THE CHLOROVINYLARSINES

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Following the announcement by Gibson and Pope (10) that ethylene is absorbed by the chlorides of sulfur, forming β,β'-dichlorodiethyl sulfide, Green and Price (12) began their study of the action of acetylene and ethylene upon inorganic, anhydrous chlorides.

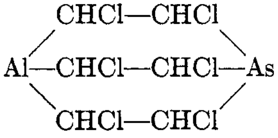
Dafert (4) studied the reaction of acetylene upon arsenic trichloride at ordinary temperature and at the boiling point of the latter and found that there was no appreciable reaction; in the presence of anhydrous aluminum chloride at ordinary temperature, however, he isolated a product, a heavy, yellow oil, boiling at 108°C. at 7 mm. and at 250°C. at 760 mm., specific gravity, $d^{15°}_{4°}$, 1.6910, with strongly irritating vapors but not marked by poisonous properties although exhibiting strong bactericidal power, to which he gave the name diacetylene arsenic trichloride and ascribed the formula, $AsCl_3 \cdot 2C_2H_2$. He apparently regarded the substance as an association product rather than a secondary arsine, although the properties correspond to those of bis(β-chlorovinyl)chloroarsine. He does not report finding the corresponding compounds of arsenic trichloride with one and three molecules of acetylene, respectively.

Lewis and Stiegler (18) likewise found that all efforts to add acetylene to arsenic trichloride directly under a wide variety of physical conditions proved ineffectual. After many catalysts employed, only two, aluminum chloride and mercuric chloride, have served to effect the addition. The addition of acetylene to arsenic trichloride, both with and without polymerization, is recorded by Baud (2), and a number of compounds of aluminum chloride, acetylene, and alcohol have been isolated by Gangloff and Henderson (7). Fischer (6) added arsenic trichloride to the acids of the acetylene series, and found that the addition of arsenic trichloride and chlorine took place at the triple bond.

As to the use of aluminum chloride in this reaction, it was shown by Lewis and Perkins (17) and confirmed by Mann and Pope (19) and Green and Price (12) that an intermediate addition compound is formed of one molecule each of arsenic trichloride and aluminum chloride with three molecules of acetylene, $Al(CHClCHCl)_3As$. This conclusion was based upon the observation that a fresh reaction mixture on processing yields more tris(β-chlorovinyl)arsine, $(ClCH{:}CH)_3As$, than is present in an equilibrium mixture of arsenic trichloride, β-chlorovinyldichloroarsine, bis(β-chlorovinyl)arsine, and tris(β-chlorovinyl)arsine, of the same acetylene content. In other words, some agency had caused more molecules of acetylene to combine with arsenic in the ratio of three of acetylene to one of arsenic than is found under equilibrium conditions. This equilibrium value was previously established by heating pure tris(β-chlorovinyl)arsine with arsenic trichloride until the system had reached a constant value for the four components present.

Moreover it was found noteworthy, that when a fresh reaction mixture of arsenic trichloride, aluminum chloride, and acetylene was allowed to stand at room temperature, or preferably warmed in the presence of free arsenic trichloride, there was an appreciable rise in the content of the primary and secondary chlorovinylarsines at the expense of the tertiary. This shift of the system in favor of the primary and secondary arsines could be increased by the addition to the fresh reaction mixture of more arsenic trichloride, before it had been allowed to stand or become warmed. Curiously enough, a number of substances, particularly metallic aluminum, increased the velocity of the change to equilibrium.

It was concluded, therefore, that the three arsines had their origin in the three following intermediate compounds:



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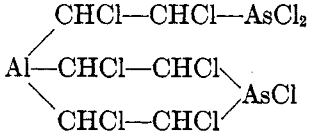

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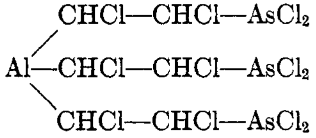


III

Compound I was believed by Lewis and Stiegler (18) to be formed when acetylene is conducted into arsenic trichloride containing aluminum chloride; compounds II and III are formed by the further reaction of compound I with one and two more molecules, respectively, of arsenic trichloride.

The arsines are obtained from these intermediate compounds by washing the reaction mixture with 20 per cent hydrochloric acid to constant volume and distilling the resulting mixture. The intermediate compounds undergo hydrolysis, the aluminum being removed in the dilute hydrochloric acid.

