[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY]

THE BETA-CHLOROVINYL-ARSINES AND THEIR DERIVATIVES[1]

BY W. LEE LEWIS AND H. W. STIEGLER

RECEIVED JANUARY 27, 1925 PUBLISHED OCTOBER 6, 1925

The pronounced physiological properties of the β-chlorovinyl-arsines and the interesting manner of their formation warranted a further study of their derivatives and of the mechanism of their synthesis from arsenic trichloride, acetylene and aluminum trichloride.

All efforts to add acetylene to arsenic chloride directly under a wide variety of physical conditions have proved ineffectual. Of the many catalysts employed, only two, aluminum chloride and mercuric chloride, have served to effect the addition. The method of their preparation from these reagents was given in a previous article by one of us[2] (with G. A. Perkins) and was confirmed as to the use of aluminum chloride in this reaction by Mann and Pope.[3]

In the former article an explanation of the reaction was offered, namely, that an intermediate addition compound is formed of one molecule each of arsenic chloride and aluminum chloride with three molecules of acetylene, $Al(CHCl.CHCl)_3As$. This conclusion was based upon the observation that a fresh reaction mixture on processing yields more *tris*-β-chlorovinyl-arsine, $(CHCl{=}CH)_3As$, than is present in an equilibrium mixture of arsenic chloride, β-chlorovinyl-dichloro-arsine, *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 together pure *tris*-β-chlorovinyl-arsine with arsenic chloride until the system had reached a constant value for the four components then present.

Moreover, it was noteworthy, that when a fresh reaction mixture of arsenic chloride, aluminum chloride and acetylene was allowed to stand at room temperature, or preferably warmed in the presence of free arsenic chloride, there was an appreciable rise in the content of the primary and secondary chlorovinyl arsines 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 chloride, 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.[2]

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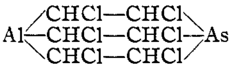
[1] This work was carried out under a grant from the Research Board of the Public Health Institute of Chicago.

[2] Lewis and Perkins, *Ind. Eng. Chem.*, **15**, 290 (1923).

[3] Mann and Pope, *J. Chem. Soc.*, **121**, 1754 (1922).

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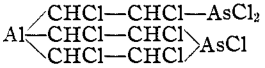
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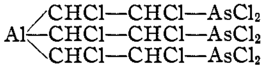

(III)

Compound I is believed to be formed when acetylene is conducted into arsenic chloride containing aluminum chloride; II and III are formed by the further reaction of I with one and two more molecules, respectively, of arsenic chloride.

The arsines are obtained from these intermediate compounds by washing the reaction mixture with 20% hydrochloric acid to constant volume and distilling the resulting mixture. The intermediate compounds undergo hydrolysis, the aluminum being removed in the dil. 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 chloride 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 chloride in the absence of a suitable catalyst. Moreover, aluminum chloride is known to add acetylene. This intermediate catalyst compound would then add arsenic chloride to form the assumed parent compound, $Al(CHCl{-}CHCl)_3As$. 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 *beta* position to the corresponding metal. On hydrolyzing, 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 compound, irrespective of the kind of aluminum halide used as a catalyst. Arsenic chloride should give a vinyl arsine containing chlorine, and arsenic bromide a compound containing bromine with either aluminum chloride or bromide. Arsenic bromide, acetylene and aluminum chloride would thus form $Al(CHBr{-}CHCl)_3As$ as an intermediate compound, while arsenic chloride and aluminum bromide should similarly give $Al(CHCl{-}CHBr)_3As$. The former would finally yield bromo-arsines and the latter chloro-arsines.

This has been found to be experimentally true and offers further experimental confirmation of this explanation of the reaction. Moreover, in no instances were organic arsenic compounds isolated containing mixed halogens.

This method will be further employed in studying the mechanism of the addition of halides of mercury and aluminum to unsaturated compounds, in general.

The bromo-vinyl arsines boil higher than the chloro homologs, and the corresponding solid derivatives melt consistently higher.

The characteristic stability of the halogen attached to the *beta* carbon containing a double bond completely prevented the modification of this part of the arsine molecule. The derivatives listed here are all due to changes on the arsenic and all contain the unchanged vinyl group. Again, the sensitivity of the substance to alkalies prevented the formation of derivatives in this medium.

