32. *The Formation of Organo-metalloidal Compounds by Micro-organisms. Part I. Trimethylarsine and Dimethylethylarsine.*

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GMELIN (*Karlsruher Ztg.*, November, 1839) ascribed certain cases of poisoning to a volatile arsenic compound liberated from mouldy wall-paper in damp rooms and mentioned the garlic odour observed under such conditions. Selmi (*Ber.*, 1874, **7**, 1642) suggested that the moulds produced hydrogen, which reduced the arsenic in the pigment to hydrogen arsenide. He appears to have been the first to ascribe an active rôle to the moulds. The production of hydrogen arsenide is mentioned by Martin (*Gazette Médicale*, 1847, Feb. 13, p. 130) and Fleck (*Z. Biol.*, 1872, **8**, 444), but from the work of Pool, Klason, and others (see below) there is no doubt that this substance is absent. Basedow (*Schmidt's Jahrbuch*, 1846, **52**, 89) suggested the presence of cacodyl oxide in the arsenical gas.

Gosio (*Arch. Ital. Biol.*, 1893, **18**, 253, 298; 1901, **35**, 201; *Ber.*, 1897, **30**, 1024) states that *Aspergillus glaucus*, *A. virens*, *Mucor mucedo*, and *M. ramosus* in addition to *Penicillium brevicaule* produce this gas (Gosio-gas), which, from the results of a combustion, he believed to be an alkyl arsine. Biginelli (*Gazzetta*, 1901, **31**, i, 58) aspirated the gas from cultures of *P. brevicaule* on potato-mash containing arsenious oxide through acidified mercuric chloride: the precipitate was assigned the composition $Et_2AsH,2HgCl_2$; and on recrystallisation two further products were obtained, one of which he believed to be $(Et_2AsH)_2O,4HgCl_2$.

On these grounds Biginelli regarded the gas as diethylarsine, Klason (*Ber.*, 1914, **47**, 2634) as diethylarsine oxide. Wigren (*Annalen*, 1924, **437**, 285) synthesised these compounds and stated that their behaviour towards acid $HgCl_2$ solution (Biginelli's solution) was different from that of Gosio-gas.

Cevey (*Dissertation*, Lausanne, 1902) and Pool (*Pharm. Weekblad*, 1912, **49**, 878) found that a garlic odour is also evolved in mould cultures containing sodium cacodylate. Puntoni (*Annali d'Igiene*, 1917, **27**, 293) noticed this odour in a liquid containing sodium cacodylate, on which a growth of a " Penicillium " had formed. The gas was not identified. He also detected, in the breath of patients receiving sodium cacodylate by the mouth, a garlic odour which he attributed to the agency of intestinal organisms, and he isolated from the fæces various bacteria (*B. mesentericus vulgatus*, *B. mes. ruber*, and *B. subtilis*), which gave this odour on media containing sodium cacodylate.

Maassen (*Arb. Kais. Gesund.*, 1902, **18**, 479), Abel and Buttenberg (*Z. Hyg.*, 1899, **32**, 449), and Huss (*ibid.*, 1914, **76**, 361) give bibliographies on arsenical moulds.

Lerrigo (*Analyst*, 1932, **57**, 155, 163) has discussed the recent Forest of Dean cases where fatal poisoning occurred in rooms of which the plaster and wall-paper contained arsenic (Daily Press, 19—20 Jan., 1932).

We have prepared diethylarsine oxide by Wigren's method (*loc. cit.*). It has a pungent odour entirely different from that of Gosio-gas. With alcoholic mercuric chloride it gives $(Et_2As)_2O,2HgCl_2$, decomposing without melting (Grischkewitsch-Trochimowski, *Rocz. Chem.*, 1928, **8**, 423). Contrary to the statements of Wigren, we find that it forms a mercurichloride with Biginelli's solution, which differs from that obtained in alcohol in being stable to hydrochloric acid.

Diethylarsine also has been prepared. Its reaction with mercuric chloride was again different from that of Gosio-gas, calomel and mercury being formed. The main product was shown by Grischkewitsch-Trochimowski (*ibid.*, 1929, **9**, 742) to be identical with that obtained directly from diethylchloroarsine. The composition given by Wigren ($Et_2AsCl,2HgCl$) is incorrect; his product probably contained calomel.