Further experimental evidence in support of this explanation of the reaction was sought on the following basis. Three molecules of acetylene may add one molecule each of arsenic trichloride and aluminum chloride simultaneously, or in two steps. Presumably, the addition takes place in two steps, the aluminum chloride adding first to form $(CHCl{:}CH)_3Al$, since acetylene cannot be made to add arsenic trichloride in the absence of a suitable catalyst. Moreover, aluminum chloride is known to add acetylene. This intermediate catalyst compound would then add arsenic trichloride to form the assumed parent compound, $Al(CHClCHCl)_3As$. It may be seen at once that if this assumption is correct the halogens on the original arsenic and aluminum, respectively, are attached to the carbon atoms in the β-position to the corresponding metal. On hydrolysis, distilling, etc., the aluminum chloride and the organic arsenic compounds would be freed with the same halogen atoms as those with which the respective metals were originally combined. Therefore, the nature of the halide of arsenic used in the reaction determines the nature of the halogen in the resulting organic arsenical compounds, irrespective of the kind of aluminum halide used as the catalyst. Arsenic trichloride should give a vinylarsine containing chlorine, and arsenic tribromide a compound containing bromine with either aluminum chloride or aluminum bromide. Arsenic tribromide, acetylene, and aluminum chloride would thus form $Al(CHBr\text{-}CHCl)_3As$ as an intermediate compound, while arsenic trichloride and aluminum bromide should simultaneously give $Al(CHClCHBr)_3As$. The former would finally yield bromoarsines and the latter chloroarsines.

This has been found by Mann and Pope (19) to be experimentally true and offers further experimental confirmation of this explanation of the reaction. Moreover, in no instance were organic arsenic compounds isolated containing mixed halogens.

β-CHLOROVINYLDICHLOROARSINE, $CHCl{:}CHAsCl_2$

The most important chlorovinylarsine, the chemical agent which created the most discussion during the latter part of the World War and about which many unauthentic stories were circulated, was "Lewisite," or, as the press and laity called it, "Methyl," chemically known as β-chlorovinyldichloroarsine and having the formula represented by $CHCl{:}CHAsCl_2$.

Preparation

β-Chlorovinyldichloroarsine has been prepared, along with the secondary and tertiary arsines, by passing acetylene into arsenic trichloride to which has been added anhydrous aluminum chloride (9, 12, 17, 18, 19, 21); by reducing a hot hydrochloric acid solution of β-chlorovinylarsinic acid, $CHCl{:}CH\text{—}AsO(OH)_2$, with sulfur dioxide using hydrogen iodide as a catalyst (9); by heating a mixture of arsenic trichloride with tris(β-chlorovinyl)arsine in a sealed tube for four hours at 220°C. according to the reaction (12):

$$(CHCl{:}CH)_3As + 2AsCl_3 \rightarrow 3CHCl{:}CHAsCl_2$$

Physical properties

β-Chlorovinyldichloroarsine is a colorless or faintly yellow liquid miscible in all proportions with absolute alcohol, benzene, kerosene, olive oil, liquid petrolatum, and the common organic solvents. It is insoluble in cold water or dilute acids, but is hydrolyzed on standing or warming in water. It is colorless and stable when pure, but in the presence of small amounts of arsenic trichloride acquires a violet to dark purple color on standing, the speed of the change and the depth of color depending upon the amount of arsenic trichloride present as an impurity (17).

It has the following physical constants. Boiling point: 203°C. (14), 190°C. (1, 17, 26, 28), 98°C. at 30 mm. (17), 96°C. at 30 mm. (12), 93–94°C. at 24 mm. (3), 93°C. at 26 mm. (12), 82°C. at 16.5 mm. (19), 79°C. at 15 mm. (17), 77–78°C. at 12 mm. (29), 76.1°C. at 10 mm. (9), 76–77°C. at 12.5 mm. (19), 72°C. at 10 mm. (17), 71–74°C. at 15 mm. (27), 69.5–70.5°C. at 10 mm. (13). Its melting point has been reported as follows: 0.1°C. (9, 15), −13°C. (1, 26, 28). Specific gravity: $d^{10.6°}_{4.0°}$, 1.8954 (13); $d^{20°}_{4°}$, 1.8880 (17); $d^{23.7°}_{4.0°}$ (vacuum), 1.8819 (15); $d^{26.1°}_{4.0°}$ (vacuum), 1.8754 (9); $d^{30°}_{4°}$ (vacuum), 1.8648 (9). Vapor pressure, log = 9.123 − 2781.69/T (17); 0.087 at 0°C. (28); 0.395 at 20°C. (28). One cubic meter of saturated vapor contains 0.395 g. at 20°C., 15.60 g. at 40°C. (1, 26, 28). The index of refraction at 10.6°C. has the following values: $n_\alpha = 1.6092$, $n_D = 1.6153$, $n_\beta = 1.6333$ (13); at 23.7°C., $n_C = 1.6025$, $n_D = 1.6092$, $n_F = 1.6251$ (15). The molecular refraction for the D sodium line is 38.14 at 10.6°C. (13), 38.16 at 23.7°C. (15); for the α and β hydrogen lines at 10.6°C., it is 37.83 and 38.98, respectively (13).

