237. *Isomers of 2-Chlorovinyldichloroarsine.*

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Two isomeric forms of 2-chlorovinyldichloroarsine have been prepared from the mixture obtained by the interaction of acetylene and arsenic trichloride in the presence of catalysts. The pure arsonic acids have also been prepared.

The possibility that 2-chlorovinylarsonic acid and the derived dichloroarsine (" lewisite ") could exist in *cis*- and *trans*-forms has been mentioned in the literature (cf. Gibson and Gibson, *J.*, 1931, 753), but no attempt had been made to prepare the two forms in a pure state.

The mixture known as " lewisite ", prepared by interaction of acetylene and arsenic trichloride in the presence of aluminium chloride (Green and Price, *J.*, 1921, **119**, 448) was reported to be highly active as a vesicant, its activity being due to the 2-chlorovinyldichloroarsine. When, however, 2-chlorovinyldichloroarsine was prepared by using mercuric chloride or cuprous chloride as a catalyst (Jones *et al.*, *Ind. Eng. Chem.*, in the press), it appeared to be somewhat less vesicant and it seemed possible that this difference might be due to different amounts of the two isomers being present. Since aluminium chloride usually favours the formation of the *trans*-compound (Zelinsky and Turowa-Pollak, *Ber.*, 1929, **62**, 1618; 1932, **65**, 1299) and since acetylene normally gives rise to *trans*-addition products (Garner, *Chem. News*, 1919, **119**, 16), it seemed probable that the aluminium chloride product would have the *trans* configuration. Backe and Beute (*Rec. Trav. chim.*, 1935, **54**, 167), however, have shown that under certain conditions propiolic acid gives rise to *cis*-addition products, and it seemed possible that mercuric chloride and cuprous chloride might give rise to more *cis*-2-chlorovinyldichloroarsine than would aluminium chloride.

2-Chlorovinyldichloroarsine prepared by all three methods was shown to consist in the main of the same isomer by oxidation, by means of hydrogen peroxide, to the same arsonic acid, m. p. 130—131°, which is presumed to have the *trans*-configuration. In each case the liquors of this acid contained a second *acid* which was extremely soluble in water and in all aqueous solvents and difficult to isolate.

Attempts to separate *cis*- and *trans*-2-chlorovinyldichloroarsine by fractional distillation indicated that the isomer presumed to have the *cis*-configuration had a lower b. p. than the other, since the lower-boiling fractions yielded less arsonic acid, m. p. 130—131°, than did the higher-boiling fractions. However, since no clear cut could be observed between the first and last fractions without a slow distillation rate, this method of separation was abandoned, since prolonged heating of the dichloroarsine causes disproportionation to arsenic trichloride and the 2 : 2′-dichlorodivinylchloroarsine.

Pure *trans*-chlorovinyldichloroarsine, prepared from the arsonic acid, liberates two molecules of hydrochloric acid with water with formation of chlorovinylarsine oxide; on treatment with cold sodium hydroxide solution a third molecule of hydrochloric acid is liberated with the formation of sodium arsenite and evolution of one molecule of acetylene. This gives a useful method of estimating the purity of *trans*-2-chlorovinyldichloroarsine; when, however, it was applied to redistilled 2-chlorovinyldichloroarsine prepared by using cuprous chloride as catalyst, it gave results of only 90%. This suggested that the other constituent, presumably the *cis*-compound, was present to the extent of 10% and had different properties.

cis-2-Chlorovinyldichloroarsine was finally prepared by a combination of fractional distillation of the dichloroarsines, and fractional crystallisation of the arsonic acids. Crude lewisite prepared with a cuprous chloride catalyst (containing arsenic trichloride and some monochloroarsine) was oxidised by means of chlorine water and the bulk of the *trans*-compound removed as arsonic acid. The acid liquors were reconverted into the chloroarsines and fractionated; this gave a product very rich in the *cis*-isomer, which dissolved in cold sodium hydroxide solution without evolution of gas and therefore contained no *trans*-compound. Direct oxidation of the dichloroarsine gave a solution of the arsonic acid in hydrochloric acid solution from which the acid was difficult to isolate; the dichloroarsine was therefore shaken with water to give the arsine oxide, which was then oxidised by means of hydrogen peroxide solution. The solution on evaporation to dryness gave an oily solid which crystallised from acetone–carbon tetrachloride to give the pure cis-2-*chlorovinylarsonic acid*, m. p. 90—91°.

