325. *Some Physical Properties of Tertiary Arsines.*

By W. J. Jones, W. J. C. Dyke, G. Davies, D. C. Griffiths, and J. H. E. Webb.

Although a number of tertiary arsines have been prepared, their physical properties have not hitherto been co-ordinated. The lack of such correlation renders the investigation of these compounds more difficult, since recorded data afford little guidance as to the probable values of those physical constants that can be taken as criteria of purity. The data and relationships now given yield approximate values of boiling point under pressures usual in the purification of these substances, of density, and of refractive index. As illustrations of the use of these relationships, the following two instances may be cited. Employing the formulæ given in the later section on physical properties, the calculated constants for *ethyldi-*n*-butylarsine* are b. p. 90°/10 mm., $d_{4^\circ}^{20^\circ}$ 0·9980, and $n_D^{20^\circ}$ 1·4742, whilst direct measurements on the freshly purified substance give b. p. 93°/10 mm., $d_{4^\circ}^{20^\circ}$ 0·9970, and $n_D^{20^\circ}$ 1·4730. Again, when *methyldi-*n*-amylarsine* is prepared from methyldihalogenoarsines and *n*-amyl Grignard reagent, it is accompanied by *n*-decane. The equation connecting the b. p. of a tri-*n*-alkylarsine with its molecular weight gives for methyldi-*n*-amylarsine the b. p. 103°/10 mm. (obs., 104°/10 mm.), whilst the b. p. of *n*-decane is 55°/10 mm., a difference which would allow of effective separation of the two products by redistillation. Similar calculations proving the difficulty of separating certain arsines from accompanying hydrocarbon are given later.

The present work has involved the preparation of several mixed arsines by the interactions between various substituted arsenic halides and Grignard reagents. Yields refer to purified products and are expressed in g. per 12 g. of magnesium used in the experiment. Thermometric readings have been corrected for errors, and weighings for air displacement. Standard manometers and barometers were used in measuring pressure. The density and refractive index of each arsine were determined as soon as possible after its final purification by distillation. This was particularly necessary, since most of these compounds readily oxidised in contact with air.

Methyldialkylarsines.—These arsines were obtained by the action of Grignard reagents on $AsMeI_2$, which was prepared by Auger's method (*Compt.*

rend., 1906, **142**, 1151) and distilled before use (b. p. 140°/30 mm.). Owing to the mildness of its interaction with the reagents, it was essential to use 4 mols. of the Mg compound to 1 of $AsMeI_2$, and to reflux the mixture for at least 3 hrs.; otherwise, the final product was contaminated with unchanged $MeAsI_2$. The proximity of the b. p. of the hydrocarbon present in the Grignard solution to that of the arsine demanded, in the case of an aliphatic compound, careful fractional redistillation for separation.

Methyldi-n-*propylarsine* (Found: C, 47·5; H, 9·7; As, 41·9. $C_7H_{17}As$ requires C, 47·7; H, 9·7; As, 42·6%) was prepared by refluxing a mixture of $AsMeI_2$ and $MgPr^{\alpha}Br$ in ethereal solution, decomposing the product with NH_4Cl aq., and fractionating the crude arsine under reduced press. (J., 1930, 2428). The purified arsine (yield, 17 g.) had b. p. 42°/10 mm., 66°/34 mm., 70°/42 mm., $d^{20^\circ}_{4^\circ}$ 1·0350, $d^{25^\circ}_{4^\circ}$ 1·0300. The following derivatives were prepared by methods already described (J., 1931, 185). In this and subsequent cases, alcohol was used for crystallisation unless otherwise stated. *Methyldi*-n-*propylarsine mercurichloride* (Found: Cl, 15·7. $C_7H_{17}As,HgCl_2$ requires Cl, 15·8%), separated from accompanying HgCl by recryst., forms white needles, m. p. 82°; *dimethyldi*-n-*propylarsonium mercuri-iodide* (Found: I, 49·2; Hg, 26·0. $C_8H_{20}IAs,HgI_2$ requires I, 49·3; Hg, 26·0%), m. p. 95°, lemon-yellow prisms.

Methyldi-n-*butylarsine* (Found: C, 52·7; H, 10·4; As, 36·2. $C_9H_{21}As$ requires C, 52·9; H, 10·4; As, 36·7%), yield 20 g., has b. p. 77°/10 mm., $d^{20^\circ}_{4^\circ}$ 1·0023. The *mercurichloride* (Found: Cl, 14·8. $C_9H_{21}As,HgCl_2$ requires Cl, 14·9%) forms bundles of prisms, m. p. 87°. *Dimethyldi*-n-*butylarsonium iodide* (Found: I, 36·6. $C_{10}H_{24}IAs$ requires I, 36·7%), has m. p. 148°; its *mercuri-iodide* (Found: I, 47·4; Hg, 25·2. $C_{10}H_{24}IAs,HgI_2$ requires I, 47·5; Hg, 25·1%), after recryst., forms pale yellow needles, m. p. 68°.

The reaction between $AsMeI_2$ and *iso*butylmagnesium bromide yielded 23 g. of purified *methyldi*iso*butylarsine* (Found: C, 52·5; H, 9·9%); b. p. 57°/10 mm., 81°/33 mm., $d^{20^\circ}_{4^\circ}$ 1·0019. On treatment of the first runnings with conc. H_2SO_4, 3 c.c. of βε-dimethylhexane, b. p. 27°/33 mm., were obtained. *Methyldi*iso*butylarsine mercurichloride* (Found: Cl, 14·8%) forms flat needles, m. p. 123°. The methiodide, after being twice recryst. from $EtOH–Et_2O$, was obtained as short needles, m. p. 174° (Dehn and Wilcox, *Amer. Chem. J.*, 1906, **35**, 18, give m. p. 155°).