Among the more common classes of derivatives isolated are the halogen derivatives, oxides, arsonic and arsinic acids, sulfides, cyanides, thiocyanates, condensation products, mixed arsines, arsonium compounds, double salts or molecular compounds, etc. As a rule, the oxides and arsonic and arsinic acids have no marked vesicant or irritating properties. The sulfides and thiocyanates possess powerful, disagreeable and sickening odors that are very persistent. The cyanides have little odor but appear to be quite toxic. Condensation products of the primary arsine with diphenylamine, phenyl-α-naphthylamine, etc., possess strongly irritating properties and induce violent sneezing. The condensation product of the primary arsine with diphenylamine bears a resemblance in structure and properties to the toxic sneeze gas, 6-chlorophenarsazine. The mixed aliphatic tertiary arsines have odors similar to that of the original *tris*-β-chlorovinyl-arsine but no apparent vesicant properties. *tris*-β-Chlorovinyl-arsine has a very strong tendency to form double salts, or compounds with silver nitrate, and its quaternary derivatives in turn form addition compounds with mercuric iodide and phenylmercuric iodide.

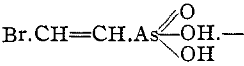
Part of this investigation was carried out in an outdoor, uncovered laboratory, other operations being conducted in special hoods with strong drafts, special precautions as to the use of rubber gloves, etc., being rigidly observed.

Experimental Part

β-Bromovinyl-dibromo-arsine, $Br.CH{=}CH.AsBr_2$.—To determine whether the halogen from the arsenic or from the aluminum goes to the beta carbon of the vinyl radical, 320 g. (4 molecular proportions) of arsenic bromide was mixed with 35 g. of finely powdered, anhydrous aluminum chloride, and acetylene, which had been washed with sodium bisulfite solution and dried with sulfuric acid, was passed into the mixture. Good agitation was maintained throughout the preparation, which consumed two and one-third hours. The temperature was 35° at the start, 42° at the end of one hour and 48° at the end of the absorption. To permit equilibrium to be reached and at the same time to increase the content of primary arsine, the reaction mixture was allowed to stand for two days. It was then poured into 200 cc. of 20% hydrochloric acid, the mixture shaken well and the heavy oily layer separated from the acid layer above it. The oily layer was washed five times with 20% hydrochloric acid to constant volume, in order to remove the catalyst and most of the arsenic tribromide. The washed product, weighing 156 g., was first distilled without fractionation at 10–12 mm. pressure, 80% distilling up to 152°. This composite was then fractionated five times at 16 mm.

Analysis of the fraction boiling between 140° and 143° proved it to be β-bromovinyl-dibromo-arsine.

Anal. Subs., 0.2282, 0.2224: AgBr, 0.3776, 0.3674. Calcd. for $C_2H_2Br_3As$: Br, 70.36. Found: 69.98, 70.27.

β-Bromovinyl-arsonic Acid,  $\mathrm{Br.CH{=}CH.As}\begin{cases}{=}O\\-OH\\-OH\end{cases}$.—To confirm further the nature of the product isolated as described above, it was oxidized to the arsonic acid as mentioned under the discussion of β-chlorovinyl-arsonic acid later in this article. The crystals formed resemble closely those of the chlorovinyl-arsonic acid; m. p., 143° and 130°, respectively.

Anal. Subs., 0.1690, 0.1768: AgBr, 0.1367, 0.1421. Calcd. for $C_2H_4O_3BrAs$: Br, 34.61. Found: 34.43, 34.22.

***bis*-β-Bromovinyl-bromo-arsine,** $(Br.CH{=}CH)_2AsBr$.—The 155–165° portion from the fractionation described above contained the *bis*-β-bromovinyl-bromo-arsine.

Anal. Subs., 0.2419, 0.2420: AgBr, 0.3738, 0.3779. Calcd. for $C_4H_4Br_3As$: Br, 65.39. Found: 65.77, 66.45.

Due possibly to the long standing of the original reaction mixture, an insufficient amount of the *tris*-β-bromovinyl-arsine was obtained for study.

β-Chlorovinyl-dichloro-arsine.—To confirm further the theory that the halogen of the catalyst does not remain in the final organic products of the reaction, either on the arsenic or the *beta*-carbon, aluminum bromide, arsenic chloride and acetylene were used in the reaction.

Because of the more vigorous action of aluminum bromide, much less was required as a catalyst than when the chloride was used. Into a solution of 38 g. of aluminum bromide in 410 g. (16 molecular proportions) of arsenic chloride, acetylene, washed and dried as described above, was passed slowly during vigorous stirring for two hours at a temperature of 25°. The reaction mixture was allowed to stand for seven hours and was then hydrolyzed by being poured into 300 cc. of approximately 25% hydrochloric acid. Considerable heat was developed at this point and the mixture was cooled in a water-bath. After the mixture had been stirred vigorously for 15 minutes, the lower oily layer was separated from the acid and fractionated thrice at 30 mm.

The 90–105° fraction proved to be crude β-chlorovinyl-dichloro-arsine entirely free from bromine. This was confirmed by oxidizing a portion of the product with nitric acid to β-chlorovinyl-arsonic acid. After one recrystallization from xylene the arsonic acid melted at 128°.