Chemical properties

(*a*) *Reaction with water.* When an alcoholic solution of β-chlorovinyldichloroarsine is added to water, complete hydrolysis of the chlorine attached to the arsenic occurs within a few minutes at 20°C.; at 5°C., 90 per cent hydrolyzes rapidly, the rest more slowly; undiluted at 20°C., it hydrolyzes similarly to the alcoholic solution at 5°C. (22).

(*b*) *Reaction with an alkali hydroxide.* A dilute solution of an alkali hydroxide, even when cold, causes a vigorous reaction, acetylene being evolved with brisk effervescence which is quantitative, according to Nekrasov and Nekrasov (21). When β-chlorovinyldichloroarsine is treated with one-half its weight of water and an excess of dilute ammonium hydroxide is added slowly, β-chlorovinylarsenious oxide, $CHCl{:}CHAs{:}O$, is formed. It is a white crystalline powder melting at 143°C. when slowly heated; it is very slightly soluble in water and carbon disulfide, more soluble in xylene and slightly soluble in alcohol, especially when boiled (18).

(*c*) *Reaction with halogens.* Halogens are rapidly absorbed with the formation of a variety of products. Thus, if a dilute solution of bromine in carbon tetrachloride be added slowly to a solution of the chloroarsine in the same solvent, the color of the bromine slowly disappears, and on shaking, or on keeping, fine leaflets of a bromo compound separate, m.p. 122°C. (12).

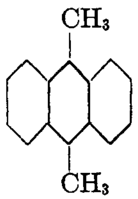
(*d*) *Reaction with nitric acid.* β-Chlorovinyldichloroarsine is vigorously oxidized when warmed with an equal volume of concentrated nitric acid; the oxidation sets in spontaneously in the cold, and the resulting solution, when chilled and scratched, deposits β-chlorovinylarsinic acid, $CHCl{:}CHAsO(OH)_2$, as a mass of colorless crystals. The acid crystallizes from a mixture of acetone and carbon tetrachloride in long needles, melting at 130°C. (19). When crystallized from organic solvents such as an equal mixture of acetone and carbon tetrachloride, the crystals appear as fine needles. Both these latter and the larger, flat, hexagonal type obtained by the action of hydrogen peroxide on β-chlorovinylarsenious oxide show the same crystallographic measurements and characteristics. Both kinds of crystals are biaxial, positive, orthorhombic, and have the same measurements: α, 1.555; β, 1.565; γ, 1.705; birefringence $\gamma - \alpha$, 150 (18). When the acid is heated in a vacuum at 110–115°C., it loses one molecular proportion of water, giving the corresponding anhydride, β-chlorovinylarsenic oxide, $CHCl{:}CHAsO_2$. It forms a fine, white hygroscopic powder and decomposes violently at 242°C. All attempts to recrystallize it result in the production of the original acid (19).

(*e*) *Reaction with hydrogen sulfide.* β-Chlorovinylarsenious sulfide, $CHCl{:}CHAs{:}S$, has been prepared by Mann and Pope (19), Lewis and Stiegler (18), and Kretov and Berlin (16) by passing hydrogen sulfide into an absolute alcohol or carbon tetrachloride solution of β-chlorovinyldichloroarsine. Neither Mann and Pope (19) nor Lewis and Stiegler (18) were able to effect a crystallization of the sulfide, obtaining a pale yellow, viscous liquid with a strong garlic-like odor; the liquid solidified to a hard resin on strong cooling. Kretov and Berlin (16), however, by bringing the mixture to a boil and then quickly cooling it, are said to have obtained light yellow plates with a repulsive odor, soluble in carbon disulfide and chloroform, slightly soluble in alcohol.

