

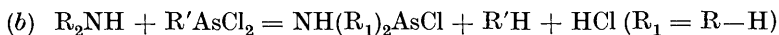
CCCXLVIII.—10-Chloro-5:10-dihydrophenarsazine and its Derivatives. Part XVI. 10-Alkyl-5:10-dihydrophenarsazines as Convenient Sources of Aliphatic Dichloroarsines.

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It has been shown (Gibson and co-workers, J., 1926, 450; *Rec. trav. chim.*, 1930, **49**, 1006; Seide and Gorski, *Ber.*, 1929, **62**, 2186) that the formation of 10-chloro-5:10-dihydrophenarsazine from diphenylamine and arsenious chloride should be written



since 10-chloro-5:10-dihydrophenarsazine is decomposed into arsenious chloride and diphenylamine hydrochloride by hydrogen chloride. When the reaction is carried out under the usual conditions, under which the hydrogen chloride produced escapes from the sphere of the reaction, it proceeds almost quantitatively from left to right. 10-Chloro-5:10-dihydrophenarsazine (or a derivative) is also produced when dichloroarsines ($\text{R}'\text{AsCl}_2$) are heated with aromatic secondary amines (R_2NH), the reaction being expressed thus:



(Burton and Gibson, J., 1926, 464; compare Lewis and Stiegler, *J. Amer. Chem. Soc.*, 1925, **47**, 2546; 1930, **52**, 4164; Seide and Gorski, *loc. cit.*; Scherlin and Epstein, *Ber.*, 1928, **61**, 1823; Gibson, *J. Amer. Chem. Soc.*, 1931, **53**, 376). Seide and Gorski (*loc. cit.*) also showed that 10-methyl- and 10-phenyl-5:10-dihydrophenarsazines (Aeschlimann, J., 1927, 413) when heated with hydrogen chloride are decomposed into diphenylamine hydrochloride and methyl- and phenyldichloroarsine respectively and therefore concluded that it is unlikely that the 10-alkyl- or 10-aryl-compounds are intermediate products in reaction (b), which was

suggested as a possibility by Burton and Gibson (*loc. cit.*); for all practical purposes, the reaction



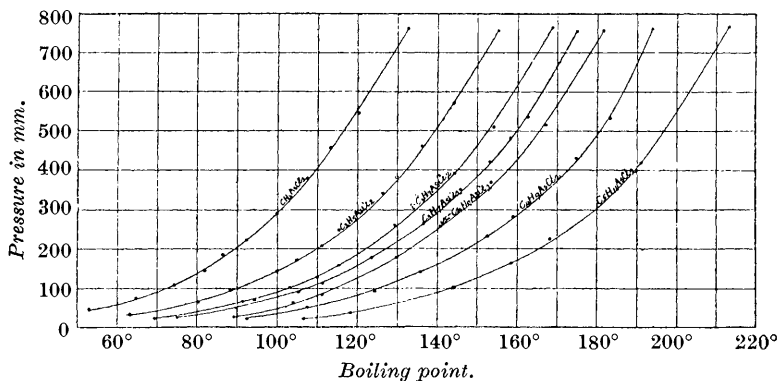
is complete.

Although Seide and Gorski only studied two examples and worked with small quantities of materials, the yields of dichloroarsines obtained by them were so good that it was considered desirable to see how far the reaction is general and to what extent it can be used for the preparation of alkyl-dichloroarsines, particularly of those not readily accessible by other methods.

10-Methyl-, -ethyl-, -propyl-, -isopropyl-, -isobutyl-, -sec.-butyl-, -n-butyl-, -n-amyl-, and -diethylmethyl-5:10-dihydrophenarsazines have been prepared by the action of the appropriate alkylmagnesium halide on 10-chloro-5:10-dihydrophenarsazine (Aeschlimann, *loc. cit.*). These are all highly crystalline compounds whose lack of colour is explained by the theory of colour of dihydrophenarsazines previously elaborated (J., 1929, 1238; *Rec. trav. chim.*, *loc. cit.*). On being kept for some months in stoppered bottles, some of them acquired a yellow colour. The yields in which these 10-alkyl-5:10-dihydrophenarsazines are obtained appear to depend on the yield of the Grignard reagent from a given quantity of alkyl halide rather than on the reaction between the Grignard reagent and the 10-chloro-compound. If the formation of the Grignard reagent did not appear to be complete, the yield of the 10-alkyl-compound was low, although an excess of the former was normally taken. This was particularly the case with the *iso*-alkyl compounds. From the *n*-alkyl bromides, high yields of the 10-alkyl-compounds are obtained. The 10-alkyl-5:10-dihydrophenarsazines have a mildly irritating effect on the skin of the face.

