, 37.4.  $C_{12}H_{21}PI$  requires I, 37.5%). *Tri- $\beta$ -methylallylphosphine-p-benzoquinone*, precipitated by ether from mixed alcoholic solutions of its components, formed pale lemon-yellow stellate crystals, which darkened in the air or on heating, becoming black at 200° (Found: C, 70.8; H, 8.5.  $C_{12}H_{21}O_2P$  requires C, 71.0; H, 8.3%).

*Phenyldi- $\beta$ -methylallylphosphine*.—The compound (15 g.) was obtained from the Grignard reagent and phenyldichlorophosphine, and had b. p. 148°/13 mm.,  $d_4^{25}$  0.9484,  $n_D^{25}$  1.5485 (Found: C, 76.8; H, 9.0; P, 14.2; *M*, 223.  $C_{14}H_{19}P$  requires C, 77.0; H, 8.8; P, 14.2%; *M*, 218). It gave the *mercurichloride*, rectangular plates, m. p. 140.5° (Found: Cl, 14.7.  $C_{14}H_{19}P, HgCl_2$  requires Cl, 14.5%). *Phenylmethyldi- $\beta$ -methylallylphosphonium iodide* separated in needles, m. p. 188° (decomp.), from alcohol-ether (Found: I, 34.9.  $C_{15}H_{23}PI$  requires I, 35.2%). On mixing hot alcoholic solutions of mercuric iodide and excess of the methiodide, *phenylmethyldi- $\beta$ -methylallylphosphonium mercuri-iodide* crystallised out on cooling as lemon-coloured needles, m. p. 133° (Found: I, 47.0; Hg, 24.5.  $C_{15}H_{23}PI, HgI_2$  requires I, 46.7; Hg, 24.6%). Similarly, cadmium iodide and the methiodide gave the *cadmi-iodide*, needles, m. p. 114° [Found: I, 46.7; Cd, 10.5.  $(C_{15}H_{23}PI)_2, CdI_2$  requires I, 46.7; Cd, 10.3%]. Addition of excess of bromine to the phosphine in ether gave a precipitate, which, on solution in hot alcohol and treatment with water until turbidity appeared, yielded *phenyldi-( $\beta$ -dibromo- $\beta$ -methylpropyl)phosphine oxide*, needles, m. p. 105°, from aqueous alcohol (Found: Br, 57.6.  $C_{14}H_{19}OBr_4P$  requires Br, 57.7%).

*p-Tolyldi- $\beta$ -methylallylphosphine*.—Prepared from the  $\beta$ -methylallyl Grignard reagent and *p*-tolyl-dichlorophosphine, the *phosphine* (11 g.) had b. p. 168°/23 mm.,  $d_4^{25}$  0.9426,  $n_D^{25}$  1.5465 (Found: C, 77.4; H, 9.3; P, 13.3; *M*, 228.  $C_{15}H_{21}P$  requires C, 77.5; H, 9.1; P, 13.4%; *M*, 232). It gave the *mercurichloride*, cubes, m. p. 164° (Found: Cl, 14.2.  $C_{15}H_{21}P, HgCl_2$  requires Cl, 14.1%). *p-Tolyldi- $\beta$ -methylallylphosphonium iodide* crystallised in needles, m. p. 94°, from alcohol-ether (Found: I, 33.8.  $C_{16}H_{24}PI$  requires I, 33.9%) and yielded *p-tolylmethyldi- $\beta$ -methylallylphosphonium mercuri-iodide*, pale-yellow prisms, m. p. 79° (Found: I, 46.1; Hg, 24.1.  $C_{16}H_{24}PI, HgI_2$  requires I, 45.9; Hg, 24.2%).

*p-Xylyldi- $\beta$ -methylallylphosphine*.—The *phosphine* (12 g.) was obtained from  $\beta$ -methylallylmagnesium bromide and *p*-xylyldichlorophosphine; it had b. p. 166°/16 mm.,  $d_4^{25}$  0.9402,  $n_D^{25}$  1.5450 (Found: C, 77.8; H, 9.4; P, 12.3.  $C_{16}H_{23}P$  requires C, 78.0; H, 9.4; P, 12.6%). The *mercurichloride* separated in prisms, m. p. 201–202° (Found: Cl, 13.7.  $C_{16}H_{23}P, HgCl_2$  requires Cl, 13.7%). *p-Xylylmethyldi- $\beta$ -methylallylphosphonium iodide* crystallised in prisms, m. p. 161°, from alcohol-ether (Found: I, 32.5.  $C_{17}H_{25}PI$  requires I, 32.7%). It gave with mercuric iodide in alcohol the *mercuri-iodide*, pale yellow rhombic plates, m. p. 71° (Found: I, 45.5; Hg, 23.6.  $C_{17}H_{25}PI, HgI_2$  requires I, 45.2; Hg, 23.8%), and with cadmium iodide, the *cadmi-iodide*, needles, m. p. 159° [Found: I, 44.0; Cd, 10.2.  $(C_{17}H_{25}PI)_2, CdI_2$  requires I, 44.4; Cd, 9.8%].