*Dimethyldi*iso*butylarsonium mercuri-iodide* (Found: I, 47·2; Hg, 25·2%) crystallised as pale yellow needles, m. p. 93°.

Methyldi-n-*amylarsine* has b. p. 104°/10 mm., 121°/21 mm., 130°/33 mm., and $d^{20^\circ}_{4^\circ}$ 0·9810 (Found: C, 56·5; H, 10·6; As, 32·0. $C_{11}H_{25}As$ requires C, 56·9; H, 10·8; As, 32·3%) (yield, 20 g.); it is only partially miscible with abs. EtOH at 15°. In the isolation of the arsine, a first fraction containing 8 g. of *n*-decane, b. p. 80°/33 mm., was obtained. Its *mercurichloride* (Found: Cl, 14·0. $C_{11}H_{25}As,HgCl_2$ requires Cl, 14·1%) forms white needles, m. p. 66°. *Dimethyldi*-n-*amylarsonium iodide* (Found: I, 33·7. $C_{12}H_{28}IAs$ requires I, 33·9%) is pptd. as an oil from an ethereal solution of its constituents. On separation from the mother-liquor, the oil rapidly crystallises, and after being kept in a vacuum for a month has m. p. 45—47°.

Methyldi-n-*hexylarsine* (Found: C, 59·7; H, 11·1; As, 28·4. $C_{13}H_{29}As$ requires C, 60·0; H, 11·2; As, 28·8%) is formed from $AsMeI_2$ and *n*-hexylmagnesium bromide. There were obtained 11 g. of *n*-dodecane, b. p. 89°/10 mm., and 29 g. of purified arsine, b. p. 134°/10 mm., $d^{20^\circ}_{4^\circ}$ 0·9662; $n^{20^\circ}_{F}$ 1·4792;

$n_{\mathrm{D}}^{20^\circ}$ 1·4718; $n_{\mathrm{C}}^{20^\circ}$ 1·4688. The arsine is not completely miscible with EtOH at 15°, but mixes freely with Et_2O and with C_6H_6. The *mercurichloride* (Found: Cl, 13·4. $C_{13}H_{29}As,HgCl_2$ requires Cl, 13·3%) crystallises as aggregated flat needles, m. p. 56°.

Diarylmethylarsines.—A yield of 15 g. of purified *dicyclohexylmethylarsine* (Found: C, 61·0; H, 9·9; As, 28·9. $C_{13}H_{25}As$ requires C, 60·9; H, 9·8; As, 29·3%) was obtained from $AsMeI_2$ and *cyclo*hexylmagnesium bromide in Et_2O. In order to separate the arsine from the accompanying di*cyclo*hexyl, the product was fractionally distilled 3 times under low pressure. The arsine has b. p. 127°/4 mm., 136°/10 mm., $d_{4^\circ}^{20^\circ}$ 1·1151; $n_{\mathrm{F}}^{20^\circ}$ 1·5385; $n_{\mathrm{D}}^{20^\circ}$ 1·5300; $n_{\mathrm{C}}^{20^\circ}$ 1·5265. The *mercurichloride* (Found: Cl, 13·4. $C_{13}H_{25}As,HgCl_2$ requires Cl, 13·4%), m. p. 162°, forms a white cryst. powder. *Dicyclohexyldimethylarsonium iodide* (Found: I, 31·9. $C_{14}H_{28}IAs$ requires I, 31·9%), recryst. from H_2O, forms white plates, m. p. 185°. The *arsonium mercuri-iodide* (Found: I, 44·8; Hg, 23·3. $C_{14}H_{28}IAs,HgI_2$ requires I, 44·7; Hg, 23·5%) crystallises as pale yellow needles, m. p. 149°.

The interaction between $AsMeI_2$ and *p*-tolylmagnesium bromide in ether gives *di-*p*-tolylmethylarsine* (Found: C, 66·3; H, 6·3; As, 27·2. $C_{15}H_{17}As$ requires C, 66·2; H, 6·3; As, 27·5%), b. p. 163°/6 mm., 174°/10 mm., $d_{4^\circ}^{20^\circ}$ 1·2011; $n_{\mathrm{F}}^{20^\circ}$ 1·6269; $n_{\mathrm{D}}^{20^\circ}$ 1·6097; $n_{\mathrm{C}}^{20^\circ}$ 1·6026. Di-*p*-tolyl cryst. from the first runnings in the preliminary distillation. The liquid residue from these was added to the arsine fraction and the combined liquids were twice fractionally redistilled in a vacuum; yield, 20 g. The *mercurichloride* (Found: Cl, 12·8. $C_{15}H_{17}As,HgCl_2$ requires Cl, 13·0%), is a white powder, m. p. not sharp. The *methiodide* (Found: I, 30·8. $C_{16}H_{20}IAs$ requires I, 30·7%) is slowly formed in cold Et_2O from its components; recryst. from either H_2O or EtOH–Et_2O, it forms prisms, m. p. 177°.

Obtained from the products of interaction of $AsMeI_2$ with benzylmagnesium chloride, *dibenzylmethylarsine* (Found: C, 66·2; H, 6·1; As, 27·0. $C_{15}H_{17}As$ requires C, 66·2; H, 6·3; As, 27·5%) has b. p. 169°/5 mm., 185°/10 mm.; m. p. *ca.* 36° (thermometer in liquid); $d_{4^\circ}^{20^\circ}$ 1·2101; $n_{\mathrm{F}}^{20^\circ}$ 1·6333; $n_{\mathrm{D}}^{20^\circ}$ 1·6156; $n_{\mathrm{C}}^{20^\circ}$ 1·6083; yield, 22 g. Similarly to tribenzylarsine (Challenger and Peters, J., 1929, 2617), this arsine yields Ph·CHO during its aerial oxidation. The *mercurichloride* (Found: Cl, 13·0. $C_{15}H_{17}As,HgCl_2$ requires Cl, 13·0%) crystallises as plates, m. p. 158°.

