XXV.—*Some Aliphatic Compounds of Arsenic.*

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The present communication contains a description of the properties of a few compounds derived from the lower tertiary arsines.

The arsines used were prepared by the action of arsenic trichloride on the Grignard reagents, and were purified by redistillation under the lowest convenient pressure. The boiling points, $t°$, of tri-*n*-propylarsine, when distilled in nitrogen under low pressures, p mm., were found to be 84°/17 mm., 92°/27 mm., and 113°/79 mm., which are related by the equation $10{\cdot}2378 - \log_{10} p = 3215/(t + 273)$. For 12 mm. the equation gives b. p. 78°, in agreement with that given by Grischkevitsch-Trochimovski and Sikorski (*Bull. Soc. chim.*, 1927, **41**, 1572), *viz.*, 78·5—79°/12 mm.; Dehn and Williams (*Amer. Chem. J.*, 1908, **40**, 112), however, give b. p. 158°/73 mm. and 167°/90 mm.

Exposed to the air, the arsine gradually deposits the oxide, which can also be prepared by shaking either an alcoholic solution of the arsine with red mercuric oxide or a similar solution of the arsine dibromide with silver oxide. *Tri*-n-*butylarsine oxide* [Found: C, 54·8; H, 10·6; As, 28·7. $(C_4H_9)_3AsO$ requires C, 54·9; H, 10·4; As, 28·6%] forms pasty crystals, insoluble in water or in ether, but soluble in alcohol. Obtained by aerial oxidation of the arsine in ether, *tri*-n-*amylarsine oxide* [Found: C, 59·3; H, 11·2; As, 24·4. $(C_5H_{11})_3AsO$ requires C, 59·2; H, 10·9; As, 24·6%] forms an oil which slowly solidifies when kept in the presence of sulphuric acid.

Prepared by the method of Hantzsch and Hibbert (*Ber.*, 1907, **40**, 1512), *tri*-n-*propylarsine sulphide* [Found: S, 13·3; As, 31·1. $(C_3H_7)_3AsS$ requires S, 13·6; As, 31·7%] and *tri*iso*butylarsine sulphide* [Found: S, 11·7. $(C_4H_9)_3AsS$ requires S, 11·5%] crystallise as long colourless needles.

When an alcoholic solution of the arsine dibromide is shaken with a slight excess of silver sulphate, the precipitated silver bromide removed, and the filtrate diluted with ether, *tri*-n-*propylarsine sulphate* [Found: SO_4, 31·6. $(C_3H_7)_3AsSO_4$ requires SO_4, 32·0%] is obtained as white hairy crystals, m. p. 84°, easily soluble in alcohol and immediately deliquescent in the air.

When a dilute solution of chlorine in carbon tetrachloride is cautiously added to a solution of an arsine in the same solvent, considerable evolution of heat ensues, and there results a solution of the arsine dichloride, which remains as white crystals on evaporation of the solvent in a vacuum. The dichlorides are easily soluble in water or alcohol; they are best recrystallised from ether. They are less hygroscopic than the corresponding dibromides. *Tri-*n*-propylarsine dichloride* [Found : C, 39·2 ; H, 7·9 ; Cl, 25·8 ; As, 27·2. $(C_3H_7)_3AsCl_2$ requires C, 39·2 ; H, 7·7 ; Cl, 25·8 ; As, 27·3%] forms elongated prisms, m. p. 84°. *Tri-*n*-butylarsine dichloride* [Found : Cl, 22·2 ; As, 23·4. $(C_4H_9)_3AsCl_2$ requires Cl, 22·4 ; As, 23·6%] has m. p. 40°. *Triiso*butylarsine dichloride* [Found : C, 45·1 ; H, 8·6 ; Cl, 22·0 ; As, 23·6. $(C_4H_9)_3AsCl_2$ requires C, 45·4 ; H, 8·6 ; Cl, 22·4 ; As, 23·6%] forms square white plates, m. p. 130°. *Tri-*n*-amylarsine dichloride* [Found: Cl, 19·4. $(C_5H_{11})_3AsCl_2$ requires Cl, 19·7%] is a sweet-smelling liquid.