*p-Ethylphenyldi- $\beta$ -methylallylphosphine*.—This compound (12 g.), prepared from the Grignard reagent and *p*-ethylphenyldichlorophosphine, had b. p. 178°/20 mm.,  $d_4^{25}$  0.9360,  $n_D^{25}$  1.5435 (Found: C, 77.7; H, 9.6; P, 12.4; *M*, 240.  $C_{16}H_{23}P$  requires C, 78.0; H, 9.4; P, 12.6%; *M*, 246). The *mercurichloride* separated in prisms, m. p. 156° (Found: Cl, 14.1.  $C_{16}H_{23}P, HgCl_2$  requires Cl, 13.7%). *p-Ethylphenylmethyldimethyl- $\beta$ -allylphosphonium iodide*, rectangular plates, m. p. 153°, from alcohol-ether (Found: I, 32.4.  $C_{17}H_{26}PI$  requires I, 32.7%), gave the *mercuri-iodide*, pale yellow needles, m. p. 82.5° (Found: I, 45.3; P, 23.5.  $C_{17}H_{26}PI, HgI_2$  requires I, 45.2; P, 23.8%).

*p-isoPropylphenyldi- $\beta$ -methylallylphosphine*.—Interaction of the Grignard reagent and *p*-isopropylphenyldichlorophosphine gave the *phosphine* (14 g.), b. p. 182.5°/19 mm.,  $d_4^{25}$  0.9279,  $n_D^{25}$  1.5350 (Found: C, 77.9; H, 9.8; P, 11.8; *M*, 263.  $C_{17}H_{25}P$  requires C, 78.4; H, 9.7; P, 11.9%; *M*, 260). Its *mercurichloride* was obtained in needles, m. p. 153° (Found: Cl, 13.4.  $C_{17}H_{25}P, HgCl_2$  requires Cl, 13.3%).

*p-Methoxyphenyldi- $\beta$ -methylallylphosphine*.—*p*-Methoxyphenyldichlorophosphine and di- $\beta$ -methylallylmagnesium bromide reacted to give the *phosphine* (12 g.), b. p. 192°/20 mm.,  $d_4^{25}$  0.9948,  $n_D^{25}$  1.5513 (Found: C, 72.3; H, 8.7.  $C_{15}H_{21}OP$  requires C, 72.6; H, 8.6%). Its *mercurichloride* separated in cubes, m. p. 181° (Found: Cl, 13.8.  $C_{15}H_{21}OP, HgCl_2$  requires Cl, 13.6%). *p-Methoxyphenylmethyldi- $\beta$ -methylallylphosphonium iodide*, needles, m. p. 134.5°, from water (Found: I, 32.3.  $C_{16}H_{24}OPI$  requires I, 32.5%) gave the *mercuri-iodide*, pale yellow prisms, m. p. 71° (Found: I, 45.0; Hg, 23.7.  $C_{16}H_{24}OPI, HgI_2$  requires I, 45.1; Hg, 23.7%), and the *cadmi-iodide*, needles, m. p. 132° [Found: I, 44.2; Cd, 10.1.  $(C_{16}H_{24}OPI)_2, CdI_2$  requires I, 44.3; Cd, 9.8%].