Di-β-phenylethylmethylarsine (Found: C, 68·3; H, 7·1; As, 24·9. $C_{17}H_{21}As$ requires C, 68·0; H, 7·1; As, 24·9%) is prep. by the addition of $AsMeI_2$ to β-phenylethylmagnesium bromide; yield, 16 g.; b. p. 190°/4 mm., 212°/10 mm.; $d_{4^\circ}^{20^\circ}$ 1·1530; $n_{\mathrm{F}}^{20^\circ}$ 1·5985; $n_{\mathrm{D}}^{20^\circ}$ 1·5843; $n_{\mathrm{C}}^{20^\circ}$ 1·5785. In the prep. there were also obtained 7 g. of PhEt, b. p. 136°, and 3 g. of αδ-diphenylbutane, b. p. 316°/760 mm. The arsine is sparingly sol. in EtOH, and possesses a pleasant odour resembling that of β-phenylethyl alcohol. The *mercurichloride* (Found: Cl, 12·5. $C_{17}H_{21}As,HgCl_2$ requires Cl, 12·4%), almost insol. in EtOH, forms white needles, m. p. 165°, from glac. AcOH.

Di-β-phenylethyldimethylarsonium iodide (Found: I, 28·7. $C_{18}H_{24}IAs$ requires I, 28·7%), sparingly sol. in H_2O, cryst. as white plates, m. p. 151°.

Diphenylmethylarsine, prepared by the method of Burrows and Turner (J., 1920, **117**, 1381) and carefully purified by fractional distillation in a vacuum, had $d_{4^\circ}^{20^\circ}$ 1·2710; $n_{\mathrm{F}}^{20^\circ}$ 1·6472; $n_{\mathrm{D}}^{20^\circ}$ 1·6290; $n_{\mathrm{C}}^{20^\circ}$ 1·6215.

Dimethylalkylarsines.—These compounds and the corresponding arylarsines were obtained from Grignard reagents (2 mols.) and $AsMe_2I$ (1 mol.)

(Burrows and Turner, *loc. cit.*), the latter having been redistilled immediately before use.

Dimethylethylarsine (Found: C, 35·9; H, 8·3. Calc. for $C_4H_{11}As$: C, 35·8; H, 8·3%) was prep. using di-*n*-amyl ether as solvent (J., 1930, 2428). It was first prepared by Cahours (*Annalen*, 1862, **122**, 219). It has b. p. 86°/760 mm., $d_{4^\circ}^{20^\circ}$ 1·0990, and forms a *mercurichloride* (Found: Hg, 49·3. $C_4H_{11}As,HgCl_2$ requires Hg, 49·5%), separated from accompanying HgCl by filtration of the alc. solution, and recryst. from glac. AcOH; needles, m. p. 154°. *Trimethylethylarsonium mercuri-iodide* (Found: I, 53·0; Hg, 27·7. $C_5H_{14}AsI,HgI_2$ requires I, 52·1; Hg, 27·5%) forms yellow needles, m. p. 92°.

With *n*-propylmagnesium bromide and $AsMe_2I$ dissolved in Et_2O, *dimethyl*-n-*propylarsine* (Found: C, 40·8; H, 8·9. $C_5H_{13}As$ requires C, 40·5; H, 8·9%) is obtained, b. p. 27°/17 mm., $d_{4^\circ}^{20^\circ}$ 1·0221. It forms a *methiodide* (Found: I, 43·7. $C_6H_{16}IAs$ requires I, 43·8%), m. p. 211°.

Dimethyl-*n*-butyl-, -*n*-amyl-, and -*dl*-amylarsines were formed in Et_2O solution from $AsMe_2I$ and the Grignard reagents, but owing to the proximity of their b. p.'s to those of *n*-octane, *n*-decane, and $\gamma\zeta$-dimethyloctane, respectively, their separation could not be effected. The difficulty that arises in this method of preparation is indicated by the values of the b. p.'s of these arsines calc. by the formula given later; *e.g.*, the b. p.'s (10 mm.) of the first two arsines are 35° and 50° respectively, whereas those of *n*-octane and *n*-decane are 20° and 55°. The following derivatives were prepared directly from the ethereal solution of the arsine. *Trimethyl*-n-*butylarsonium iodide* (Found: I, 41·4. $C_7H_{18}IAs$ requires I, 41·7%), m. p. 163°; the *mercuri-iodide* (Found: I, 50·3; Hg, 26·1. $C_7H_{18}IAs,HgI_2$ requires I, 50·2; Hg, 26·4%) forms yellow needles, m. p. 120°. *Dimethyl*-n-*amylarsine mercurichloride* (Found: Cl, 15·6; Hg, 45·2. $C_7H_{17}Cl_2AsHg$ requires Cl, 15·8; Hg, 44·8%) forms rods, m. p. 87°, from glac. AcOH. *Trimethyl*-n-*amylarsonium iodide* (Found: C, 29·9; H, 6·2; I, 39·9. $C_8H_{20}IAs$ requires C, 30·2; H, 6·3; I, 39·9%), recryst. from EtOH–Et_2O, forms fine needles, m. p. 172°; the *cadmi-iodide* (Found: C, 18·7; H, 3·7. $2C_8H_{20}IAs,CdI_2$ requires C, 19·2; H, 4·0%), m. p. 186° (from EtOH). *Trimethyl*-dl-*amylarsonium iodide* (Found: I, 40·1%) has m. p. *ca.* 145°.