The mercurichlorides obtained from both diethylarsine and its oxide behave towards sodium hydroxide differently from those yielded by Gosio-gas, reduction occurring without production of odour.

The properties of the mould gas are also different from those of methylarsine or ethylarsine (Dehn, *Amer. Chem. J.*, 1905, **33**, 127; 1908, **40**, 88), which oxidise in air to form red solids and with mercuric chloride solution give calomel and mercury methylarsonate and ethyldichloroarsine respectively.

The synthesis of *hydroxytriethylarsonium picrate* and *benzyltriethylarsonium picrate* conclusively showed that triethylarsine is not the arsenical ingredient of Gosio-gas.

In our study of the nature of Gosio-gas, four strains of *Penicillium brevicaule* (*Scopulariopsis brevicaulis*) were cultivated on sterile bread-crumbs containing arsenious oxide and all gave rise to trimethylarsine, no other arsenical gas being detected. The gases were aspirated through Biginelli's solution by means of sterile air. The precipitate (B_1), m. p. 264°, appeared to be identical with Biginelli's second compound, m. p. 270°, and consisted of trimethylarsine dimercurichloride. On passage of the gas for some weeks, the m. p. fell to about 221°, recrystallisation giving trimethylarsine monomercurichloride (B_2), m. p. 224—226°.

Trimethylarsine with Biginelli's solution gave a precipitate which, alone or with B_1, melted at 265°. The mercurichloride, m. p. 224—226°, precipitated from dilute Biginelli's solution was identical with B_2, similarly obtained from Gosio-gas.

When the arsenious oxide is replaced by sterilised solutions of sodium methylarsonate or sodium cacodylate (free from inorganic arsenic), but without other alteration of the experimental procedure, a gas is evolved giving a mercurichloride identical in m. p., mixed m. p., and behaviour on crystallisation with that obtained from arsenious oxide.

The identity of Gosio-gas has been confirmed by several independent observations: (a) Compounds B_1, m. p. 264°, and B_2, m. p. 226°, with nitric acid give hydroxytrimethylarsonium nitrate, m. p. 128—129°, which is also obtained from Gosio-gas and nitric acid.

(b) Both these nitrates give hydroxytrimethylarsonium picrate, m. p. and mixed m. p. 218—219°.

(c) Synthetic trimethylarsine and hydrogen peroxide give trimethylarsine oxide and thence the picrate, m. p. and mixed m. p. 218—219°.

(d) Evaporation of B_1 with hydrogen peroxide gives *hydroxytrimethylarsonium chloride mercurichloride*, m. p. and mixed m. p. 135—136°, identical with that obtained from synthetic trimethylarsine.

(e) Gosio-gas and benzyl chloride give a quaternary salt and thence a picrate, m. p. and mixed m. p. with benzyltrimethylarsonium picrate, 173—174° (Ingold, Shaw, and Wilson, J., 1928, 1280). This was kindly supplied by Dr. E. H. Ingold, and had been obtained from benzyldimethylarsine and methyl iodide. This picrate is also identical with a specimen obtained from synthetic trimethylarsine and benzyl chloride (m. p. and mixed m. p. 173—174°).

Benzyltriethylarsonium chloride, m. p. 167—168°, and *picrate*, m. p. 83—84°, were prepared from triethylarsine for comparison.

Since aliphatic arsines are oxidised in air, it was necessary in order fully to establish the identity of Gosio-gas (which is obtained in highly aerated cultures) to show that trimethylarsine volatilises unchanged in air. On passage of air over or through its solution in *iso*amyl ether–xylene and then into Biginelli's solution, the precipitate obtained had m. p. and mixed m. p. 265° with B_1 obtained from Gosio-gas. With greatly diluted Biginelli's solution the air–synthetic arsine mixture gave the monomercurichloride B_2, m. p. 224—226°.

The behaviour of sodium ethylarsonate to cultures of the mould on sterile bread-crumbs has been studied. A garlic odour was evolved and Biginelli's solution gave a solid (B_4), m. p. 240—241°, which depressed the m. p. 264° of the mercurichloride (B_1) obtained from the methylarsonate cultures, to 247°. B_4 was also obtained when air was drawn through an *iso*amyl ether solution of dimethylethylarsine into Biginelli's solution.