The 10-alkyl-5:10-dihydrophenarsazines were readily decomposed by treatment at 110–130° with dry hydrogen chloride. Indications of the preliminary formation of an addition compound were observed, a crystalline solid being deposited on the surface of the flask as soon as hydrogen chloride was bubbled through the liquid. By means of a special apparatus, action of the dichloroarsines on the rubber stoppers was prevented throughout the work. Methyl-, ethyl-, *n*-propyl-, isopropyl-, *n*-butyl-, isobutyl-, sec.-butyl-, and *n*-amyl-dichloroarsines were obtained crude in yields varying from 65 to 85% of the theoretical and, after distillation under diminished pressure, they were obtained as colourless liquids in yields varying from 50 to 67%. This method seems admirably suited for the preparation of normal and branched-chain alkyl-

dichloroarsines. The physical constants of the alkyldichloroarsines were determined on twice-distilled specimens.



In the table are given the densities (reduced to vacuum standard) and the boiling points under various pressures of the above eight dichloroarsines. For the density determinations specially calibrated weights were used, and about 10 c.c. of liquid in each case. The determination of the boiling points at reduced pressures was carried out by means of the pressure regulator described in the following paper. From the slope of the boiling point–pressure curves (which are not quite accurately represented by an equation of the form $A - \log_e p = K/T$), the molecular heats of vaporisation and Trouton's constant at 760 mm. are calculated to be: MeAsCl_2 , 7890 cal. and 19.4; EtAsCl_2 , 9180 cal. and 21.4; Pr^nAsCl_2 , 10,400 cal. and 23.1; Pr^iAsCl_2 , 11,500 cal. and 26.0; $n\text{-BuAsCl}_2$, 12,200 cal. and 26.2; sec.-BuAsCl_2 , 10,700 cal. and 23.5; and $n\text{-AmAsCl}_2$, 11,950 cal. and 24.6 respectively. The somewhat high values in some cases of Trouton's constant may indicate some association in the liquid state. If the densities of the n -alkyldichloroarsines are plotted against the number of carbon atoms, an anomaly is revealed in the case of the butyl compound.

Substance.	D_{4}^{20} (vac.).	M. p.	Boiling points at :					
			20 mm.	50 mm.	100 mm.	200 mm.	400 mm.	760 mm.
MeAsCl_2	1.8358	-42.5°	—	55.5°	72.1°	89.1°	109.1°	132.5°
EtAsCl_2	1.6595	—	—	74.0	90.0	109.6	131.2	155.3
$n\text{-PrAsCl}_2$...	1.5380	-28.2	—	88.8	107.5	126.9	151.2	175.3
$iso\text{-PrAsCl}_2$	1.4900	—	67.0°	85.5	102.6	121.0	145.0	168.6
$n\text{-BuAsCl}_2$...	1.4664	—	90.5	105.0	125.6	147.2	172.0	194.1
$iso\text{-BuAsCl}_2$	1.4465	—	77.8	95.8	—	—	—	—
sec.-BuAsCl_2	1.4128	—	85.0	99.4	113.7	132.1	156.7	181.8
$n\text{-AmAsCl}_2$...	1.4035	-45.5	103.0	123.1	142.6	164.1	189.0	212.9

(Densities should not be in error by more than 1 part in 10,000.)

EXPERIMENTAL.

The general procedure for the preparation of the 10-alkyl-5 : 10-dihydrophenarsazines was as follows. The alkylmagnesium bromide (2 mols.; 1 g.-mol. in 480 c.c. of ether) was prepared in a 3-litre flask fitted with a reflux condenser of wide diameter. The flask was held above a vessel containing ice and water, and purified 10-chloro-5 : 10-dihydrophenarsazine (1 mol.) added in small quantities. Each addition produced a momentarily vigorous reaction and the "wetting" of its wall soon resulted in a blockage of the condenser. This was most conveniently removed by pouring ether down the condenser until a column of about 10 cm. remained above the solid. By cooling the flask in ice-water, the whole of the chloro-compound was sucked into the flask. When the addition of the chloro-compound was complete the mixture was heated for 30 minutes on the water-bath and finally ice and dilute sulphuric acid were added. In those reactions which did not proceed so well, some solid remained at this stage and this was removed by filtration and the ethereal solution was washed with dilute sulphuric acid and then with dilute sodium hydroxide solution. Any precipitated solid was removed by filtration and the ethereal solution was then washed with water, dried with potassium carbonate, and evaporated. The residue readily solidified and was usually crystallised from alcohol; for the *sec.*-butyl and *isobutyl* compounds aqueous alcohol was used, these compounds having a tendency to separate as oils.