Aryldimethylarsines.—A yield of 8 g. of purified cyclo*hexyldimethylarsine* (Found: C, 51·2; H, 8·9; As, 39·8. $C_8H_{17}As$ requires C, 51·0; H, 9·1; As, 39·9%) was obtained from *cyclo*hexylmagnesium bromide and $AsMe_2I$. The arsine has b. p. 65°/9 mm., $d_{4^\circ}^{20^\circ}$ 1·2390. It catches fire when introduced into the air. Its *methiodide* (Found: I, 38·2. $C_9H_{20}IAs$ requires I, 38·5%) has m. p. 259° (decomp.), needles from EtOH–Et_2O; cyclo*hexyltrimethylarsonium mercuri-iodide* (Found: I, 48·6; Hg, 25·4. $C_9H_{20}I_3AsHg$ requires I, 48·5; Hg, 25·6%), m. p. 138°; the *arsonium cadmi-iodide* [Found: C, 20·9; H, 4·2; Cd, 11·1. $2C_6H_{11}As(CH_3)_3I,CdI_2$ requires C, 21·1; H, 3·9; Cd, 10·9%] m. p. 198°.

p-Dibromobenzene with Mg in Et_2O gives *p*-bromophenylmagnesium bromide (Bodroux, *Compt. rend.*, 1903, **136**, 1138), which, on treatment with $AsMe_2I$, yields p-*bromophenyldimethylarsine* (Found: C, 36·4; H, 4·1; As, 28·5. $C_8H_{10}BrAs$ requires C, 36·8; H, 3·9; As, 28·7%), b. p. 134—136°/9 mm., $d_{4^\circ}^{20^\circ}$ 1·5918; yield of purified arsine, 15 g.

Addition of $AsMe_2I$ to *o*-tolylmagnesium bromide yielded 27 g. of purified o-*tolyldimethylarsine* (Found: C, 54·8; H, 6·8; As, 38·4. $C_9H_{13}As$ requires C, 55·1; H, 6·7; As, 38·2%), b. p. 93°/10 mm., $d_{4^\circ}^{20^\circ}$ 1·1993; $n_F^{20^\circ}$ 1·5833; $n_D^{20^\circ}$

1·5690; $n_{\mathrm{C}}^{20^\circ}$ 1·5631. o-*Tolyldimethylarsine dibromide* (Found : Br, 44·5. $C_9H_{13}Br_2As$ requires Br, 44·9%), recryst. from anhyd. acetone, forms rhombs, m. p. 104°. The *hydroxybromide* [Found : Br, 27·4. $C_7H_7·As(CH_3)_2(OH)Br$ requires Br, 27·3%] separates as rectangular prisms, m. p. 182°, when H_2O–EtOH solutions of the dibromide are concentrated. o-*Tolyltrimethylarsonium iodide* (Found : I, 37·3. $C_{10}H_{16}IAs$ requires I, 37·6%) forms fibrous crystals, m. p. 290°; the *cadmi-iodide* [Found : C, 23·1; H, 3·0; I, 48·4; Cd, 11·4. $2C_7H_7·As(CH_3)_3I,CdI_2$ requires C, 23·0; H, 3·1; I, 48·7; Cd, 10·8%] white silky needles, m. p. 179°; the *mercuri-iodide* (Found : I, 48·2; Hg, 25·6. $C_{10}H_{16}IAs,HgI_2$ requires I, 48·1; Hg, 25·3%) yellow needles, m. p. 164°.

Similarly obtained, m-*tolyldimethylarsine* (Found : C, 55·4; H, 6·9; As, 38·2%) has b. p. 88°/10 mm., 115°/34 mm.; $d_{4^\circ}^{20^\circ}$ 1·1906; $n_{\mathrm{F}}^{20^\circ}$ 1·5792; $n_{\mathrm{D}}^{20^\circ}$ 1·5645; $n_{\mathrm{C}}^{20^\circ}$ 1·5584; yield, 24 g. Its *dibromide* (Found : Br, 44·8%) forms rectangular plates, m. p. 120°. m-*Tolyltrimethylarsonium iodide* (Found : I, 37·3%) crystallises in cubic form, m. p. 240°; the *cadmi-iodide*, $2C_7H_7·As(CH_3)_3I,CdI_2$ (Found : I, 49·0; Cd, 10·6%), needles, m. p. 119°; the *mercuri-iodide* (Found : I, 48·1; Hg, 25·6%), silky yellow crystals, m. p. 127°.

m-*Xylyldimethylarsine* (Found : C, 56·7; H, 7·2; As, 35·7. $C_{10}H_{15}As$ requires C, 57·1; H, 7·2; As, 35·7%) (yield, 24 g.), from the products of interaction of the Grignard reagent derived from 4-bromo-*m*-xylene and $AsMe_2I$, has b. p. 101°/10 mm., 113°/17 mm.; $d_{4^\circ}^{20^\circ}$ 1·1928; $n_{\mathrm{F}}^{20^\circ}$ 1·5793; $n_{\mathrm{D}}^{20^\circ}$ 1·5650; $n_{\mathrm{C}}^{20^\circ}$ 1·5591. Its *methiodide* (Found : I, 35·8. $C_{11}H_{18}IAs$ requires I, 36·1%) forms prisms, m. p. 203°; m-*xylyltrimethylarsonium mercuri-iodide* (Found : I, 47·6; Hg, 24·6. $C_{11}H_{18}IAs,HgCl_2$ requires I, 47·2; Hg, 24·9%) yellow flakes, m. p. 108°.