Dimethylethylarsine (Jones, J., 1932, 2284) forms two mercurichlorides, $Me_2EtAs,HgCl_2$, m. p. 154°, and $Me_2EtAs,2HgCl_2$, m. p. 240—241° and at 240° in admixture with B_4 (m. p. 240—241°).

The gas from the ethylarsonate cultures with benzyl chloride yielded a picrate, m. p. and mixed m. p. 113—114° with synthetic *benzyldimethylethylarsonium picrate*, prepared from dimethylethylarsine and benzyl chloride.

Absorption of the mould gas in nitric acid gives a nitrate and thence a picrate, m. p. and mixed m. p. 162—163° with synthetic *hydroxydimethylethylarsonium picrate*.

In the search for a possible mechanism of the production of Gosio-gas attempts have been made to correlate this change with the processes of carbohydrate breakdown (see also, Gosio, *loc. cit.*, 1901, **35**, 211). The production of acetic acid by way of pyruvic acid and acetaldehyde being assumed, its condensation with arsenious acid might yield trimethylarsine in a reaction analogous to Cadet's synthesis of cacodyl (Morgan, "Organic Derivatives of Arsenic and Antimony," 1918, 1—15): $3Me{\cdot}CO_2H + As(OH)_3 = 3CO_2 + Me_3As + 3H_2O$. Acetic acid is not a frequent product of mould metabolism, nor, apart from the production of methane by various bacteria from calcium acetate (Stephenson, " Bacterial Metabolism," 1930, 133), is it readily decarboxylated by micro-organisms.

A more attractive hypothesis is that formaldehyde, the methylating action of which is generally assumed in the higher plants, may be produced by the mould from the carbohydrate or the protein of the bread and undergo condensation with arsenious acid, $H{\cdot}AsO(OH)_2$, giving hydroxymethylarsonic acid, $CH_2(OH){\cdot}AsO(OH)_2$, which might undergo reduction first to methylarsonic acid and then to $CH_3{\cdot}As(OH)_2$ or $CH_3{\cdot}AsHO(OH)$, which could again react with formaldehyde, finally yielding cacodylic acid, $(CH_3)_2AsO{\cdot}OH$, from which trimethylarsine oxide, $(CH_3)_3AsO$, and by reduction trimethylarsine could arise. This suggestion is put forward with all reserve.

The scheme presents analogies with the method for the alkylation of arsenious oxide (Morgan, *op. cit.*, p. 29; Auger, *Compt. rend.*, 1903, **137**, 925; Wigren, *Annalen*, 1924, **437**, 287).

The formation of α-hydroxyethylphosphonic acid, $OH{\cdot}CHMe{\cdot}PO(OH)_2$, from paracetaldehyde and phosphorous acid, and of similar compounds (Ville, *Ann. Chim. Phys.*, 1891, **23**, 350; Marie, *ibid.*, 1904, **3**, 407), furnishes some support for this suggestion.

Hausmann (*Beitr. Chem. Phys. Path.*, 1904, **5**, 397) found that the actinia *Aiptasia diaphana*, Rapp, produces a garlic odour in sea-water containing arsenious oxide. This he attributed chiefly to the brown algæ (Zooxanthellen) living in symbiosis with the animal. The brown and green algæ contain chlorophyll and build up their protoplasm from carbon dioxide, water, and a source of nitrogen like the green plants. If, as is probable, this proceeds by way of formaldehyde, the production of volatile arsenic compounds by these organisms and by moulds may be explicable along similar lines. This question is under investigation and the research is being extended to include compounds of selenium and tellurium (Rosenheim, P., 1902, 138).

EXPERIMENTAL.

Two of the strains of *Penicillium brevicaule*, designated *P. brevicaule* Saccardo and *P. brevicaule* var. *alba*, Thom, were obtained from the Centraal Bureau voor Schimmelcultures, Baarn. The first strain (A) was usually employed and was originally isolated by Professor Biourge and sent to Baarn in August, 1929. The second (B) was isolated by Dr. Church from Camembert cheese and sent to Baarn in April, 1925. These are now registered in the Baarn List of Fungi, 1932, as *Scopulariopsis brevicaulis* (Sacc.) Bainier and *Scopulariopsis brevicaulis* (Sacc.) Bainier var. *alba* Thom.