Anal. Subs., 0.2012, 0.2456: AgCl, 0.4093, 0.5010. Calcd. for $C_2H_2Cl_3As$: Cl, 51.31. Found: 50.33, 50.47.

***bis*-β-Chlorovinyl-chloro-arsine.**—The 130–140° portion of the fractionation described above contained the *bis*-β-chlorovinyl-chloro-arsine.

Anal. Subs., 0.2118, 0.2338: AgCl, 0.3882, 0.4264. Calcd. for $C_4H_4Cl_3As$: Cl, 45.59. Found: 45.35, 45.12.

***tris*-β-Chlorovinyl-arsine.**—The 155–163° fraction contained the *tris*-β-chlorovinyl-arsine.

Anal. Subs., 0.1853, 0.2368: AgCl, 0.3098, 0.3967. Calcd. for $C_6H_6Cl_3As$: Cl, 41.01. Found: 41.36, 41.44.

Thus, no chloro-arsines resulted from mixture of arsenic bromide, aluminum chloride and acetylene, and no bromo-arsines when arsenic chloride, aluminum bromide and acetylene were brought together. The halogen on the arsenic halide used in the reaction determines the halogen in the resulting organic arsenic compound.

Derivatives of the β-Chlorovinyl-arsines

β-Chlorovinyl-arsenious Oxide, Cl.CH=CH.As=O.—Because of the ease of hydrolysis of the chlorine atoms attached to the arsenic of β-chlorovinyl-dichloro-arsine the oxide can be formed by the action of water or weak alkali. Where water alone is used, the hydrochloric acid formed brings the reaction to early equilibrium. In order to obtain complete hydrolysis it is necessary to use a large volume of water or, better some weak base to remove the acid. Strong alkali breaks up the compound liberating acetylene. The oxide is best obtained by mixing the β-chlorovinyl-dichloro-arsine with one-half its weight of water and adding an excess of dil. ammonium hydroxide slowly, during stirring, and cooling. The insoluble β-chlorovinyl-arsenious oxide that is formed is purified by being ground to a fine powder, and washed repeatedly with water and finally with alcohol. It is a white, crystalline powder; m. p. 143°, 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.

Anal. Calcd. for C_2H_2OAsCl: C_2H_2, 17.07; As, 49.17; Cl, 23.26. Found: C_2H_2, 16.99; As, 49.17, 49.30; Cl, 22.66, 22.80.

β-Chlorovinyl-di-iodo-arsine, Cl—CH=CH—AsI$_2$.—To 245 g. of β-chlorovinyl-dichloro-arsine (94%) 20 g. of potassium iodide in 250 cc. of hydriodic acid (d., 1.5) was added, in small portions during shaking. Considerable heat was evolved. After being separated, the oily layer was washed with 200 cc. of hot ligroin to remove any unchanged material. This washing was repeated twice and the product was recrystallized from 20 cc. of methyl alcohol by cooling in an ice-salt mixture. The crystals, m. p. 37.5–38.5°, were yellow-brown, somewhat soluble in ligroin and very soluble in alcohol and benzene.

Anal. Calcd. for $C_2H_2ClI_2As$: C_2H_2, 6.67; As, 19.31; I, 65.04. Found: C_2H_2, 6.54, 6.57, 6.60; As, 19.60; I, 66.00.

β-Chlorovinyl-dibromo-arsine, Cl.CH=CH.AsBr$_2$.—This compound is prepared from β-chlorovinyl-arsenious oxide and hydrobromic acid. To 70 g. of the oxide was added slowly a solution of 10 g. of potassium bromide in 200 cc. of hydrobromic acid (40%). The evolution of heat was slight. The oxide was gradually converted into a dark, oily liquid which was agitated and warmed with the hydrobromic acid solution for two or three hours. After being cooled, the oily layer was collected on a dry filter paper; yield, 92.3%. It was distilled at 15 mm. pressure and the 114–116° fraction analyzed. The compound is soluble in absolute alcohol and slightly soluble in ligroin, but did not crystallize from these solvents at 80°.

Anal. Calcd. for $C_2H_2ClBr_2As$: C_2H_2, 8.78; As, 25.30; Cl, 11.97; Br, 53.95. Found: C_2H_2, 8.36, 8.37; As, 25.20; Cl, 12.40; Br, 53.70.