p-*Xylyldimethylarsine* (Found : C, 56·7; H, 7·3; As, 35·7%) was obtained similarly from bromo-*p*-xylene; yield, 27 g.; b. p. 113°/7 mm., 120°/10 mm.; $d_{4^\circ}^{20^\circ}$ 1·1896; $n_{\mathrm{F}}^{20^\circ}$ 1·5813; $n_{\mathrm{D}}^{20^\circ}$ 1·5670; $n_{\mathrm{C}}^{20^\circ}$ 1·5611. Its *dibromide* is hygroscopic and melts at 106° (Found : Br, 42·7. $C_{10}H_{15}Br_2As$ requires Br, 43·2%). p-*Xylyltrimethylarsonium iodide* (Found : I, 36·0%) cryst. as plates, m. p. 223°; the *mercuri-iodide* (Found : I, 46·9; Hg, 24·8%), stout yellow needles, m. p. 129°.

β-Phenylethyldimethylarsine (Found : C, 56·9; H, 7·2; As, 35·6. $C_{10}H_{15}As$ requires C, 57·1; H, 7·2; As, 35·7%) is derived from β-bromo-α-phenylethane. It has b. p. 103°/10 mm., 119°/20 mm.; $d_{4^\circ}^{20^\circ}$ 1·1621; $n_{\mathrm{F}}^{20^\circ}$ 1·5634; $n_{\mathrm{D}}^{20^\circ}$ 1·5505; $n_{\mathrm{C}}^{20^\circ}$ 1·5452. Yield, 15 g. The *hydroxybromide* [Found : Br, 25·9. $C_{10}H_{15}·As(OH)Br$ requires Br, 26·0%] has m. p. 118° (from acetone); the *methiodide* (Found : I, 36·2. $C_{11}H_{18}IAs$ requires I, 36·2%), m. p. 202°. *β-Phenylethyltrimethylarsonium cadmi-iodide* (Found : C, 25·0; H, 3·5; I, 47·2; Cd, 10·7. $2C_{11}H_{18}·AsI,CdI_2$ requires C, 24·7; H, 3·4; I, 47·4; Cd, 10·5%) forms silvery needles, m. p. 158°. Two different mercuri-iodides were obtained from alc. solutions by varying the proportions of the components used. With equimol. proportion, *β-phenylethyltrimethylarsonium mercuri-iodide* (Found : I, 47·1; Hg, 24·7. $C_{11}H_{18}AsI,HgI_2$ requires I, 47·2; Hg, 24·9%) is obtained after recrystn. as yellow needles, m. p. 116°. From 2 mols. of methiodide to 1 of HgI_2, *bis-β-phenylethyltrimethylarsonium mercuri-iodide* (Found : I, 44·0; Hg, 17·5. $2C_{11}H_{18}AsI,HgI_2$ requires I, 43·8; Hg, 17·3%) (white needles) resulted; m. p. 155° (recryst.).

Tri-β-phenylethylarsine (Found : C, 74·2; H, 6·7; As, 19·1. $C_{24}H_{27}As$ requires C, 73·8; H, 7·0; As, 19·2%) also was prepared from $AsCl_3$; yield, 12 g. It has b. p. 281°/10 mm.; $d_{4^\circ}^{20^\circ}$ 1·1545. Its *methiodide* (Found: I, 23·8. $C_{25}H_{30}IAs$ requires I, 23·8%), needles, has m. p. 115°; its *methomercuri-iodide* (Found: I, 38·8; Hg, 20·5. $C_{25}H_{30}IAs,HgI_2$ requires I, 38·6; Hg, 20·3%), yellow needles, m. p. 90°; its *dibromide* (Found: Br, 29·3. $C_{24}H_{27}Br_2As$ requires Br, 29·1%) white plates from ether, m. p. 117°.

From the products of the interaction of β-naphthylmagnesium bromide with $AsMe_2I$, *β-naphthyldimethylarsine* (Found: C, 61·7; H, 5·7; As, 32·5. $C_{12}H_{13}As$ requires C, 62·0; H, 5·6; As, 32·3%) is isolated as a liquid, b. p. 177°/10 mm.; $d_{4^\circ}^{20^\circ}$ 1·2995; $n_F^{20^\circ}$ 1·6731; $n_D^{20^\circ}$ 1·6502; $n_C^{20^\circ}$ 1·6407. The *methiodide* (Found: I, 34·2. $C_{13}H_{16}IAs$ requires I, 33·9%), fibrous crystals, has m. p. 251° (decomp.); the *methomercuri-iodide* (Found: I, 46·5; Hg, 24·5. $C_{13}H_{16}IAs,HgI_2$ requires I, 46·0; Hg, 24·2%) forms yellow needles, m. p. 154°.

Ethyldialkylarsines.—These compounds were prepared, similarly to the methylarsines, from $AsEtI_2$ (McKenzie and Wood, J., 1920, **117**, 408), which was redistilled before use (b. p. 160°/50 mm.).

Ethyldi-n-*butylarsine* (Found: C, 54·7; H, 10·6; As, 34·6. $C_{10}H_{23}As$ requires C, 55·0; H, 10·6; As, 34·4%), yield, 24 g., has b. p. 93°/10 mm., 120°/34 mm.; $d_{4^\circ}^{20^\circ}$ 0·9970; $n_F^{20^\circ}$ 1·4801; $n_D^{20^\circ}$ 1·4730; $n_C^{20^\circ}$ 1·4699. Its aerial oxidation gives the *oxide* (Found: As, 32·2. $C_{10}H_{23}OAs$ requires As, 32·0%), which after recrystn. forms plates, m. p. 133°. The *methiodide* (Found: I, 35·2. $C_{11}H_{26}IAs$ requires I, 35·2%) crystallises as needles, m. p. 168°.