Other strains used were *P. brevicaule* (strain Derx) (C) and *P. brevicaule* Saccardo (strain Washington 2) (D), being Nos. 1362 and 580, National Collection of Type Cultures, Lister Institute, respectively. No. 1362 was isolated from air by Dr. Derx, Delft, and No. 580 from cheese by Dr. Church. These were maintained in a virile condition by occasional sub-culturing onwort-agar or potato-agar media.

Procedure.—Fresh bread crumbs (with or without added H_2O) were used in conical flasks such that after sterilisation (25—30 min. at 120°) a layer 1—1·5 in. deep was obtained. 150—200 G., 250—300 g., and 400—500 g. of fresh crumbs were required for the 1, 3, and 4 l. flasks respectively. These were inoculated with an aq. spore suspension of the mould A or D from a potato-agar slope culture, incubated for 3—4 days at 32° to obtain a good mycelial growth and then at room temp. for 4—5 days more until spores just tinged with brown were obtained. B and C grew very poorly at 32° and cultures were grown at room temp. for 16 days (B) and for 7 days (C).

Aq. solutions of the As compounds, sterilised for 25—30 min. at 120°, were added direct or from a sterile pipette, and the cotton-wool plugs replaced by rubber bungs carrying tubes lightly plugged with cotton-wool. These had been sterilised at 120° for 25—30 min., and dried at 50° or at room temp. The flasks were arranged in series (or two sets of 3 or 4 flasks in series were placed in parallel), connected to an empty bottle and then to the absorption flasks. A continuous stream of air, sterilised by passage through H_2SO_4, sterile cotton-wool, $HgCl_2$ aq. (1 in 1000), and again sterile cotton-wool (Raistrick, *Phil. Trans.*, 1931, *B*, **220**, 15), was passed through and volatile As compounds were absorbed in suitable reagents. Sterilised solutions of all As compounds, other than As_2O_3, were found to be free from inorg. As. The average concn. of the As_2O_3 was 0·2—0·25 g., of the methylarsonate 1—1·5 g., and of the cacodylate 0·1—0·3 g.

per 100 g. of fresh crumbs. The ethylarsonate was used in concns. of 0·2—0·25 and 0·5 g. of the acid sodium and potassium salts respectively, per 100 g. of crumbs.

Mould Products.—Trimethylarsine dimercurichloride, $Me_3As,2HgCl_2$ (B_1). The action of all four strains of *P. brevicaule* on media containing As_2O_3, and of Mould A (Baarn strain) on media containing sodium methylarsonate or sodium cacodylate, produces a volatile compound which in Biginelli's solution (10 pts. $HgCl_2$; 20 pts. HCl; 80 pts. H_2O) gives a white cryst. ppt., m. p. 262—264° (decomp.). Recryst. from hot dil. aq. $HgCl_2$, it gives white plates, m. p. 264—265° (decomp.), not depressing the m. p. of $Me_3As,2HgCl_2$ obtained from synthetic Me_3As and Biginelli's solution (see p. 100). From hot H_2O alone this product tends to lose Me_3As, and on long boiling a little HgCl is formed. Mixed m. p. determinations and analyses indicate that the products from all the sources are identical. Repeated treatment of B_1 with hot acetone gives B_2 [Found: (As_2O_3) C, 5·6; H, 1·55; Cl, 21·3; Hg, 60·7; (arsonate) C, 5·6; H, 1·5; Cl, 21·1; (cacodylate) C, 5·5; H, 1·3; Cl, 21·55, 21·0. $C_3H_9Cl_4AsHg_2$ requires C, 5·4; H, 1·4; Cl, 21·4; Hg, 60·5%].

Trimethylarsine monomercurichloride, $Me_3As,HgCl_2$ (B_2). With Gosio-gas and Biginelli's solution, from which a considerable quantity of $Me_3As,2HgCl_2$ has already separated, a second product, m. p. 220—222°, is obtained which, recryst. from hot H_2O, gives needles, m. p. 224—226°, not depressing the m. p. of authentic $Me_3As,HgCl_2$ (see p. 100). This product was noticed during the action of Mould A on sodium methylarsonate (Found: C, 9·3; H, 1·7; Cl, 17·7, 18·4. $C_3H_9Cl_2AsHg$ requires C, 9·2; H, 2·3; Cl, 18·1%).