Arsine dibromides are produced when carbon tetrachloride solutions of their components are mixed, and the solvent is expelled ; excess of bromine gives a deep red coloration, due probably to the formation of perbromide. When recrystallised from acetone, the arsine dibromides form colourless, highly hygroscopic crystals, which are easily soluble in alcohol, in ether, and in carbon tetrachloride. When the crystals are exposed to chlorine, or are treated with nitric or sulphuric acid, bromine is expelled. *Tri-*n*-propylarsine dibromide* [Found : C, 29·4 ; H, 5·9 ; Br, 43·4 ; As, 20·5. $(C_3H_7)_3AsBr_2$ requires C, 29·7 ; H, 5·8 ; Br, 43·9 ; As, 20·6%] forms stout rods, m. p. 95° ; *tri-*n*-butylarsine dibromide* (Found : Br, 39·3 ; As, 18·2. $C_{12}H_{27}Br_2As$ requires Br, 39·4 ; As, 18·5%) crystallises as cubes, m. p. 55° ; *triiso*butylarsine dibromide* (Found : C, 35·4 ; H, 7·1 ; Br, 39·4. $C_{12}H_{27}Br_2As$ requires C, 35·5 ; H, 6·7 ; Br, 39·4%), rhombs, m. p. 135° ; *tri-*n*-amylarsine dibromide* (Found : Br, 35·2. $C_{15}H_{33}Br_2As$ requires Br, 35·7%) is a liquid.

Yellow flocculent precipitates of arsine di-iodides are obtained on mixing solutions of iodine and of the arsines in light petroleum. The di-iodides are very soluble in water and in alcohol, but insoluble in ether. On short exposure to the air, they become dark brown. *Tri-*n*-propylarsine di-iodide* (Found : I, 55·6. $C_9H_{21}I_2As$ requires I, 55·4%), m. p. *ca.* 130° (after previous darkening) ; *tri-*n*-butylarsine di-iodide* (Found : I, 51·1. $C_{12}H_{27}I_2As$ requires I, 50·8%), m. p. 124° ; *triiso*butylarsine di-iodide* (Found : I, 50·6%), m. p. 117—119° (after previous darkening).

With mercuric chloride, trialkylarsines yield double compounds of the general formula $R_3As,HgCl_2$. These compounds slowly separate from alcoholic solutions of equivalents of their components, and may be recrystallised from alcohol. There were thus obtained the *mercurichlorides* of tri-*n*-propylarsine, $(C_3H_7)_3As,HgCl_2$ (Found : Cl, 14·9. Calc. : Cl, 14·9%), m. p. 106°, of tri-*n*-butylarsine, $(C_4H_9)_3As,HgCl_2$ (Found : Cl, 13·8. Calc. : Cl, 13·7%), m. p. 70°, and of tri*iso*butylarsine, $(C_4H_9)_3As,HgCl_2$ (Found : Cl, 13·5. Calc. : Cl, 13·7%), m. p. 158°.

Landolt (*Annalen*, 1854, **92**, 370) claimed to have prepared a double compound of triethylarsine dichloride with mercurous oxide (Found : C, 16·59, 17·05 ; H, 4·24, 4·63 ; Cl, 16·37, 17·19 ; Hg, 48·22, 47·06%). From his method of preparation, *viz.*, mixing alcoholic solutions of mercuric chloride and of triethylarsine, there is little doubt that he was dealing with an impure specimen of triethylarsine mercurichloride [$(C_2H_5)_3As,HgCl_2$ requires C, 16·61 ; H, 3·49 ; Cl, 16·35 ; Hg, 46·26%].

Methiodides are readily obtained when equivalents of arsine and methyl iodide are mixed in ethereal solution. They may be recrystallised from water or alcohol or alcohol–ether. *Methyltriethylarsonium iodide* (Found : I, 41·7. $C_7H_{18}IAs$ requires I, 41·7%) has m. p. 270°. *Methyltri*-n-*propylarsonium iodide* (Found : I, 36·6. $C_{10}H_{24}IAs$ requires I, 36·7%) forms hexagonal prisms, m. p. 204°. *Methyltri*iso*butylarsonium iodide* (Found : I, 32·6. $C_{13}H_{30}IAs$ requires I, 32·7%) forms well-developed tabular crystals, m. p. 254° (after previous darkening). The following were prepared in less pure condition : *methyltri*-n-*butylarsonium iodide* (Found : I, 32·7. $C_{13}H_{30}IAs$ requires I, 32·7%) ; *ethyltri*-n-*butylarsonium iodide* (Found : I, 31·6. $C_{14}H_{32}IAs$ requires I, 31·6%), m. p. *ca.* 107° ; *methyltri*-n-*amylarsonium iodide* (Found : I, 30·1. $C_{16}H_{36}IAs$ requires I, 29·5%), obtained as an oil.