When added to *n*-amylmagnesium bromide, $AsEtI_2$ gives *ethyldi*-n-*amylarsine* (Found: C, 58·7; H, 11·1; As, 30·5. $C_{12}H_{27}As$ requires C, 58·5; H, 11·1; As, 30·5%), yield, 28 g.; b. p. 119°/10 mm., 152°/39 mm.; $d_{4^\circ}^{20^\circ}$ 0·9886. The *oxide* (Found: As, 28·5. $C_{12}H_{27}OAs$ requires As, 28·6%) forms plates, m. p. 74°.

There were also prepared *dicyclohexylethylarsine* (Found: C, 61·6; H, 10·0; As, 27·7. $C_{14}H_{27}As$ requires C, 62·2; H, 10·1; As, 27·7%), yield 15 g., b. p. 161°/10 mm., 183°/23 mm.; and the *methiodide* (Found: I, 30·8. $C_{15}H_{30}IAs$ requires I, 30·8%), needles, m. p. 135°.

n-*Butyldialkylarsines.*—Prepared from purified *n*-butyldichloroarsine (Quick and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 805), *diethyl*-n-*butylarsine* (Found: C, 50·7; H, 10·1; As, 39·3. $C_8H_{19}As$ requires C, 50·5; H, 10·1; As, 39·4%) has b. p. 64°/10 mm., 97°/48 mm.; $d_{4^\circ}^{20^\circ}$ 1·0193; $n_F^{20^\circ}$ 1·4837; $n_D^{20^\circ}$ 1·4752; $n_C^{20^\circ}$ 1·4717; yield, 23 g. The *oxide* (Found: As, 36·4. $C_8H_{19}OAs$ requires As, 36·4%) forms feathery crystals, m. p. 103°; the *methiodide* (Found: I, 38·2. $C_9H_{22}IAs$ requires I, 38·2%), needles, m. p. 128°.

Di-n-*propyl*-n-*butylarsine* (Found: C, 55·0; H, 10·6; As, 34·0. $C_{10}H_{23}As$ requires C, 55·0; H, 10·6; As, 34·4%) has b. p. 88°/10 mm., 117°/36 mm.; $d_{4^\circ}^{20^\circ}$ 0·9945; $n_F^{20^\circ}$ 1·4812; $n_D^{20^\circ}$ 1·4731; $n_C^{20^\circ}$ 1·4697; yield, 23 g. The *oxide* (Found: As, 31·9. $C_{10}H_{23}OAs$ requires As, 32·0%) forms plates, m. p. 106°; the *methiodide* (Found: I, 35·5. $C_{11}H_{26}IAs$ requires I, 35·3%) needles, m. p. 190°; the *ethiodide* (Found: I, 34·3. $C_{12}H_{28}IAs$ requires I, 33·9%) needles, m. p. 192°.

Phenyldialkylarsines.—$AsPhCl_2$ (Morgan and Vining, J., 1920, **117**, 780) reacts with *n*-propyl- and *n*-amyl-magnesium bromide to give *phenyldi*-n-*propylarsine* (Found: C, 60·5; H, 7·9. $C_{12}H_{19}As$ requires C, 60·5; H, 8·0%) and *phenyldi*-n-*amylarsine* (Found: As, 25·9. $C_{16}H_{27}As$ requires As, 25·5%) respectively. The former has b. p. 125°/10 mm., 141°/19 mm.; $d_{4^\circ}^{20^\circ}$ 1·1078; $n_F^{20^\circ}$ 1·5595; $n_D^{20^\circ}$ 1·5463; $n_C^{20^\circ}$ 1·5409; the latter has b. p. 174°/10 mm., 186°/16 mm.

Diphenylalkylarsines.—With *n*-propylmagnesium bromide, $AsPh_2Cl$ (Morgan and Vining, *loc. cit.*) gives *diphenyl*-n-*propylarsine* (Found : C, 66·3; H, 6·2; As, 27·5. $C_{15}H_{17}As$ requires C, 66·2; H, 6·3; As, 27·5%); yield, 20 g.; b. p. 177°/10 mm.; $d_{4^\circ}^{20^\circ}$ 1·1964; $n_F^{20^\circ}$ 1·6220; $n_D^{20^\circ}$ 1·6054; $n_C^{20^\circ}$ 1·5986. The *mercurichloride* (Found: Hg, 36·7. $C_{15}H_{17}As,HgCl_2$ requires Hg, 36·9%) forms prisms, m. p. 152°. *Diphenylmethyl*-n-*propylarsonium iodide* (Found : I, 31·0. $C_{16}H_{20}IAs$ requires I, 30·7%), on recryst. from H_2O, separates as needles, m. p. 153°.

There is similarly obtained *diphenyl*-n-*butylarsine* (Found : C, 66·7; H, 6·4; As, 26·0. $C_{16}H_{19}As$ requires C, 67·1; H, 6·7; As, 26·2%); yield, 6 g.; b. p. 183°/10 mm., 197°/17 mm. Its *methiodide* (Found : I, 28·9. $C_{17}H_{22}IAs$ requires I, 29·6%) has m. p. 140°.