β-Chlorovinyl-arsonic Acid, Cl—CH=CH—As(=O)(OH)$_2$.—This compound can be made by oxidizing β-chlorovinyl-arsenious oxide with hydrogen peroxide and evaporating the clear solution to crystallization. The crystals thus obtained are flat and hexagonal. The arsonic acid can also be obtained by oxidation of β-chlorovinyl-dichloro-arsine with nitric acid,[3] either concentrated or dilute. When concentrated acid is used, the reaction is apt to become too vigorous and cooling is necessary. When dil. nitric acid is used, warming may be necessary to start the reaction, after which it proceeds spontaneously until the arsine layer has all been decomposed. When the substance is 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 hydrogen-peroxide method show the same crystallographic measurements and characteristics. Both kinds of crystals are bi-axial, positive, orthorhombic, and have the same measurements; α, 1.555; β, 1.565; γ, 1.705; birefringence γ-α, 150. The crystals melt at 130°, are very soluble in water and alcohol and can be readily crystallized from a mixture of equal volumes of acetone and carbon tetrachloride.

Anal. Subs., 0.2891, 0.2817: AgCl, 0.2254, 0.2190. Calcd. for $C_2H_4O_3AsCl$: Cl, 19.2. Found: 19.28, 19.23.

β-CHLOROVINYL-SILVER-ARSONATE, $Cl.CH{=}CH.{-}As({=}O)(OAg)_2$.—This salt was prepared by the action of an ammoniacal solution of silver oxide on the arsonic acid in aqueous solution. Four g. of silver nitrate was converted to the oxide with sodium hydroxide in the usual manner. After being washed, the precipitate was dissolved in ammonium hydroxide and a water solution of 2.5 g. of the arsonic acid was added. The solution was filtered and slightly acidified with nitric acid. The disilver salt separated as a creamy white, finely crystalline precipitate which was thoroughly washed by being stirred with water. After a final washing with absolute alcohol, the precipitate was dried at about 70°. The salt is insoluble in water and in cold and hot alcohol but soluble in dil. nitric acid and ammonium hydroxide. When pure it appears to be fairly stable toward light. When heated alone or with concd. nitric acid it decomposes violently.

Anal. Subs., 0.2480, 0.2582: AgCl, 0.0878, 0.0865. Calcd. for $C_2H_2O_3ClAsAg_2$: Cl, 8.86. Found: 8.76, 8.59.

Subs., 0.3916, 0.3156: AgCl, 0.2572, 0.2247. Calcd.: Ag, 53.91. Found: 53.55, 53.58.

β-Chlorovinyl-arsenious Sulfide, $Cl.CH{=}CH.As{=}S$.—This compound may be obtained by treating either β-chlorovinyl-arsenious oxide or β-chlorovinyl-dichloro-arsine with hydrogen sulfide. The latter method proved the more satisfactory and gave about a 50% yield. Forty-one g. of the dichloro-arsine was dissolved in about 60 cc. of absolute alcohol, and hydrogen sulfide was bubbled through the solution for two hours. The pale yellow sulfide separated as a thick, sticky mass. The alcohol was decanted and the sulfide washed once with absolute alcohol. It was then dissolved in freshly distilled carbon disulfide and precipitated by adding absolute alcohol. This procedure was repeated thrice. The β-chlorovinyl-arsenious sulfide was left as a clear, golden-yellow oil which, however, persistently retained traces of carbon disulfide, even after being warmed for some time. This was finally removed by subjecting the material to 5 mm. pressure for one hour, the containing flask being immersed in a boiling water-bath. The pure compound is a clear, amber-colored plastic, insoluble in common solvents except carbon disulfide, in which it dissolves readily. It cannot be distilled, even under a high vacuum, without decomposition. The compound has an extremely irritating and nauseating odor, which persists in the skin for days. No vesicant action was noted.

Anal. Subs., 0.2716, 0.3387: AgCl, 0.2331, 0.2860. Calcd. for C_2H_2AsClS: Cl, 21.08. Found: 20.89, 20.87.

Subs., 0.4515, 0.3085, 0.3428, 0.3508: $BaSO_4$, 0.6347, 0.4278, 0.4758, 0.4827. Calcd.: S, 19.00. Found: 19.26, 18.99, 19.02, 19.15.

7-β-Chlorovinyl-7,12-dihydro-γ-benzophenarsazine (IV).—The hypothetical parent compound for derivatives of this type is γ-benzophenarsazine[4] (V). To 5 g. of β-chlorovinyl-dichloro-arsine, 6 g. of phenyl-α-naphthylamine was added. Marked cooling was noted. The mixture was heated gently under an air condenser for 15 minutes. Copious fumes of hydrogen chloride were evolved. After the mixture had stood overnight, a little xylene was added to the thick mass to permit filtration. The bright yellow product was washed with a small quantity of absolute alcohol, then crystallized from

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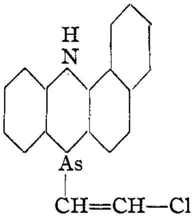
[4] Lewis and Hamilton, THIS JOURNAL, **43**, 2218 (1921).

xylene, in which it is fairly soluble at boiling temperature. The well-defined, needle-like crystals thus separated were ground and dried at 100°; m. p., 213°.