*p-Bromophenyldi- $\beta$ -methylallylphosphine*.—Obtained from di- $\beta$ -methylallylmagnesium bromide and *p*-bromophenyldichlorophosphine, this *phosphine* (14 g.) had b. p. 189°/18 mm.,  $d_4^{25}$  1.2094,  $n_D^{25}$  1.5752 (Found: C, 56.7; H, 6.3; P, 10.3; *M*, 293.  $C_{14}H_{13}BrP$  requires C, 56.6; H, 6.1; P, 10.4%; *M*, 297). The *mercurichloride* was obtained in cubes, m. p. 194° (Found: Cl, 12.4.  $C_{14}H_{13}BrP, HgCl_2$  requires Cl, 12.5%). *p-Bromophenylmethyldi- $\beta$ -methylallylphosphonium iodide*, cubes, m. p. 174°, from alcohol-ether (Found: I, 28.8.  $C_{15}H_{21}BrPI$  requires I, 28.9%), yielded the *mercuri-iodide*, pale yellow needles, m. p. 67° (Found: I, 42.8; Hg, 22.4.  $C_{15}H_{21}BrPI, HgI_2$  requires I, 42.6; Hg, 22.4%) and the *cadmi-iodide*, needles, m. p. 178° [Found: I, 40.8; Cd, 9.3.  $(C_{15}H_{21}BrPI)_2, CdI_2$  requires I, 40.8; Cd, 9.0%]. On adding bromine to the phosphine in ether until a brown colour persisted, there was deposited an oil which solidified on being kept in a vacuum; on dissolving the solid in alcohol, adding water until turbidity developed, and allowing the mixture to stand, there formed crystals of *p-bromophenyldi-( $\beta$ -dibromo- $\beta$ -methylpropyl)phosphine oxide*, needles, m. p. 152°, from alcohol (Found: C, 26.6; H, 2.9; Br, 63.2; non-nuclear Br, 51.3.  $C_{14}H_{13}OBr_2P$  requires C, 26.6; H, 2.9; Br, 63.1; non-nuclear Br, 50.5%).

*Preparation of the Arsines.*—To the allyl or  $\beta$ -methylallyl Grignard reagent, prepared as already described, was added arsenic trichloride (6.8 c.c.) in ether (50 c.c.) or phenyldi-iodoarsine (51 g., obtained by the method of Steinkopf and Smie, *Ber.*, 1926, **59**, 1461) in ether (200 c.c.). The isolation and purification of the arsine were also effected by redistillation under low pressure in carbon dioxide.

*Phenyldiallylarsine.*—This arsine (9 g.) was prepared by the interaction of allylmagnesium bromide and phenyldi-iodoarsine; it had b. p.  $131^\circ/10$  mm. (Found: C, 61.3; H, 6.4; As, 31.3.  $C_{12}H_{15}As$  requires C, 61.5; H, 6.5; As, 32.0%). It formed the *mercurichloride*, needles, m. p.  $120^\circ$  (Found: Cl, 13.8.  $C_{12}H_{15}As, HgCl_2$  requires Cl, 14.0%).

*Tri- $\beta$ -methylallylarsine.*—The compound (6 g.), obtained from  $\beta$ -methylallylmagnesium bromide and arsenic trichloride, had b. p.  $114^\circ/15$  mm. (Found: C, 59.3; H, 8.7; As, 31.4.  $C_{15}H_{21}As$  requires C, 60.0; H, 8.8; As, 31.2%). It yielded the *mercurichloride*, needles, m. p.  $96-97^\circ$  (decomp.), from glacial acetic acid (Found: Cl, 14.2.  $C_{15}H_{21}As, HgCl_2$  requires Cl, 13.9%), and *methyltri- $\beta$ -methylallylarsonium iodide*, long rectangles, m. p.  $129^\circ$  (slight decomp.), from alcohol (Found: I, 33.0.  $C_{15}H_{24}AsI$  requires I, 33.2%).

*Phenyldi- $\beta$ -methylallylarsine.*—Interaction of the  $\beta$ -methylallyl Grignard reagent and phenyldi-iodoarsine gave the arsine (15 g.), b. p.  $153^\circ/13$  mm.,  $d_4^{20}$  1.1200 (Found: C, 63.7; H, 7.5; As, 28.7.  $C_{14}H_{19}As$  requires C, 64.1; H, 7.3; As, 28.6%). It formed *phenylmethyl-di- $\beta$ -methylallylarsonium iodide*, needles, m. p.  $163^\circ$  (slight decomp.), from water (Found: I, 31.4.  $C_{15}H_{22}AsI$  requires I, 31.4%).