Chloroplatinates as follows have been obtained from the arsonium chlorides. *Methyltri*-n-*propylarsonium chloroplatinate*,

$$[CH_3\cdot As(C_3H_7)_3]_2PtCl_6$$

(Found : C, 28·2 ; H, 5·7 ; Cl, 24·9. $C_{20}H_{48}Cl_6As_2Pt$ requires C, 28·3 ; H, 5·7 ; Cl, 25·1%), m. p. 219° (decomp.), forms elongated orange plates. *Methyltri*iso*butylarsonium chloroplatinate*,

$$[CH_3\cdot As(C_4H_9)_3]_2PtCl_6$$

(Found : C, 33·3 ; H, 6·7 ; Cl, 23·0. $C_{26}H_{60}Cl_6As_2Pt$ requires C, 33·5 ; H, 6·5 ; Cl, 22·9%), m. p. 224° (decomp.), orange needles. *Methyltri*-n-*amylarsonium chloroplatinate*, $[CH_3\cdot As(C_5H_{11})_3]_2PtCl_6$ (Found : C, 37·6 ; H, 7·3 ; Cl, 20·8. $C_{32}H_{72}Cl_6As_2Pt$ requires C, 37·8 ; H, 7·2 ; Cl, 21·0%), orange plates, m. p. 114°. These chloroplatinates were recrystallised from alcohol.

When hot alcoholic solutions of cadmium iodide and of arsine methiodide are mixed and then cooled, white arsonium cadmi-iodide crystallises. These compounds are fairly soluble in boiling water or alcohol, and easily in cold acetone ; they are best recrystallised from alcohol. *Methyltriethylarsonium cadmi-iodide*, $2CH_3\cdot As(C_2H_5)_3I,CdI_2$ (Found : C, 17·2 ; H, 3·7 ; I, 52·3 ; Cd, 11·6. $C_{14}H_{36}I_4As_2Cd$ requires C, 17·2 ; H, 3·7 ; I, 52·1 ; Cd, 11·5%) crystallises as flakes, m. p. 283° (with volatilisation). *Methyltri*-n-*propylarsonium cadmi-iodide*, $2CH_3\cdot As(C_3H_7)_3I,CdI_2$ (Found : C, 22·7 ; H, 4·8 ; I, 48·1 ;

Cd, 10·7. $C_{20}H_{48}I_4As_2Cd$ requires C, 22·7; H, 4·6; I, 47·9; Cd, 10·6%) forms needles which volatilise a few degrees above their m. p. 279°. *Methyltri*-n-*butylarsonium cadmi-iodide*, $CH_3\cdot As(C_4H_9)_3I,CdI_2$ (Found: C, 20·5; H, 4·1; I, 50·3; Cd, 14·6. $C_{13}H_{30}I_3AsCd$ requires C, 20·7; H, 4·0; I, 50·5; Cd, 14·9%) forms stellate needles, m. p. 100°. *Methyltri*iso*butylarsonium cadmi-iodide*, $CH_3\cdot As(C_4H_9)_3I,CdI_2$ (Found: C, 20·7; H, 4·3; I, 50·4; Cd, 15·2. $C_{13}H_{30}I_3AsCd$ requires C, 20·7; H, 4·0; I, 50·5; Cd, 14·9%), needles, m. p. 138°. It is noteworthy that, whilst the methyltriethyl and methyltri-*n*-propyl compounds are of the type $2MeR_3AsI,CdI_2$, similarly to the compounds $2Me_4AsI,CdI_2$ and $2Et_4AsI,CdI_2$ (Cahours, *Annalen*, 1862, **122**, 207, 201), the more easily fusible methyltributyl compounds have the formula $MeBu_3AsI,CdI_2$.

Methyltri-n-*propylarsonium mercurichloride* [Found: Cl, 20·6; Hg, 38·1. $CH_3\cdot As(C_3H_7)_3Cl,HgCl_2$ requires Cl, 20·2; Hg, 38·1%] is obtained on adding a hot alcoholic solution of mercuric chloride to a similar solution of the methochloride, and cooling. On recrystallisation from alcohol, the mercurichloride separates as white needles, m. p. 141°.

With mercuric iodide, the methiodides of the arsines give yellow compounds of the general formula MeR_3AsI,HgI_2 (Cahours, *loc. cit.*; Mannheim, *Annalen*, 1905, **341**, 182; Dehn and Williams, *loc. cit.*). Prepared by mixing hot alcoholic solutions of its components, and recrystallised from alcohol, *methyltriethylarsonium mercuri-iodide* [Found: I, 50·1; Hg, 26·4. $CH_3\cdot As(C_2H_5)_3I,HgI_2$ requires I, 50·2; Hg, 26·4%] forms needles, m. p. 61°; *methyltri*-n-*propylarsonium mercuri-iodide* (Found: I, 47·6; Hg, 24·5. $C_{10}H_{24}I_3AsHg$ requires I, 47·6; Hg, 25·0%), needles, m. p. 90°; *methyltri*-n-*butylarsonium mercuri-iodide* (Found: I, 45·1; Hg, 23·7. $C_{13}H_{30}I_3AsHg$ requires I, 45·2; Hg, 23·8%) and *methyltri*iso*butylarsonium mercuri-iodide* (Found: I, 45·2; Hg, 23·8%) have m. p.'s 76° and 117° respectively.

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