Very prolonged passage of the gas dissolves the ppt., forming a solution (B_3). This with $HgCl_2$ aq. gives B_2, which in aq. solution gives B_1 on treatment with more $HgCl_2$. On evaporating B_3 under diminished press., B_1 is pptd.

With NaOH, B_1 and B_2 give an intense garlic odour (resembling that of the polymethylene sulphides), and yellow HgO is pptd., which quickly blackens owing to reduction to Hg_2O. NH_3 aq. gives the same odour, but no blackening occurs, indicating the absence of HgCl.

Hydroxytrimethylarsonium nitrate, $Me_3As(OH){\cdot}NO_3$. (a) Direct absorption in HNO_3 of the volatile product from the action of Mould A on As_2O_3, sodium methylarsonate, and sodium cacodylate and of *P. brevicaule* var. *alba* and *P. brevicaule* (Derx strain) on As_2O_3 gives on concn. and recrystn. of the residue from acetone–Et_2O, long needles, m. p. 128—129°, not depressing the m. p. of the *hydroxy-nitrate* obtained indirectly (see below) or from synthetic Me_3As.

(b) The same product was obtained indirectly: (1) from B_1 and B_2 and HNO_3, extraction with acetone, and recrystn. from acetone–Et_2O; (2) from B_1 and NaOH aq., filtration, and evapn. with HNO_3 (Found: C, 18·65, 18·3; H, 4·45, 5·1; N, 6·5, 6·3. $C_3H_{10}O_4NAs$ requires C, 18·1; H, 5·1; N, 7·0%).

Hydroxytrimethylarsonium picrate, $Me_3As(OH){\cdot}O{\cdot}C_6H_2(NO_2)_3$. Addition of sat. aq. sodium picrate to conc. aq. hydroxy-nitrate gives a *picrate*, m. p. 218—219° after recrystn. from hot H_2O (Found: C, 29·7; H, 3·45; N, 11·5. $C_9H_{12}O_8N_3As$ requires C, 29·6; H, 3·3; N, 11·5%).

Benzyltrimethylarsonium picrate, $CH_2Ph{\cdot}AsMe_3{\cdot}O{\cdot}C_6H_2(NO_2)_3$. (a) The volatile product from cultures of Mould A and sodium methylarsonate was absorbed in alc. CH_2PhCl. After several days the EtOH was removed, the quaternary salt extracted with H_2O, the solution washed with Et_2O, and sodium picrate added. The ppt. had m. p. 169—171°, and 173—174° after crystn. from hot H_2O. It did not depress the m. p. of benzyltrimethylarsonium picrate (173—174°). (b) The solid B_1 from cultures of Mould A and As_2O_3, sodium methylarsonate, or sodium cacodylate was suspended in EtOH–CH_2PhCl in CO_2 and treated with H_2S. The HgS was separated, and EtOH removed from the filtrate, which, treated as in (a), gave in each case a picrate, m. p. 173—174° on recrystn. and mixed m. p. 173—174° with authentic $CH_2Ph{\cdot}AsMe_3{\cdot}O{\cdot}C_6H_2(NO_2)_3$, m. p. 173—174°, or with a second specimen obtained from Me_3As and CH_2PhCl (see p. 100) (Found: C, 43·95; H, 4·0; N, 9·3. Calc.: C, 43·75; H, 4·1; N, 9·6%).

Mercurichloride of Hydroxytrimethylarsonium Chloride, $Me_3As(OH)Cl,HgCl_2$.—Crude B_1, m. p. 264°, from cultures of Mould A (Baarn strain) and sodium methylarsonate was suspended in H_2O and H_2O_2, boiled under reflux, and filtered. The residue contained unchanged mercurichloride and HgCl. The evaporated filtrate, extracted with EtOH or acetone, gave a solid, m. p. 133—134°, which, recryst. from MeOH–light petroleum (b. p. 40—60°), had m. p. 135—136° and did not depress the m. p. (135—136°) of the product obtained from synthetic Me_3AsO and Biginelli's solution. It was also obtained from the (mould) mercurichloride B_1 with HCl aq. and a few drops of HNO_3 and extraction with EtOH (Found: C, 8·1; H, 2·3; Cl, 23·6, 24·2; Hg, 44·7. $C_3H_{10}OCl_3AsHg$ requires C, 8·1; H, 2·3; Cl, 24·0; Hg, 45·2).