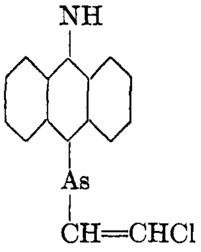
(*f*) *Reaction with potassium iodide.* Upon adding a concentrated hydrochloric acid (density 1.5) solution of potassium iodide to β-chlorovinyldichloroarsine there is formed β-chlorovinyldiiodoarsine, $CHCl{:}CHAsI_2$, yellowish-brown crystals, melting at 37.5–38.5°C., somewhat soluble in ligroin and very soluble in alcohol and benzene (18).

(*g*) *Reaction with potassium thiocyanate.* On treating a hot alcoholic solution of potassium thiocyanate with an absolute alcoholic solution of β-chlorovinyldichloroarsine, Lewis and Stiegler (18) obtained β-chlorovinylhydroxythiocyanoarsine, $CHCl:CHAs(OH)CNS$, an oil, soluble in water but unstable in air.

(*h*) *Reaction with benzene.* When β-chlorovinyldichloroarsine is allowed to react with benzene in the presence of anhydrous aluminum chloride there is formed 9, 10-dimethylanthracene, m.p. 180–181°C. (9).

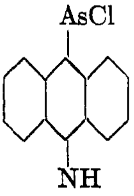


(*i*) *Reaction with diphenylamine.* (1) When a mixture of β-chlorovinyldichloroarsine and diphenylamine is heated gently, hydrogen chloride fumes are freely evolved and on cooling a thick mass of green crystals of 6-β-chlorovinylphenarsazine



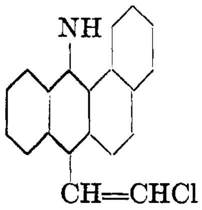
is formed. The compound is soluble in hot xylene, in acetone–carbon tetrachloride mixture, and in absolute alcohol; it is insoluble in ether. It melts at 186–187°C. It is decidedly irritating to the eyes and nostrils (18).

(2) 10-Chloro-5,10-dihydrophenarsazine,



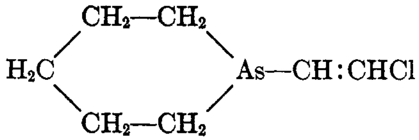
is prepared by boiling a mixture of diphenylamine, β-chlorovinyldichloroarsine, and *o*-dichlorobenzene under a reflux for twelve hours (3, 25). It boils at 120–121°C. at 9–10 mm.; its specific gravity, $d_{20^\circ}^{20^\circ}$, is 1.6766 (25).

(*j*) *Reaction with phenyl-α-naphthylamine.* Upon adding phenyl-α-naphthylamine to β-chlorovinyldichloroarsine there separate the well-defined, bright yellow, needle-like crystals of 7-β-chlorovinyl-7, 12-dihydro-γ-benzophenarsazine.



The melting point of the compound has been given as 213°C. (18) and as 218–220°C. (3).

(*k*) *Reaction with α,ε-dichloropropane.* Cyclopentamethylene-β-chlorovinylarsine,



is prepared by treating magnesium with α, ε-dichloropropane in ether with β-chlorovinyldichloroarsine; its melting point is 89–91°C. at 5 mm. (11).

Qualitative test

Nametkin and Nekrasov (20) found that when a 0.1 per cent solution of β-chlorovinyldichloroarsine is treated with a saturated aqueous solution of hydrogen sulfide a white amorphous precipitate of the arsine sulfide resulted, according to the reaction:

$$RAsCl_2 + H_2S \rightarrow 2HCl + RAsS$$

From solutions of 90 per cent alcohol the precipitate is crystalline. Using an aqueous solution of mercurous nitrate instead of the hydrogen sulfide a white precipitate was formed which turned gray in twelve hours.

Physiological properties

When β-chlorovinyldichloroarsine in the form of lecithin-emulsin is intravenously injected into dogs, in doses of 0.003 g. per kilogram of body weight, a violent apnea and a sudden drop in blood pressure occurs; after vagotomy, however, the compound has no effect on blood pressure or respiration (5).