Too long heating, too high temperatures and the use of catalysts caused the formation of tar. Practically no reaction took place in boiling xylene.

Anal. Subs., 0.2264, 0.2281: AgCl, 0.0889, 0.0891. Calcd. for $C_{18}H_{13}ClNAs$: Cl, 10.03. Found: 9.71, 9.64.

6-β-Chlorovinyl Phenarsazine (VI).—A mixture of 25 g. of β-chlorovinyl-dichloroarsine with 15 g. of diphenylamine was heated gently for 25 minutes. Hydrogen chloride fumes were freely evolved. On cooling, a thick mass of crystals formed. About 15 cc. of absolute alcohol was added to the mixture to facilitate filtration. The green crystals left on the filter were washed with a small amount of absolute alcohol. After two crystallizations from xylene, the product was washed with ether and dried. The compound is soluble in hot xylene, in a mixture of acetone and carbon tetrachloride and in absolute alcohol, and is insoluble in ether; m. p., 186–187°. It is decidedly irritating to the eyes and nostrils.



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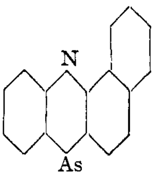

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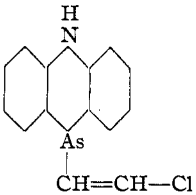

(VI)

Anal. Subs., 19.78, 18.38: AgCl, 0.0960, 0.0879. Calcd. for $C_{14}H_{11}NClAs$: Cl, 12.00. Found: 12.03, 11.86.

β-Chlorovinyl-hydroxythiocyano-arsine, Cl.CH=CH.—As(OH)CNS.—A mixture of 15 g. of potassium thiocyanate in hot alcohol with 10 g. of β-chlorovinyl dichloro-arsine in absolute alcohol was shaken for one hour. The solution was separated from potassium chloride by filtration. The filtrate was diluted with water and then extracted with ether. The ether layer was washed several times with a little water. On evaporation, an oil was left, that was soluble in water and rather unstable in air.

Anal. Subs., 0.2185, 0.2193: AgCl, 0.1508, 0.1510. Calcd. for $C_3H_3OClNSAs$: Cl, 16.76. Found: 17.07, 17.05.

Subs., 0.2185, 0.2193: $BaSO_4$, 0.2615, 0.2602. Calcd.: S, 15.16. Found: 16.38, 16.27.

***bis*-β-Chlorovinyl-arsenious Oxide, $(Cl.CH{=}CH)_2As.O.As.(CH{=}CH.Cl)_2$.**—This compound was obtained as a result of an attempt to form the ethoxy compound of *bis*-β-chlorovinyl-chloro-arsine by treatment with sodium alcoholate. It can also be prepared by stirring an alcoholic solution of the arsine with sodium hydroxide solution. One hundred and fifty g. of *bis*-β-chlorovinyl-chloro-arsine was treated with 19 g. of sodium alcoholate in alcohol, in small portions. The mixture was filtered and the precipitate washed with alcohol and finally with water. After being thrice crystallized from hot alcohol, the substance melted at 62–63°. The compound is soluble in ether and hot alcohol, slightly soluble in cold alcohol and insoluble in water.

Anal. Calcd. for $C_8H_8OCl_4As$: Cl, 34.44; As, 36.4. Found: Cl, 34.21, 34.24; As, 35.95.

***bis*-β-Chlorovinyl-arsinic Acid, $(Cl.CH{=}CH)_2As({=}O)OH$.**—An excess of dil. nitric acid (equal volumes of concd. acid and water) was poured over a quantity of *bis*-β-chlorovinyl-chloro-arsine. The reaction proceeded rapidly and required cooling in an ice-bath. When the arsine layer was completely decomposed, the solution stood for a short time and crystallization was induced by cooling, and scratching the sides of the beaker. The mother liquor was separated from the colorless crystals by filtration. The crystals were washed, crystallized thrice from water and finally dried thoroughly in a vacuum desiccator over sulfuric acid; m. p., 114–115°.

Anal. Subs., 0.2376, 0.2046: AgCl, 0.2924, 0.2521. Calcd. for $C_4H_5O_2Cl_2As$: Cl, 30.71. Found: 30.38, 30.40.

***bis*-β-Chlorovinyl-arsenious Sulfide,** $(Cl.CH{=}CH)_2As.S.As(CH{=}CH.Cl)_2$.—Five cc. of *bis*-β-chlorovinyl-chloro-arsine was dissolved in 40 cc. of absolute alcohol, and hydrogen sulfide was bubbled through the solution for one hour. Considerable heat was evolved. The product precipitated as an oil by the addition of water to the reaction mixture. The oil was washed well, separated carefully and dried in a desiccator. The sulfide is yellow-brown, viscous, soluble in alcohol, insoluble in water and has an extremely irritating effect on the mucous membrane. The odor is powerful, penetrating and disagreeable.