The figures in parentheses indicate the yields in grams of the pure 10-alkyl-5 : 10-dihydrophenarsazine obtained from 100 g. of 10-chloro-5 : 10-dihydrophenarsazine. 10-Methyl-, m. p. 106—107° (64); 10-ethyl-, m. p. 75° (68); 10-*n*-propyl-, m. p. 85·5—86·5° (79); 10-*isopropyl*-, m. p. 87—88° (38) (Found : As, 26·2. C₁₅H₁₆NAs requires As, 26·3%); 10-*n*-butyl-, m. p. 94—95° (69) (Found : As, 25·4. C₁₆H₁₈NAs requires As, 25·1%); 10-*isobutyl*-, m. p. 73—74° (51 g., crude) (Found : As, 25·4%); 10-*sec.*-butyl-, m. p. 85—86° (74 g., crude) (Found : As, 25·2%); 10-*n*-amyl-, m. p. 90—92° (55) (Found : C, 64·6; H, 6·5; As, 24·6. C₁₇H₂₀NAs requires C, 65·1; H, 6·4; As, 24·0%); 10-*diethylmethyl*-, m. p. 110—111° (4) (Found : As, 24·3%). From 64 g. of 10-chloro-2-methyl-5 : 10-dihydrophenarsazine and propylmagnesium bromide, 50 g. of pure 2-*methyl*-10-*propyl*-5 : 10-*dihydrophenarsazine*, m. p. 83·5—84·5°, were obtained (Found : As, 25·3. C₁₆H₁₈NAs requires As, 25·1%).

In concentrated sulphuric acid, all the alkyl derivatives yield deep red solutions; those of the ethyl, *isopropyl*, *sec.*-butyl, and *diethylmethyl* compounds become green on addition of a little

concentrated nitric acid; in all cases the colour changes to brown or reddish-brown with excess of concentrated nitric acid.

The decomposition of the 10-alkyl-5 : 10-dihydrophenarsazines was carried out in a vacuum distillation flask of the Claisen type. The necks of the flask were elongated and of such a diameter that the thermometer and leading-in tube were of sliding fit for a length of 5—6 cm. This arrangement prevented any action of the dichloroarsines on the stoppers. A similar arrangement was made for the side arm (provided with a short condenser) leading to the all-glass receiver of the Perkin type. The leading-in tube for the hydrogen chloride was provided with a glass stopper, as was the capillary tube which replaced this tube of ordinary dimensions for the redistillation of the dichloroarsines. The flask, about half-filled with the alkyl compound, was heated in an oil-bath at 110—130°. When the compound had melted, a rapid stream of hydrogen chloride was bubbled through it. After a time the inlet tube invariably became blocked and its tap was then turned off. The melt was then automatically sucked into the tube and this was frequently cleared by this means. If this failed, the temperature of the bath was raised to 140—180° (the higher temperature in the case of the higher homologues) and the pressure in the apparatus reduced. The contents of the flask finally melted and the dichloroarsine distilled. When all volatile material appeared to have passed over, the temperature of the bath was lowered to about 130° and the passage of the hydrogen chloride recommenced. These operations were repeated until no more distillate was obtained or the contents of the flask had decomposed extensively. The distillate was usually coloured and contained some solid. After one distillation under reduced pressure the dichloroarsine was obtained pure, but it was submitted to a second distillation in each case.

The figures in parentheses give the percentage yields of pure dichloroarsine obtained in each case. Methyl- (67); ethyl- (65); *n*-propyl- (64) (Found : Cl, 37.2. $C_3H_7Cl_2As$ requires Cl, 37.5%); *isopropyl*- (67) (Found : Cl, 37.8%); *n*-butyl- (52); *isobutyl*- (starting from crude 10-*isobutyl*-5 : 10-dihydrophenarsazine, 55) (Found : Cl, 34.2. $C_4H_9Cl_2As$ requires Cl, 34.9%); *sec*-butyl- (starting from crude 10-*sec*-butyl-5 : 10-dihydrophenarsazine, 54) (Found : Cl, 35.2%); *n*-amyl- (51) (Found : Cl, 32.2. $C_5H_{11}Cl_2As$ requires Cl, 32.7%).

Owing to an accident resulting in loss of the material during the determination of its boiling points the data for *isobutyldichloroarsine* are omitted from the table in the introductory portion of the paper. All the dichloroarsines are readily superheated and supercooled. Only three crystallised in a mixture of solid carbon dioxide and acetone, although the others became very viscous.

They all possess a very pungent odour which at the same time is reminiscent of decaying fungus.

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