β-Chlorovinyldichloroarsine produces lesions on the skin similar to those caused by "mustard gas," but after a shorter time and of more serious symptoms. It is more toxic (23) and more irritating than "mustard" (24). It is a strong vesicant; its vapor is likewise vesicant and extremely irritating to the nose, throat, and bronchi, producing constitutional symptoms (17). A small quantity, even in dilute solution, applied to the skin causes painful blistering. It is also a very powerful respiratory irritant, the mucous membrane of the nose being attacked and violent sneezing induced. More prolonged exposure to the vapor leads to severe pain in the throat and chest (12).

Use

Its possible use in aeroplane bombs led General Fries, former chief of Chemical Warfare Service, to apply the term "The Dew of Death" to its use in this way.

β,β'-DICHLORODIVINYLCHLOROARSINE, BIS(β-CHLOROVINYL)CHLOROARSINE, $(CHCl{:}CH)_2AsCl$

Preparation

This compound is prepared along with the primary and tertiary arsines when acetylene is passed into arsenic trichloride containing anhydrous aluminum chloride (9, 12, 17, 18, 19, 29); by the reduction of a hot hydrochloric acid solution of β,β'-dichlorodivinylarsinic acid with sulfur dioxide, using hydrogen iodide as a catalyst (9); by heating tris(β-chlorovinyl)arsine and arsenic trichloride in a sealed tube at 220°C. for four hours according to the following equation:

$$2(CHCl{:}CH)_3As + AsCl_3 \rightarrow 3(CHCl{:}CH)_2AsCl \quad (12)$$

and upon heating bis(β-chlorovinyl)dimethylarsonium iodide, $(CHCl{:}CH)_2As(CH_3)_2I$ (18).

Physical properties

It is a colorless or pale yellow liquid, insoluble in water and dilute acids but soluble in all proportions in the common organic solvents. Its boiling point has been given as: 230°C. (17), 136°C. at 30 mm. (17), 130–133°C. at 26 mm. (12), 120–121°C. at 17 mm. (19), 119°C. at 15 mm. (17), 116–117°C. at 15 mm. (19), 115–116°C. at 13 mm. (9), 113°C. at 11 mm. (29), 112°C. at 10 mm. (17), 108.5–109.5°C. at 12 mm. (13), 108–109° C.at 10.5 mm. (19). Specific gravity: $d^{11°}_{4°}$, 1.7047 (13); $d^{20°}_{4°}$, 1.7020 (17); $d^{23.4°}_{4.0°}$, (vacuum), 1.6936 (15); $d^{24.1°}_{4.0°}$, (vacuum), 1.6926 (9); $d^{27.1°}_{4.0°}$ (vacuum), 1.6884 (9). Its index of refraction: at 11°C., $n_\alpha = 1.6032$, $n_D = 1.6096$, $n_\beta =$

1.6262 (13); at 23.4°C., $n_C = 1.6014$, $n_D = 1.6080$, $n_F = 1.6250$, $n_G = 1.6401$ (15). The molecular refraction values at 11°C. for the D line of sodium and the α and β hydrogen lines are 47.47, 47.06, and 48.50, respectively (13). Vapor pressure, $\log = 9.983 - 3295.3/T$ (17).

Chemical properties

(*a*) *Reaction with nitric acid.* By the action of dilute nitric acid (equal volumes of concentrated acid and water) on the secondary arsine, bis(β-chlorovinyl)arsenic acid, $(CHCl{:}CH)_2AsOOH$, is produced as colorless, needle-shaped crystals, m.p. 97°C. (12), 99°C. (19), 114–115°C. (18). It decomposes when dissolved in water (19).

(*b*) *Reaction with sodium hydroxide.* On treating an alcoholic solution of the secondary arsine with sodium hydroxide, bis(β-chlorovinyl)arsenious oxide, $[(CHCl{:}CH)_2As]_2O$, is produced, m.p. 62–63°C. It is soluble in ether and hot alcohol, slightly soluble in cold alcohol, and insoluble in water (18).

(*c*) *Reaction with halogens.* Halogens are rapidly absorbed with the formation of additive compounds, such as $(CHCl{:}CH)_2AsClX_2$ (12).

(*d*) *Reaction with potassium cyanide.* On treating an absolute alcohol solution of the secondary arsine with an aqueous solution of potassium cyanide, considerable heat is evolved and potassium chloride separates almost at once as a fine white precipitate; bis(β-chlorovinyl)arsenious cyanide, $(CHCl{:}CH)_2AsCN$, is obtained as a colorless oil from the filtrate (18).