Anal. Subs., 0.3613, 0.4142: AgCl, 0.4822, 0.5530. Calcd. for $C_8H_8Cl_4As_2S$: Cl, 33.15. Found: 32.93, 33.02.

Subs., 0.3613, 0.4142: $BaSO_4$, 0.2012, 0.2276. Calcd.: S, 7.48. Found: 7.47, 7.48.

***bis*-β-Chlorovinyl-arsenious Cyanide,** $(Cl.CH{=}CH)_2As.CN$.—Ten g. of *bis*-β-chlorovinyl-chloro-arsine was dissolved in absolute alcohol. Four g. of potassium cyanide (calcd., 2.8 g.) was dissolved in 15 cc. of water and the solution poured into the alcoholic solution of the arsine. Considerable heat was evolved by the reaction and potassium chloride separated almost at once as a fine, white precipitate. After a few minutes the liquid was filtered and water added. A colorless oil separated which was washed thrice with water and finally dried over calcium chloride. It gave a very strong test for nitrogen.

Anal. Subs., 0.3664, 0.2450: AgCl, 0.4704, 0.3163. Calcd. for C_5H_4ClNAs: Cl, 31.67. Found: 31.74, 31.91.

***bis*-β-Chlorovinyl-ethylarsine,** $(Cl.CH{=}CH)_2As.C_2H_5$.—This compound is made by the action of the Grignard reagent on *bis*-β-chlorovinyl-chloro-arsine. Four g. of ethyl iodide was converted into the Grignard reagent in the usual manner, and 4 g. of *bis*-β-chlorovinyl-chloro-arsine in dry ether added drop by drop. The reaction was violent. The reaction mixture stood for a day in a well-stoppered flask. It was then poured into water and the ether layer separated. On evaporation of the ether a colorless oil remained, resembling *tris*-β-chlorovinyl-arsine in appearance and penetrating odor.

Anal. Subs., 0.2455, 0.2654: AgCl, 0.3084, 0.3327. Calcd. for $C_6H_9Cl_2As$: Cl, 31.25. Found: 31.07, 31.01.

***bis*-β-Chlorovinyl-methylethyl-arsonium Iodide,** $(ClCH{=}CH)_2As(CH_3)(C_2H_5)I$.—This quaternary compound was made by heating *bis*-β-chlorovinyl-ethylarsine with an excess of methyl iodide, in which it is soluble, in a sealed tube at about 90°, for one and one-half hours. When cooled, the contents of the tube became solid with crystals, which were crystallized thrice from absolute alcohol. At 234° the white material sublimed with no evidence of charring or decomposition. The compound is soluble in water, alcohol, hot absolute alcohol and common organic solvents.

Anal. Subs., 0.1978, 0.2290: AgI, 0.1249, 0.1454. Calcd. for $C_7H_{12}Cl_2IAs$: I, 34.41. Found: 34.12, 34.32.

***bis*-β-Chlorovinyl-methyl-arsine,** $(Cl.CH{=}CH)_2As.CH_3$.—Five g. of *bis*-β-chlorovinyl-chloro-arsine was allowed to react with 5 g. of methyl iodide in the form of the Grignard reagent. The Grignard solution was dropped slowly into the cooled, dry ether solution of the arsine. After two hours the reaction mixture was cautiously poured into water and the ether layer separated, washed thrice with water and dried with calcium chloride. After the ether had been filtered and evaporated, a thin, colorless oil remained. It had a powerful, disagreeable odor, similar to that of *tris*-β-chlorovinyl-arsine. It is insoluble in water and soluble in ether and in absolute alcohol.

Anal. Subs., 0.2358, 0.2416: AgCl, 0.3187, 0.3263. Calcd. for $C_5H_7Cl_2As$: Cl, 33.31. Found: 33.42, 33.40.

***bis*-β-Chlorovinyl-dimethyl-arsonium Iodide,** $(ClCH{=}CH)_2As(CH_3)_2I$.—*bis*-β-Chlorovinyl-methyl-arsine was sealed in a tube with an excess of methyl iodide and heated in a water-bath at about 100° for three hours. An almost solid mass of crystals formed. These were removed from the tube and boiled with a little absolute alcohol, in which they were almost insoluble. The compound was then crystallized twice from about 70% alcohol. At 243° the material did not melt but changed without charring, probably breaking up into methyl iodide and the original arsine. The compound is soluble in water and dil. alcohol but only very slightly soluble in absolute alcohol.

Anal. Subs., 0.0696, 0.2488: AgI, 0.0461, 0.1638. Calcd. for $C_6H_{10}Cl_2IAs$: I, 35.77. Found: 35.77, 35.57.