Pure cis-2-*chlorovinyldichloroarsine*, m. p. — 46°, prepared from this acid, dissolved in cold sodium hydroxide solution with formation of the sodium salt of the arsine oxide without evolution of gas, but on warming to 40° vinyl chloride was liberated, the liberation being brisk at 80°. Thus the *cis*-compound liberates no further hydrochloric acid on treatment with sodium hydroxide solution and agrees in properties with the 10% of impurity in the *trans*-compound formed by interaction of acetylene and arsenic trichloride in the presence of cuprous chloride.

An impure specimen of the *cis*-acid was isolated by similar means from the 2-chlorovinyldichloroarsine prepared by the use of mercuric chloride as catalyst.

The evidence for the configuration of this pair of isomers is given by McDowell, Moelwyn-Hughes, and Emblem (following paper); however, the *trans*-isomer normally has the higher m. p.

The *arsine oxides* of the two isomers have been prepared in a crystalline state by allowing a dilute solution of the dichloroarsine in water to stand for a long time; the *trans*-compound has m. p. 140°, and the *cis*-, m. p. 130—131°.

The *cis*-isomer can be determined in a mixture of the two by taking advantage of the fact that it dissolves in cold sodium hydroxide solution with formation of the sodium salt of the arsine oxide which can be reconverted into the dichloroarsine with hydrochloric acid, whereas the *trans*-compound decomposes to sodium arsenite. The dichloroarsine can be titrated by means of iodine in the presence of the arsenic chloride without interference. Any secondary or tertiary arsine present will not dissolve in sodium hydroxide solution and can be extracted with a solvent.

Attempts to isomerise the *trans*-dichloroarsine to the *cis*- by irradiation with ultra-violet light, which often converts the stable form into the labile, met with no success, the main reaction was disproportionation, although analysis indicated that some *cis*-compound was formed. In the presence of air the arsonic acid was formed, which was unaffected by ultra-violet light.

Treatment of the *trans*-arsonic acid with phosphorus oxychloride gave a mixture of the *cis*- and *trans*-isomers together with arsenic trichloride, *cis*- and *trans*-dichloroethylene, and tetrachloroethane.

EXPERIMENTAL.

trans-2-*Chlorovinylarsonic Acid*.—(*a*) 2-Chlorovinyldichoroarsine (" lewisite-I "; 182 g.) prepared by the method of Green and Price (*loc. cit.*) from arsenic trichloride, acetylene, and aluminium chloride, was oxidised by stirring it with water whilst chlorine was passed in to excess. The clear solution was evaporated under reduced pressure several times with distilled water, and the residue crystallised from water in colourless needles, m. p. 130—131°. Yield, 123 g.

(*b*) 2-Chlorovinyldichloroarsine prepared by the use of mercuric chloride as catalyst (Jones *et al.*, *Ind. Eng. Chem.*, in the press) was oxidised as above and yielded the same acid, m. p. 130—131°.

(*c*) 2-Chlorovinyldichloroarsine, prepared by using cuprous chloride as catalyst (*idem, ibid.*), on similar oxidation gave the same arsonic acid, m. p. 130—131°. In each case this was the preponderating product, but the liquors contained a more soluble isomer.