*Diphenyl*iso*butylarsine* (Found : C, 67·1; H, 6·7; As, 26·2%) has b. p. 185°/10 mm.; $d_{4^\circ}^{20^\circ}$ 1·1819; yield, 15 g. The *hydroxybromide* [Found : Br, 21·1. $C_{16}H_{19}As(OH)Br$ requires Br, 20·9%] crystallised as needles, m. p. 116°, from acetone; the *methiodide* (Found : I, 29·9%) forms hexagonal plates, m. p. 152°, from aq. EtOH.

Diphenyl-n-*amylarsine* (Found : C, 67·2; H, 7·0; As, 24·8. $C_{17}H_{21}As$ requires C, 68·0; H, 7·1; As, 24·9%) has b. p. 194°/10 mm., $d_{4^\circ}^{20^\circ}$ 1·1617; $n_F^{20^\circ}$ 1·5993; $n_D^{20^\circ}$ 1·5846; $n_C^{20^\circ}$ 1·5786. *Diphenyl*-dl-*amylarsine* (Found : As, 25·0%) boils at 195°/10 mm.; $d_{4^\circ}^{20^\circ}$ 1·1624. Yields of both, 10 g.

Saturated Vapour Pressures, Molecular Volumes, and Refractivities of Tertiary Arsines.

The following table incorporates results obtained by the authors, and by previous investigators, of whom the chief have been Landolt (*Annalen*, 1854, **54**, 301); Winmill (J., 1912, **101**, 718); Turner, Burrows, Roberts, and Bury (J., 1920, **117**, 1378; 1921, **119**, 426; 1926, 1443); Steinkopf, Schwen, Donat, and Jaeger (*Ber.*, 1921, **54**, 1437; 1922, **55**, 2597); Mills and Raper (J., 1925, **127**, 2479); Gryszkiewicz-Trochimowski, Zambrzycki, and Sikorski (*Rocz. Chem.*, 1926, **6**, 794; 1927, **7**, 54; 1928, **8**, 250; *Bull. Soc. chim.*, 1927, **41**, 1570).

As will be seen from the table, for arylarsines containing one or more complete benzene rings in the molecule, the mol. vol. at 20°, V_{20°, is approx. given by the equation, $V_{20^\circ} = 50{\cdot}50 + 63{\cdot}72r + 16{\cdot}128c$, wherein r denotes the number of such rings, and c the number of *additional* C atoms in saturated alkyl groups. For instance, tri-β-phenylethylarsine contains 3 rings and 6 additional C atoms, whence the calc. value of $d_{4^\circ}^{20^\circ}$ is 1·1528 (obs., 1·1545). For aliphatic arsines containing 3 saturated alkyl groups, including cases where such groups are *iso*, the mol. vol. is given by $V_{20^\circ} = 57{\cdot}26 + 16{\cdot}128C$, wherein C denotes the *total* number of carbon atoms in the mol.

The b. p./10 mm., $t_{10\ \text{mm.}}$, of an arsine containing 3 *n*-alkyl groups is approx. given by $t_{10\ \text{mm.}} = 18{\cdot}30M^{0{\cdot}555} - 273{\cdot}1$, where M denotes the mol. wt. of the arsine. If 1 phenyl group and 2 *n*-alkyl groups

Arsine.	B. p./10 mm.		Mol. vol., c.c. at 20°.		$[R_L]_\lambda$, found.		
	Found.	Calc.	Found.	Calc.	F.	D.	C.
Trimethyl	−30°	−12°	106·6	105·6	—	—	—
Triethyl	+36	+35	141·2	154·0	43·18	42·47	42·20
Tri-*n*-propyl	75	77	198·5	202·4	57·08	55·83	55·50
Tri-*n*-butyl	116	116	247·6	250·8	70·83	69·81	69·42
Tri-*n*-amyl	150	151	294·1	299·2	84·21	83·06	82·61
Tri-*n*-hexyl	181	184	341·0	347·6	98·16	96·87	96·44
Tri-*n*-heptyl	202	216	390·3	395·9	111·63	110·04	109·48
Tri-*n*-octyl	243	246	443·2	444·3	126·27	124·68	124·02
Tri*iso*butyl	94	—	255·3	250·8	71·67*	70·66*	70·24*
Tri-*dl*-amyl	135	—	299·8	299·2	85·19*	84·03*	83·55*
Tri*iso*amyl	142	—	301·6	299·2	85·71*	84·52*	84·02*
Tri*iso*hexyl	175	—	352·8	347·6	99·72*	98·42*	97·88*
Dimethylethyl	− 5	+ 4	122·0	121·8	—	—	—
Dimethyl-*n*-propyl	+18	+20	144·8	137·9	—	—	—
Methyldi-*n*-propyl	42	50	170·1	170·2	—	—	—
Methyldi-*n*-butyl	77	77	203·6	202·4	—	—	—
Methyldi-*n*-amyl	104	103	236·6	234·7	—	—	—
Methyldi-*n*-hexyl	134	128	269·2	266·9	76·39*	75·38*	74·97*
Methyldi*iso*butyl	57	—	203·8	202·4	—	—	—
Diethyl-*n*-butyl	64	64	186·3	186·3	53·32*	52·52*	52·19*
Ethyldi-*n*-propyl	58	64	—	—	—	—	—
Ethyldi-*n*-butyl	93	90	218·8	218·5	62·16*	61·37*	61·03*
Ethyldi-*n*-amyl	119	115	249·0	250·8	—	—	—
Di-*n*-propyl-*n*-butyl	88	90	219·3	218·5	62·44*	61·54*	61·15*
Di*cyclo*hexylmethyl	136	—	229·7	—	71·91*	70·96*	70·56*
Di*cyclo*hexylethyl	161	—	—	—	—	—	—
Triallyl	76	—	179·9	—	56·66	55·55	55·04
Phenyldimethyl	80	87	—	—	48·27	47·25	46·80
Phenyldiethyl	106	103	—	—	58·89	57·72	57·24
Phenyldi-*n*-propyl	125	127	214·9	211·0	69·44	68·08	67·52
Phenyldi-*n*-amyl	174	172	—	—	—	—	—
Phenylmethylethyl	92	90	—	—	—	—	—
Phenylmethyl-*n*-propyl	102	103	—	—	—	—	—
Phenylethyl-*n*-propyl	114	115	—	—	—	—	—
p-Tolylmethylethyl	108	—	—	—	—	—	—
Diphenylmethyl	157	155	192·0	194·1	69·80†	68·23†	67·58†
Diphenylethyl	163	165	—	—	74·78	73·13	72·45
Diphenyl-*n*-propyl	177	175	227·4	226·3	80·09	78·36	77·64
Diphenyl-*n*-butyl	183	184	—	—	—	—	—
Diphenyl-*n*-amyl	194	194	258·4	258·6	88·31	86·55	85·82
Diphenyl-*dl*-amyl	195	—	258·2	258·6	—	—	—
Diphenyl*iso*butyl	185	—	242·1	242·4	—	—	—
o-Tolyldimethyl	93	—	163·4	162·6	54·65	53·55	53·09
m-Tolyldimethyl	88	—	164·6	162·6	54·73	53·59	53·11
p-Tolyldimethyl	95	—	—	—	—	—	—
p-Tolyldiethyl	118	—	—	—	—	—	—
Di-*o*-tolylmethyl	175	—	—	—	—	—	—
Di-*p*-tolylmethyl	174	—	226·5	226·3	80·29	78·51	77·77
Benzyldimethyl	115	—	—	—	—	—	—
Dibenzylmethyl	185	—	224·8	226·3	80·33	78·53	77·78
m-Xylyldimethyl	101	—	176·1	178·7	58·55	57·36	56·87
p-Xylyldimethyl	120	—	176·6	178·7	58·88	57·68	57·19
β-Phenylethyldimethyl	103	—	180·7	178·7	58·74	57·63	57·16
Di-β-phenylethylmethyl	212	—	260·3	258·6	88·87	87·15	86·45
Tri-β-phenylethyl	281	—	337·9	338·4	—	—	—
α-Naphthyldimethyl	157	—	—	—	—	—	—
β-Naphthyldimethyl	177	—	178·5	—	66·94	65·14	64·39