P. Brevicaule, *Sacc. (Baarn Strain) with Sodium Ethylarsonate.—Dimethylethylarsine dimercurichloride.* The gas from the cultures with Biginelli's solution gave white crystals, m. p.

238° (decomp.), which after recrystn. from hot H_2O containing a little $HgCl_2$ melted and decomposed at 240—241° and did not depress the m. p. (240—241°) of synthetic $Me_2EtAs,2HgCl_2$ (see p. 101) (Found : C, 7·3; H, 1·6; Cl, 21·0. $C_4H_{11}Cl_4AsHg_2$ requires C, 7·1; H, 1·6; Cl, 20·9%).

Hydroxydimethylethylarsonium picrate. Absorption in HNO_3 and evapn. gave an oil solidifying in a few days. This was deliquescent and with sat. aq. sodium picrate gave a *picrate* of const. m. p. 161—162·5° on recrystn. from hot H_2O, not depressing the m. p. of a specimen similarly prepared from synthetic dimethylethylarsine (Found : C, 31·8; H, 3·8; N, 11·15. $C_{10}H_{14}O_8N_3As$ requires C, 31·7; H, 3·7; N, 11·1%).

Benzyldimethylethylarsonium picrate. The alc. CH_2PhCl used for absorption was treated as before. With sodium picrate it gave a ppt. which, recryst. from hot H_2O, had m. p. and mixed m. p. 113—114° with synthetic *benzyldimethylethylarsonium picrate*, m. p. 113—114° (see p. 101) (Found : C, 45·1; H, 4·5; N, 9·2. $C_{17}H_{20}O_7N_3As$ requires C, 45·0; H, 4·45; N, 9·3%).

Control Experiments.—Mould A on As-free bread crumbs gave no garlic odour and no ppt. in Biginelli's solution. Uninoculated bread crumbs containing (a) As_2O_3, (b) sodium methylarsonate, (c) sodium cacodylate in the concns. used in the mould expts. gave no garlic odour and no ppt. in Biginelli's solution.

Preparation of Reference Compounds from Synthetic Arsines.—(1) *Benzyltrimethylarsonium picrate.* Trimethylarsine in xylene and *iso*amyl ether (XI solution) was prepared as described by Dyke and Jones (J., 1930, 2428). A slow stream of air was passed over the XI solution and through (a) CH_2PhCl in EtOH, (b) dil. NaOH aq., (c) Biginelli's solution for 48 hr. The liquid in (a) was treated as on p. 99 and gave a picrate which, cryst. from hot H_2O, had m. p. 173°, and 173—174° in admixture with benzyltrimethylarsonium picrate.

(2) *Trimethylarsine dimercurichloride.* The arsine was not completely absorbed in (a) and a ppt. formed in (c), m. p. 263° (decomp.) and 264—265° on crystn. from hot H_2O containing $HgCl_2$. The same compound was obtained from pure liquid Me_3As (Found : C, 5·5; H, 1·3; Cl, 21·6; Hg, 61·1. Calc. for $C_3H_9Cl_4AsHg_2$: C, 5·4; H, 1·4; Cl, 21·4; Hg, 60·5%).

(3) Trimethylarsine monomercurichloride was obtained from the calc. quantities of Me_3As and $HgCl_2$ in EtOH and also in dil. HCl aq. The ppt. sintered slightly at 218°, melted at 224—226°, and at the same temp. after recrystn. from H_2O, from which it separated in needles entirely different from the plates of the dimercurichloride (Found : C, 9·3; H, 2·3; Cl, 18·3. Calc. for $C_3H_9Cl_2AsHg$: C, 9·2; H, 2·3; Cl, 18·1%).

(4) *Hydroxytrimethylarsonium nitrate.* The XI solution was heated at 100°, and CO_2 passed through it into HNO_3. Evapn. of the latter left white needles, the hydroxy-nitrate, m. p. 128—129° after recrystn. from acetone–Et_2O (Found : C, 18·3; H, 5·1; N, 6·4. Calc. for $C_3H_{10}O_4NAs$: C, 18·1; H, 5·1; N, 7·0%).