***bis*-β-Chlorovinyl-α-naphthyl-arsine,** $(Cl.CH{=}CH)_2As.C_{10}H_8$.—A Grignard reagent of 4.2 g. of α-bromonaphthalene solution was prepared in the usual manner, using a trace of iodine to start the reaction. A solution of 4 g. of *bis*-β-chlorovinyl-chloroarsine in absolute ether was dropped slowly into the Grignard solution. A vigorous reaction took place and heat was generated. After standing overnight, the reaction mixture was poured into cold water. The ether layer was separated and filtered through a dry filter paper. On evaporation, 2 cc. of a yellow oil was left. The oil was insoluble in water and could not be crystallized or even fractionated at 25 mm. pressure.

Anal. Subs., 0.2371, 0.2505: AgCl, 0.2088, 0.2298. Calcd. for $C_{14}H_{11}Cl_2As$: Cl, 21.75. Found: 22.39, 22.71.

***tris*-β-Chlorovinyl-arsine-hydroxynitrate,** $(Cl.CH{=}CH)_3As(OH)NO_3$.—*tris*-β-Chlorovinyl-arsine was oxidized with nitric acid in the same way and with the same precautions as described under β-chlorovinyl-arsonic acid. After the acid layer had decomposed the layer of *tris*-β-chlorovinyl-arsine, the solution was allowed to stand for a short time. An oily layer that separated in the bottom of the tube crystallized quickly when a little water was added. After the liquid was filtered the compound was crystallized twice from water, then ground and dried; m. p., 103°. The crystals are soluble in cold absolute alcohol and in hot water.

Anal. Subs., 0.2790, 0.2061: AgCl, 0.3553, 0.2612. Calcd. for $C_6H_7O_4NClAs$: Cl, 31.44. Found: 31.43, 31.29.

***tris*-β-Chlorovinyl-methyl-arsonium Iodide,** $(Cl{-}CH{=}CH)_3As(CH_3)I$.—Ten g. of *tris*-$\beta$-chlorovinyl-arsine and 5.5 g. of methyl iodide were sealed in a tube which was heated in a water-bath at 80° for 22 hours, then at 100° for two hours. The contents of the tube became almost solid with a mass of crystals. These were removed from the tube and collected on a filter. The mother liquor was again heated in a sealed tube with more methyl iodide and a second crop of crystals was obtained. The crystals were washed with absolute alcohol, then crystallized several times from alcohol. The product melted at 202°, and is only very slightly soluble in absolute alcohol, either cold or hot, but is readily dissolved in 95% alcohol. It is very soluble in water.

Anal. Subs., 0.3048, 0.2090: AgI, 0.1779, 0.1223. Calcd. for $C_7H_9Cl_3IAs$: I, 31.62. Found: 31.56, 31.56.

Double Salt of *tris*-β-Chlorovinyl-methyl-arsonium Iodide and Mercuric Iodide, $(Cl.CH{=}CH)_3As(CH_3)I.HgI_2$.—Molecular proportions of *tris*-β-chlorovinyl-methyl-arsonium iodide and mercuric iodide were dissolved separately in alcohol and the solutions mixed and warmed for a short time. As the solution cooled a heavy, granular, light yellow precipitate formed. The mother liquor was filtered, the precipitate crystallized from alcohol, and the crystals were washed with absolute alcohol; they melted between 150° and 156°, and were soluble in hot absolute alcohol and somewhat soluble in hot 95% alcohol. They were insoluble in cold absolute alcohol and in hot and cold water.

Anal.[5] Subs., 0.1914, 0.2099: Hg, 0.0446, 0.0498. Calcd. for $C_7H_9Cl_3I_3AsHg$: Hg, 23.44. Found: 23.30, 23.25.

Double Salt of *tris*-β-Chlorovinyl-methyl-arsonium Iodide and Phenylmercuric iodide, $(Cl.CH{=}CH)_3As(CH_3)I.C_6H_5HgI$.—The replacement of a mercury halogen with a phenyl group did not diminish the tendency to form a double salt. Molecular proportions of *tris*-β-chlorovinyl-methyl-arsonium iodide in absolute alcohol and phenylmercuric iodide were heated in a sealed tube for 12 hours at 90°. Long, thick, needle-like, yellow crystals formed when the contents of the tube were allowed to cool. These crystals were separated from the excess of insoluble phenylmercuric iodide by warming the reaction mixture. The crystals dissolved and the solution was filtered. The filtrate deposited the crystals of the double salt. It is soluble in warm absolute alcohol and insoluble in water. The melting point of the double salt is not sharp but is near 147–148°.