* See p. 2292.

† Gryszkiewicz-Trochimowski and Sikorski (*Bull. Soc. chim.*, 1927, **41**, 1574) give 69·80, 68·21, and 67·58, respectively.

are present, the relationship becomes $t_{10\ \mathrm{mm.}} = 25{\cdot}96M^{0{\cdot}500} - 273{\cdot}1$, and if 2 phenyl groups and 1 *n*-alkyl, $t_{10\ \mathrm{mm.}} = 43{\cdot}90M^{0{\cdot}4144} - 273{\cdot}1$. These relationships are of the type proposed by Walker (J., 1894, **65**, 193). The extent of agreement of b. p.'s thus calculated with those observed is indicated in the table.

For pressures from 5 mm. to 50 mm., a range which includes pressures usual in the distillation of organic arsines, the saturated v. p., *p* mm., of tri-*n*-amylarsine is related to temp., $t°$, by the equation, $8{\cdot}6780 - \log_{10}p = 3256{\cdot}1/(t + 273{\cdot}1)$. This equation permits of the calculation of b. p.'s of arsines under pressures other than 10 mm., by the assumption that the ratio of the abs. b. p.'s of two arsines under one press. is equal to that under another. For instance, taking tri-*n*-amylarsine as a standard of reference, the calc. b. p.'s are 151°/10 mm., 184°/36 mm., 164°/17 mm., and 167°/19 mm., whilst the b. p.'s/10 mm., $t_{10\ \mathrm{mm.}}$, of di-*n*-propyl-*n*-butyl-, diphenyl-*n*-butyl-, and phenyldi-*n*-propyl-arsine given by the previous equations are 90°, 184°, and 127° respectively; whence are calculated, as indicated, the following b. p.'s; di-*n*-propyl-*n*-butylarsine, 118°/36 mm. (obs., 117°); diphenyl-*n*-butylarsine, 198°/17 mm. (obs., 197°); phenyldi-*n*-propylarsine, 142°/19 mm. (obs., 141°).

Comparison of the b. p. of an *iso*alkylarsine with that of the corresponding *n*-alkyl compound shows that, in general, branching of the carbon chain confers increased volatility, although the influence becomes less marked with increased mol. wt. and with the presence of aryl groups.

The general effect of increased mol. wt. in lowering volatility and density in the case of arsines is obvious throughout the table, and although good agreement is usually found between the results of direct determinations and the values calculated by the relationships here given, yet the lowest members of the homologous series show the greatest discrepancies.

The values of $[R_L]$ asterisked in the table include all the non-exaltative systems investigated in the present work, and, after the deduction from them of the values of the atomic refractivity of C and H (Eisenlohr, *Z. physikal. Chem.*, 1910, **75**, 585) there are left consistent values for the atomic refractivity of arsenic in these compounds, of which the following are the mean: for F, 12·30; for D, 11·96; for C, 11·83.

As Gryszkiewicz-Trochimowski and Sikorski (*Bull. Soc. chim.*, 1927, **41**, 1570) have already indicated, the presence of aryl groups, in general, causes optical exaltation, and this constitutive effect precludes the inclusion of calculated values of mol. refractivity in the above table.

In conclusion, it has to be pointed out that the regularities indicated in the present work do not extend to cacodyls or to arsepidines.

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