(*e*) *Reaction with hydrogen sulfide.* When hydrogen sulfide is bubbled into an absolute alcohol solution of the secondary arsine, considerable heat is evolved. The yellow-brown, viscous bis(β-chlorovinyl)arsenious sulfide, $[(CHCl{:}CH)_2As]_2S$, separates. It is insoluble in water but soluble in alcohol. It has an extremely irritating effect on the mucous membrane. The odor is powerful, penetrating, and disagreeable (18).

(*f*) *Reaction with chloramine-T.* When equivalent quantities of chloramine-T and the secondary arsine are boiled together, a clear solution results from which only β,β'-dichlorodivinylarsinic acid and p-toluenesulfonamide can be isolated (19).

(*g*) *Reaction with methyl iodide.* When the Grignard reagent resulting from the action of methyl iodide and magnesium reacts with the secondary arsine, bis(β-chlorovinyl)methylarsine, $(CHCl{:}CH)_2AsCH_3$, results as a thin, colorless oil, having a powerful, disagreeable odor, similar to that of the secondary arsine. It is insoluble in water, and soluble in ether and absolute alcohol. Upon heating in a sealed tube with excess of methyl iodide on a water bath, an almost solid mass of crystals is formed. At 243°C., the bis(β-chlorovinyl)dimethylarsonium iodide, $(CHCl{:}CH)_2$-

$As(CH_3)_2I$, changed, without charring, into methyl iodide and the original arsine. The compound is soluble in water and dilute alcohol but only slightly soluble in absolute alcohol (18).

(*h*) *Reaction with ethyl iodide.* By the action of the Grignard reagent made from ethyl iodide and magnesium on the secondary arsine, bis(β-chlorovinyl)ethyl arsine, $(CHCl:CH)_2AsC_2H_5$, a colorless oil resembling the secondary arsine in appearance and penetrating odor, is prepared. Upon heating with an excess of methyl iodide, in which it is soluble, in a sealed tube at about 90°C. for 1.5 hours, bis(β-chlorovinyl)methylethylarsonium iodide, $(CHCl:CH)_2As(CH_3)C_2H_5I$, is obtained as white crystals. At 234°C. sublimation occurs with no evidence of charring or decomposition. The compound is soluble in water, alcohol, and the common organic solvents (18).

(*i*) *Reaction with α-bromonaphthalene.* An absolute ether solution of the secondary arsine poured into the Grignard reagent made from α-bromonaphthalene results in bis(β-chlorovinyl)-α-naphthylarsine, $(CHCl:CH)_2AsC_{10}H_8$, a yellow oil, which is insoluble in water and can not be crystallized nor even fractionated at 25 mm. (18).

(*j*) *Reaction with benzene.* The condensation of β,β′-dichlorodivinylarsine with benzene, in the presence of anhydrous aluminum chloride, results in the formation of the hydrocarbon 9,10-dimethylanthracene, m.p. 180–181°C. (8).

Physiological properties

Applied to the skin, the substance has vesicating properties, but is much less powerful in this respect than chlorovinyldichloroarsine. Its irritant properties on the respiratory system, on the other hand, although similar to those of chlorovinyldichloroarsine, are much more intense (12).

β,β′,β″-TRICHLOROTRIVINYLARSINE, TRIS(β-CHLOROVINYL)ARSINE, $(CHCl:CH)_3As$

Preparation

This substance is prepared as the main product when acetylene is passed into arsenic trichloride containing anhydrous aluminum chloride (9, 12, 17, 18, 19, 29), but the mono- and secondary-arsines are also present. It is also made by the action of hydrogen sulfide on a chloroform solution of β,β′,β″-trichlorotrivinylarsine dibromide, in accordance with the equation:

$$(CHCl:CH)_3AsBr_2 + H_2S \rightarrow (CHCl:CH)_3As + 2HBr + S \quad (19)$$

Physical properties

It is a colorless liquid, insoluble in water, dilute acids, and alcohol. In the last respect it differs from the primary and secondary chloroarsines, both of which mix in all proportions with alcohol. With the exception of alcohol, it is soluble in all the common organic solvents. Its boiling point has been given as: 260°C. (17), 162°C. at 30 mm. (17), 151–155°C. at 28 mm. (12), 145–146°C. at 18 mm. (13), 144°C. at 15 mm. (17), 144°C. at 16 mm. (19), 139–140°C. at 13 mm. (19), 138°C. at 12 mm. (29), 136.5–137.5°C. at 12 mm. (9), 136°C. at 10 mm. (17). On cooling it crystallizes in long, white needles, melting at 23°C. (19), 18°C. (9), 13°C. (29), 3–4°C. (12). Specific gravity: $d_{4.0^\circ}^{16.2^\circ}$, 1.5800 (13); $d_{4.0^\circ}^{21.5^\circ}$, 1.5727 (13); $d_{4^\circ}^{20^\circ}$, 1.5720 (17); $d_{4^\circ}^{22^\circ}$ (vacuum), 1.5685 (9); $d_{4.0^\circ}^{23.7^\circ}$ (vacuum), 1.5664 (15); $d_{4.0^\circ}^{26.3^\circ}$ (vacuum), 1.5631 (9). Index of refraction: $n_\alpha = 1.5925$ (16.2°C.), $n_D = 1.5985$ (16.2°C.), $n_D = 1.5942$ (21.5°C.), $n_\beta = 1.6140$ (16.2°C.) (13); at 23.7°C., $n_C = 1.5939$; $n_D = 1.6005$; $n_F = 1.6158$ (15). The molecular refraction: $MR_\alpha = 55.62$ (16.2°C.), $MR_D = 56.07$ (16.2°C.), $MR_D = 56.01$ (21.5°C.), $MR_\beta = 57.24$ (16.2°C.) (13). Vapor pressure, $\log = 9.159 - 3312.43/T$ (17).

Chemical properties

(*a*) *Reaction with arsenic trichloride.* When it is heated with arsenic trichloride at 200–220°C. and the product is fractionated, a mixture of both chlorovinyldichloroarsine and dichlorodivinylchloroarsine is obtained, the amount depending upon the proportions of trichlorotrivinylarsine and arsenic trichloride used; when the ratio of arsenic trichloride and trichlorotrivinylarsine is 45.3:54.7, the proportion of chlorovinyldichloroarsine and dichlorodivinylchloroarsine is 33.55 per cent and 41.34 per cent respectively (25.11 per cent being arsenic trichloride remaining unattacked); when the ratio of arsenic trichloride and the tertiary arsine is 58.24:41.76, the proportion of the primary and secondary arsines is 48.16 per cent and 16.25 per cent respectively (35.59 per cent being unattacked arsenic trichloride) (12). The reactions may be expressed as follows:

$$(CHCl:CH)_3As + 2AsCl_3 \rightarrow 3CHCl:CHAsCl_2$$
$$2(CHCl:CH)_3As + AsCl_3 \rightarrow 3(CHCl:CH)_2AsCl \quad (12)$$

(*b*) *Reaction with nitric acid.* On heating the tertiary arsine with concentrated nitric acid, β,β',β''-trichlorotrivinylhydroxyarsonium nitrate, $(CHCl:CH)_3As(OH)NO_3$, forms as an oily layer that separates on the bottom of the vessel but which crystallizes quickly when a little water is added. The white crystals are soluble in cold absolute alcohol and hot water. They melt at 103°C. (16, 17). When an aqueous solution of the nitrate is treated with an equivalent quantity of sodium hydroxide, the solution extracted with chloroform, and the chloroform solution evaporated, a crystalline residue of β,β′,β″-trichlorotrivinylarsenic oxide, $(CHCl:CH)_3AsO$, is formed. It separates on crystallization from benzene containing a little carbon tetrachloride, in long colorless needles or in small plates which melt with decomposition at 154°C. (19).

(*c*) *Reaction with bromine.* When a ligroin solution of the tertiary arsine in a freezing mixture is cautiously treated with a ligroin solution of bromine, β,β′,β″-trichlorotrivinylarsine dibromide, $(CHCl:CH)_3AsBr_2$, separates in colorless needles which melt at 107°C. (19).

(*d*) *Reaction with methyl iodide.* On heating trichlorotrivinylarsine with an equimolecular proportion of methyl iodide in a sealed tube on a water bath at 80°C. for twenty-two hours and then at 100°C. for two hours (16) or at 100°C. for twenty-seven hours (17) β,β′,β″-trichlorotrivinylmethylarsonium iodide, $(CHCl:CH)_3AsCH_3I$, is formed. The contents of the tube become almost solid with a mass of needle-shaped crystals which are very slightly soluble in absolute alcohol, either hot or cold, but dissolve readily in 95 per cent alcohol and in water; the melting point has been given as 202°C. (18) and 209°C. (19).