(5) *Hydroxytrimethylarsonium picrate.* The nitrate gave a picrate, m. p. 218—219° after crystn. from H_2O (Valeur gives m. p. 219·5°; *Bull. Soc. chim.*, 1927, **41**, 1489) (Found : C, 29·6; H, 3·3; N, 11·2. Calc. for $C_9H_{12}O_8N_3As$: C, 29·6; H, 3·3; N, 11·5%). The same picrate was obtained from Me_3As by conversion into the dibromide, solution in H_2O, and treatment with sodium picrate.

CO_2 was passed through heated XI solution into H_2O_2 (20 vol.) for 6 hr. Evapn. left a hygroscopic solid (S), m. p. about 110° (decomp.). In MeOH this gave with sat. methyl-alc. picric acid a picrate, m. p. and mixed m. p. 218—219° with the hydroxytrimethylarsonium picrate from (5) (Found: C, 29·6; H, 3·3; N, 11·2%). (S) was therefore trimethylarsine oxide or dihydroxide.

(6) Hydroxytrimethylarsonium chloride mercurichloride, m. p. 136°, was obtained from the synthetic dimercurichloride both with H_2O_2 and with HCl aq. containing a little HNO_3 and from Me_3AsO and Biginelli's solution (Found: C, 8·3; H, 2·3; Cl, 23·8; Hg, 45·1. Calc. for $C_3H_{10}OCl_3AsHg$: C, 8·1; H, 2·3; Cl, 24·0; Hg, 45·2%).

(7) *Benzyltriethylarsonium chloride and picrate.* The arsine (1 c.c.) and CH_2PhCl (1 c.c.) were heated in CO_2 at 100° for a few hours. The solid was dissolved in H_2O and washed with Et_2O, and the aq. solution evaporated. Crystn. from acetone–Et_2O gave deliquescent leaflets, m. p. 167—168° after drying over H_2SO_4 (Found : by Volhard's method : Cl, 12·8. $C_{13}H_{22}ClAs$ requires Cl, 12·3%).

The *chloride* gave *benzyltriethylarsonium picrate*, m. p. 83—84·5° after recrystn. from aq. MeOH (Found : C, 47·4; H, 4·8; N, 8·6. $C_{19}H_{22}O_7N_3As$ requires C, 47·4; H, 5·0; N, 8·7%).

(8) *Hydroxytriethylarsonium picrate.* Et_3As (1·5 c.c.) in EtOH (25 c.c.) was shaken with red HgO (4 g.) in CO_2 for 24 hr. The liquid was filtered, heated to coagulate Hg, again filtered, and concentrated. The residue gave with aq. sodium picrate golden needles, m. p. 121—122° after two crystns. from MeOH. The mixed m. p. with picric acid (m. p. 121—122°) was 84—115° (Found : C, 35·2; H, 4·5; N, 10·1. $C_{12}H_{18}O_8N_3As$ requires C, 35·4; H, 4·5; N, 10·3%).

(9) *Benzyldimethylethylarsonium picrate.* During the distillation of dimethylethylarsine from the *iso*amyl ether (Jones, J., 1932, 2287) some escaped with the CO_2 stream and was absorbed in alc. CH_2PhCl. The quaternary compound gave the picrate as before, m. p. 113—114° after crystn. from hot H_2O (Found : C, 45·15; H, 4·25; N, 9·85. Calc. for $C_{17}H_{20}O_6N_3As$: C, 45·0; H, 4·45; N, 9·3%).

(10) *Dimethylethylarsine dimercurichloride.* The arsine in CO_2 as above gave a white ppt. with Biginelli's solution, m. p. 238° (decomp.). Recryst. from H_2O containing $HgCl_2$, this had m. p. 240—241° (Found : C, 7·15; H, 1·5; Cl, 21·0. Calc. for $C_4H_{11}Cl_4AsHg_2$: C, 7·1; H, 1·6; Cl, 20·9%).

The CO_2 stream gave with diluted Biginelli's solution the monomercurichloride, m. p. 154° (Jones, *loc. cit.*).

(11) *Hydroxydimethylethylarsonium picrate.* The synthetic arsine in CO_2 was passed through HNO_3 (*d* 1·41) for several hours. The solution was then concentrated, and the deliquescent solid converted into picrate, which, cryst. from H_2O, had m. p. 162—163° (Found : C, 31·7; H, 3·7; N, 11·3. Calc. for $C_{10}H_{14}O_8N_3As$: C, 31·7; H, 3·7; N, 11·1%).

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