cis-2-*Chlorovinylarsonic Acid*.—The mixture (40 kg.) obtained by interaction of acetylene and a solution of arsenic trichloride in tetrachloroethane with cuprous chloride in triethanolamine hydrochloride solution (*idem, ibid.*) was distilled, and the first 16 kg. to distil collected; the boiling range was up to 60°/5 mm. The distillate was a mixture of tetrachloroethane, arsenic trichloride, *cis*-lewisite-I, *trans*-lewisite-I, and some 2 : 2′-dichlorodivinylchloroarsine (" lewisite-II "). It was stirred with its own volume of water and chlorine passed in to excess. The tetrachloroethane and arsenic trichloride were then removed under reduced pressure, and the aqueous solution concentrated; on cooling, the *trans*-arsonic acid separated and was recrystallised from water. Yield, 1·9 kg. The mother liquors were then concentrated to a syrup, dissolved in concentrated hydrochloric acid, and reduced with sulphur dioxide and a trace of iodine to the chloroarsines. The mixture was then distilled once and then fractionated twice up a 4 ft. × 1 in. column packed with glass cuts and fitted with a total reflux head operating at an 8 : 1 ratio. Separation of the *cis*-lewisite-I from the *trans*-compound and lewisite-II was sharp, and a fraction, b. p. 57·2—57·6°/7 mm., was obtained (225 g.). After removal of this fraction the temperature of the vapour rose rapidly to 65° while only 20 g. distilled; this was mainly *trans*-compound.

This crude *cis*-lewisite-I was shaken with water (1 l.), and the crude arsine oxide separated as an oil which rapidly solidified. The oxide was broken up and washed with water and added in small amounts to excess of hydrogen peroxide solution (20 vols.) cooled in ice. The clear solution of arsonic acids was then evaporated under reduced pressure to a syrup which slowly crystallised. The semi-solid mass was dissolved in acetone (40 c.c.), chloroform (20 c.c.) added, and the solution cooled to − 40°. After some hours at − 40°, the crystals were filtered off on a Buchner funnel cooled to − 40° and recrystallised from acetone at − 40°. The cis-*chlorovinylarsonic acid* separated as colourless needles, m. p. 90—91° (Found: Cl, 19·0; As, 38·2. $C_2H_4O_3ClAs$ requires Cl, 19·0; As, 40·2%. The arsenic was very difficult to determine). This arsonic acid is extremely soluble in water and difficult to crystallise when water is present.

cis-2-*Chlorovinyldichloroarsine.*—*cis*-2-Chlorovinylarsonic acid (87 g.) was dissolved in concentrated hydrochloric acid (250 c.c.) and reduced with sulphur dioxide and a trace of iodine with stirring and external cooling. The cis-2-*chlorovinyldichloroarsine* distilled as a colourless liquid (92 g.), b. p. 51—52°/5 mm., m. p. − 46·6° (Found: Cl, 51·2; As, 36·0. $C_2H_2Cl_3As$ requires Cl, 51·3; As, 36·1%). *cis*-2-Chlorovinyldichloroarsine dissolves in cold sodium hydroxide solution without evolution gas and with removal of two chlorine atoms by hydrolysis (Found: Cl, 34·35. Calc. for two Cl atoms, 34·2%); addition of hydrochloric acid regenerates the dichloroarsine. The *trans*-isomer dissolves in cold sodium hydroxide solution with evolution of acetylene and liberation of three chlorine atoms; arsenic trichloride is obtained by addition of hydrochloric acid. The solution obtained by dissolving the *cis*-isomer in sodium hydroxide solution on heating to 40° slowly liberates vinyl chloride, b. p. − 18°; no acetylene was detected.

cis-2-*Chlorovinylarsine Oxide.*—When *cis*-2-chlorovinyldichloroarsine is shaken with a large volume of water, it dissolves, and the *arsine oxide* slowly separates in quantitative yield in colourless plates, m. p. 131°. The *trans*-isomer prepared in a similar manner has m. p. 143°.