(*1*) *Double salt formed with mercuric iodide.* Molecular proportions of the two iodides are dissolved separately in alcohol and then mixed and warmed for a short time. As the solution cools a heavy, granular, light yellow precipitate is formed, $(CHCl:CH)_3AsCH_3I \cdot HgI_2$, which, when recrystallized from alcohol, melts between 150°C. and 156°C. It is soluble in hot absolute alcohol, somewhat soluble in hot 95 per cent alcohol, and insoluble in cold absolute alcohol and in hot and cold water (18).

(*2*) *Double salt formed with phenylmagnesium iodide.* Molecular proportions of the two iodides, the arsonium iodide dissolved in absolute alcohol, are heated in a sealed tube for twelve hours at 90°C. Long, thick, needle-like, yellow crystals of $(CHCl:CH)_3AsCH_3I \cdot C_6H_5HgI$ form when the contents of the tube are allowed to cool. It is soluble in warm, absolute alcohol and insoluble in water; its melting point is not sharp but is near 147–148°C. (18).

(*e*) *Reaction with benzene.* The condensation of the tertiary arsine with benzene in the presence of anhydrous aluminum chloride results in the formation of the hydrocarbon, 9,10-dimethylanthracene, m.p. 180–181°C. (8).

(*f*) *Reaction with chloramine-T.* When an acetone solution of the tertiary arsine is boiled with chloramine-T for twenty minutes, filtered, and the filtrate evaporated to dryness, colorless plates of β,β′,β″-trichlorotrivinylarsine-*p*-toluenesulfonylimine, $(CHCl:CH)_3As:NSO_2C_6H_4(CH_3) \cdot H_2O$, result, m.p. 124°C. (19).

(*g*) *Reaction with metallic compounds.* (*1*) *With silver nitrate.* The double salts of trichlorotrivinylarsine and silver nitrate, $(CHCl{:}CH)_3As \cdot AgNO_3$ and $[(CHCl{:}CH)_3As]_2 \cdot AgNO_3$, are prepared by dissolving separately the tertiary arsine and silver nitrate in absolute alcohol and adding an excess of the latter to the former. Long, fine, silky needles form at once in such quantity that the solution becomes thick and semi-solid; the crystals meet at 144°C. In hot water the crystals melt and form an oil which, on cooling, quickly crystallizes again, but in the form of short, thick, needle-like crystals. The compounds are stable toward light when pure and dry (18).

(2) With potassium aurichloride. On adding an alcoholic solution of potassium aurichloride to a cooled alcoholic solution of the tertiary arsine, the mixture rapidly becomes colorless and then slowly deposits small, heavy, white crystals of β,β',β''-trichlorotrivinylarsine aurichloride, $(CHCl{:}CH)_3As \cdot AuCl$, which melt at 123°C. with decomposition. When the colorless crystals are exposed to light for several days, they gradually acquire a purplish-gray color (19).

(3) With palladous chloride. When an alcoholic solution of palladous chloride is added to a cooled alcoholic solution of the tertiary arsine, long, yellowish-brown needles of bis(β,β',β''-trichlorotrivinylarsine) palladichloride, $[(CHCl{:}CH)_3As]_2PdCl_2$, begin to form within a few seconds; these are soluble in ether and acetone, and melt at 196°C. with decomposition. The formation of this characteristic compound furnishes a ready means for detecting the presence of the tertiary arsine (19).

(4) With chloroplatinic acid. When a dilute alcoholic solution of chloroplatinic acid is added to an alcoholic solution of the tertiary arsine, long, very pale yellow needles of platinum bis(β-chlorovinyl)-bis(β,β',β''-trichlorotrivinyl)arsine, $[(CHCl{:}CH)_3As]_2Pt(CHCl{:}CH)_2$, separate, followed later by short, lemon-yellow prisms; on recrystallizing from alcohol, very pale yellow, almost white, needles separate, m.p. 198°C. (19).

Physiological properties

Trichlorotrivinylarsine is neither a strong vesicating agent nor a powerful respiratory irritant. At the same time its odor is pungent and most unpleasant, and induces violent sneezing (12).

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