*Preparation of the Stannanes.*—Triethylchlorotin, b. p.  $209-210^\circ$ , and diethyldichlorotin, m. p.  $84^\circ$ , were obtained by the methods of Kocheshkov (*J. Gen. Chem. Russia*, 1934, **4**, 1359; 1935, **5**, 211). *Tri- $n$ -butylchlorotin* (40 g.) was prepared by heating (oil-bath) a mixture of tetra- $n$ -butyltin (39 c.c.) and tin tetrachloride (4.6 c.c.) at  $230^\circ$  for 3 hours, and fractionating the product under low pressure; it had b. p.  $172^\circ/25$  mm. (Found: Cl, 11.1.  $C_{12}H_{27}SnCl$  requires Cl, 10.9%). *Di- $n$ -butyldichlorotin* (20 g.) was obtained by heating a mixture of tetra- $n$ -butyltin (16.5 c.c.) and tin tetrachloride (5.9 c.c.) for 3 hours at  $240^\circ$ , and recrystallising the product from light petroleum with cooling to  $-20^\circ$ ; it formed plates, m. p.  $40.5^\circ$  (Found: Cl, 23.3.  $C_8H_{18}SnCl_2$  requires Cl, 23.3%).

The chlorotin in benzene or ether was added to the allyl Grignard solution under hydrogen. After removal of the solvent and diallyl by distillation in carbon dioxide, the residue was dissolved in benzene (80 c.c.), the solution shaken with dilute sodium hydroxide solution to remove any traces of chloro-compound and then dried ( $CaCl_2$ ), and the stannane isolated by distillation under low pressure in carbon dioxide.

*Triethylallyltin.*—This compound (21 g.) was prepared from the allyl Grignard solution and triethylchlorotin (30 g.) in benzene (90 c.c.), and had b. p.  $76-77^\circ/10$  mm. (Found: C, 43.9; H, 8.3; Sn, 48.0.  $C_9H_{20}Sn$  requires C, 43.8; H, 8.1; Sn, 48.1%).

*Diethyldiallyltin.*—Obtained by the action of the Grignard solution on diethyldichlorotin (16.8 g.) in benzene (60 c.c.), this compound (9 g.) had b. p.  $99-100^\circ/17$  mm. (Found: C, 46.0; H, 7.7; Sn, 45.9.  $C_{10}H_{20}Sn$  requires C, 46.3; H, 7.8; Sn, 45.9%).

*Tri- $n$ -butylallyltin.*—The interaction of allylmagnesium bromide and tri- $n$ -butylchlorotin (40 g.) in ether (120 c.c.) gave this compound as a liquid (30 g.), b. p.  $155^\circ/17$  mm. (Found: C, 54.1; H, 9.8.  $C_{15}H_{32}Sn$  requires C, 54.4; H, 9.8%).

*Di- $n$ -butyldiallyltin.*—This compound (9.6 g.), prepared from the Grignard reagent and di- $n$ -butyldichlorotin (19 g.) in ether (60 c.c.), had b. p.  $145-146^\circ/17$  mm. (Found: C, 53.2; H, 9.1.  $C_{14}H_{28}Sn$  requires C, 53.2; H, 9.0%).

The following derivatives were also prepared. *Ethyltrichlorotin* (6 g.) was obtained by refluxing tetraethyltin (7.9 c.c.) and tin tetrachloride (42 c.c.) for 24 hours and fractionating the product; it had b. p.  $196-198^\circ$  (Found: Cl, 42.3.  $C_2H_5SnCl_3$  requires Cl, 41.9%). After standing, a solution of 15 g. of allylstannonic acid (Found: Sn, 62.4. Calc. for  $C_3H_5O_2Sn$ : Sn, 61.5%) in a mixture of 50 c.c. of hydrobromic acid ( $d$  1.5) and 50 c.c. of water deposited 40 g. of *allylpentabromostannic acid* (Found: Br, 71.2.  $C_3H_7Br_5Sn$  requires Br, 71.2%); it separated in small, pale yellow cubes, soluble in water but not in organic solvents, and decomposed on heating.

The physical measurements here recorded were carried out with standardised apparatus, and all relevant corrections were applied. The yields given are not of crude, but of fully purified substance. Combustions were carried out by using lead chromate-copper oxide mixtures, determinations of phosphorus by the method of Davies and Davies (*J.*, 1931, 1207), of arsenic by that of Lewis and Davis (*J.*, 1939, 286), of tin by that of Gilman and King (*J. Amer. Chem. Soc.*, 1929, **51**, 1213), and of mercury, cadmium, and iodine in complex salts by the method of Mannheim (*Annalen*, 1905, **341**, 192).