Determination of cis-2-*Chlorovinyldichloroarsine.*—The dichloroarsine (0·4598 g.) was dissolved in chloroform (20 c.c.) and shaken with cold sodium hydroxide solution (4N, 20 c.c.). The aqueous solution was washed twice with chloroform (20 c.c. each time), made just faintly acid to Congo-red, diluted to 300 c.c., and titrated with iodine solution using starch as an indicator. Provided the acid concentration is kept very low, the end point is reasonably sharp. The titre for pure *cis*-isomer was 41·4 c.c. of 1·05N-iodine which gives 98%. The chloroform washings had zero iodine titre. This method is suitable for estimating the *cis*-isomer in the presence of the *trans*-isomer, arsenic trichloride, 2 : 2′-dichlorodivinylchloroarsine, and 2 : 2′ : 2″-trichlorotrivinylarsine, even when all are present in solution, since the *trans*-isomer is converted into sodium arsenite by sodium hydroxide solution and does not therefore react with iodine after acidification. The other materials are insoluble in sodium hydroxide solution and are extracted by the chloroform.

Attempted Isomerisations.—(*a*) Pure *trans*-2-chlorovinyldichloroarsine (55 g.) (prepared by reduction of the pure *trans*-arsonic acid in hydrochloric acid solution) was dissolved in carbon disulphide (250 c.c.), and aluminium chloride (35 g.) added slowly with cooling. After ½ hour in ice and 24 hours at room temperature, the clear layer was decanted and decomposed with ice–hydrochloric acid. Distillation yielded arsenic trichloride (4·5 g.) and *trans*-2-chlorovinyldichloroarsine (9·2 g.). The aluminium chloride sludge after decomposition with ice and hydrochloric acid yielded a mixture of 2 : 2′-dichlorodivinylchloroarsine and 2 : 2′ : 2″-trichlorotrivinylarsine (8·7 g.); there was considerable high-boiling residue.

(*b*) The pure *trans*-isomer (prepared from the arsonic acid) was irradiated in an open dish with light from a mercury vapour lamp; after 24 hours the whole of the dichloroarsine had been converted into the *trans*-arsonic acid. Irradiation in a closed vessel at 1 ft. from the light source gave a product which was mainly the product of disproportionation, but some isomerisation had also occurred as was shown by analysis (arsenic trichloride, 16·1%; *trans*-isomer, 54·6%; *cis*-isomer, 8·5%; 2 : 2′-dichlorodivinylchloroarsine, 19·8%). The arsonic acid was recovered unchanged after irradiation.

(*c*) The *trans*-arsonic acid (100 g.) was treated with phosphorus oxychloride (170 g.) in small amounts with cooling; the product was then distilled. Fraction (i), b. p. 55° (7 g.); (ii), b. p. 100—110° (35 g.); (iii), b. p. 120—130° (88 g.); (iv), b. p. 35—75°/6 mm. (35 g.). Fraction (i) was a mixture of *cis*- and *trans*-dichloroethylene; (ii) was unchanged phosphorus oxychloride; (iii) was arsenic trichloride containing some tetrachloroethane; and (iv) was tetrachloroethane and 2-chlorovinyldichloroarsine. Fraction (iv) on refractionation gave 11 g. of tetrachloroethane and 24 g. of 2-chlorovinyldichloroarsine, b. p. 85—86°/11 mm., which contained only a small amount of *cis*-isomer as determined by above method.

Preliminary Investigation.—2-Chlorovinyldichloroarsine (2400 g.) of boiling range 40—65°/4 mm., prepared by using a cuprous chloride catalyst, was oxidised by stirring with water and passing in chlorine. Solvent and arsenic chloride were removed under reduced pressure and most of the *trans*-arsonic acid removed by crystallisation. The liquors were reconverted into the dichloroarsines and distilled into three fractions: (i) 40—48°/3 mm. (180 g.); (ii) b. p. 48—60°/3 mm. (283 g.); (iii) b. p. > 60°/3 mm. (81 g.). Each fraction was oxidised with water and chlorine. Fraction (i) yielded only 15 g. of *trans*-acid; fraction (ii) yielded 253 g. of the *trans*-acid. Thus the *cis*-isomer is the lower-boiling. The mother liquors of the *trans*-acid from fraction (i) on reconversion into the dichloroarsine gave a product which liberated only 28% of the theoretical amount of acetylene with cold sodium hydroxide solution.

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