Anal. Subs., 0.1899, 0.2020: Hg, 0.0451, 0.0469. Calcd. for $C_{13}H_{14}Cl_3I_2AsHg$: Hg, 24.34. Found: 23.76, 23.22.

Double Salts of *tris*-β-Chlorovinyl-arsine and Silver Nitrate, $(Cl{-}CH{=}CH)_3As.AgNO_3$ and $[(Cl{-}CH{=}CH)_3As]_2.AgNO_3$.—The compound containing equimolar proportions of the tertiary arsine and silver nitrate was prepared by dissolving the *tris*-β-chlorovinyl-arsine in absolute alcohol and adding to it an excess of silver nitrate dissolved in boiling absolute alcohol. Long, fine, silky needles formed at once in such quantity that the solution became thick and semi-solid. The liquid was filtered and the solid remaining was crystallized from a small amount of absolute alcohol and dried at 60°; m. p., 144°. 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 compound is stable toward light when pure and dry.

Anal. Subs., 0.1377, 0.1716: AgCl, 0.1372, 0.1674. Calcd. for $C_6H_6O_3Cl_3NAsAg$: Cl, 24.78. Found: 24.66, 24.12.

Subs., 0.1597, 0.1709: AgCl, 0.0534, 0.0567. Calcd.: Ag, 25.13. Found: 25.17, 24.98.

The compound containing two molecules of *tris*-β-chlorovinyl-arsine to one of silver nitrate is made as described above except that an excess of the arsine is used. The character of the crystals and other physical properties are similar to those described above.

Anal. Subs., 0.1301, 0.1200: AgCl, 0.1639, 0.1501. Calcd. for $C_{12}H_{12}O_3Cl_6NAs_2Ag$: Cl, 30.89. Found: 30.97, 30.92.

Summary

Experimental evidence is presented in support of the previously published theory of the reaction of acetylene, arsenic chloride and aluminum chloride. The β-bromovinyl-bromo-arsines have been prepared and also β-bromovinyl-arsonic acid. A number of derivatives of the β-chloro-

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[5] F. C. Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., **1921**, p. 365.

vinyl-arsines have been prepared and studied. β-Chlorovinyl-dichloroarsine has been shown to resemble arsenic trichloride in its condensations with diphenylamine and phenyl-α-naphthylamine. The strong tendency of the *tris*-β-chlorovinyl-arsine to form molecular compounds has been demonstrated.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF NEBRASKA]

PREPARATION OF 6-METHYLCOUMARIN AND ITS DERIVATIVES

BY T. J. THOMPSON AND R. HERBERT EDEE

RECEIVED MAY 29, 1925 PUBLISHED OCTOBER 6, 1925

The purpose of this investigation was the determination of the most favorable procedure for the preparation of 6-methylcoumarin, and the study of its derivatives.

In 1883 and 1884 von Pechmann[1] and others found that phenols condense with ethyl aceto-acetate and malic acid in the presence of concd. sulfuric acid to form members of the coumarin series. Different phenols were found to condense with various degrees of readiness. Thus, phenol, *o*- and *p*-cresols, quinol and thymol gave extremely poor yields, but resorcinol, orcinol and pyrogallol condensed readily. Later, Fries and Klostermann[2] condensed *m*-cresol with malic acid and ethyl aceto-acetate, and showed that a much better yield was obtainable.

Chuit and Bolsing[3] prepared coumarins by Knoevenagel's reaction. They condensed hydroxy-aldehydes with the appropriate ketonic acid or ester in the presence of an amine (aniline or piperidine). In this way, they prepared acids which on heating lost a molecule of water, forming the coumarin. From 5-methyl-salicylaldehyde and ethyl aceto-acetate, 6-methylcoumarin-carboxylic acid was prepared. This, when heated to 250–300°, yielded a very small amount of 6-methylcoumarin. Still more recently, Bailey and Boettner[4] modified the method of von Pechmann and applied it to the condensation of *m*-cresol and malic acid. They obtained yields of more than 50%. They were not able, however, to condense phenol with maleic acid. Ponndorf[5] in 1921 condensed *p*-cresol with maleic and fumaric acids, using sulfuric acid and zinc chloride as condensing agents. He reports a 50% yield, but his calculation is not based upon the purified product.

We have found that a yield of 80% of purified 6-methylcoumarin is obtained by heating equimolecular quantities of fumaric acid and *p*-cresol

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[1] Von Pechmann, *Ber.*, **16**, 2119 (1883); **17**, 929, 1646 (1884).

[2] Fries and Klostermann, *Ber.*, **39**, 871 (1906).

[3] Chuit and Bolsing, *Bull. soc. chim.*, [III] **36**, 76 (1906).

[4] Bailey and Boettner, *J. Ind. Eng. Chem.*, **13**, 905 (1921).

[5] Ponndorf, Ger. pat. 338,737, **1921.**