

268. *Carboxymethyldichloroarsine and Related Carboxylic Acids containing Arsenic.*

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The reported formation of carboxymethyldichloroarsine by the action of phosphorus trichloride on carboxymethylarsonic acid, which involves the reduction of quinquevalent arsenic to the trivalent state, has been examined and confirmed. The structure, stability, and infrared spectra of the dichloroarsine are discussed and two new related acids reported.

CARBOXYMETHYLDICHLOROARSINE (dichloroarsinoacetic acid), $\text{Cl}_2\text{As}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, was prepared by Steinkopf and Schmidt¹ by the action of phosphorus trichloride on carboxymethylarsonic acid, $(\text{HO})_2\text{AsO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The preparation was repeated by Marquez² but these workers did not establish the constitution except by elemental analysis. Braunholtz and Mann³ commented that reduction of the arsenic to the trivalent state, in preference to the formation of the chloride of the carboxylic acid, was surprising.

¹ Steinkopf and Schmidt, *Ber.*, 1928, **61**, 675.

² Marquez, *Rev. Fac. Cienc. quim., Univ. nac. La Plata*, 1941, **16**, 109.

³ Braunholtz and Mann, *J.*, 1957, 3285.

We have now found that, provided the conditions are carefully controlled, the dichloroarsine can be satisfactorily prepared. The structure of the acid has been established and dibromocarboxymethylarsine and 2-carboxyethylchloroarsine have been similarly obtained.

Carboxymethylarsonic acid was prepared by a modification of Palmer's method,⁴ being separated as its barium salt. It was then converted into the dichloroarsine by phosphorus trichloride in carbon tetrachloride. The manipulative stages were critical, a feature not reported by earlier workers: with suitable precautions, reasonable yields (ca. 25%) were obtained. The dichloroarsine was stable when pure if moisture was excluded.

Analytical results for the dichloroarsine were variable owing to the instability of the compound but all support a value of 205 for the molecular weight and the trivalent state of the arsenic. Direct titration with barium hydroxide gave an equivalent weight of 69.9. Non-aqueous titration with potassium methoxide gave a value of 105.5 on rapid titration but the compound slowly reacted further with the methoxide and (after back-titration with benzoic acid) an equivalent weight of 70 was obtained. Determination of the equivalent weight with iodine and with bromate gave equivalent weights of 208.2 and 204.2 for the trivalent arsenic compound. The molecular weight was also confirmed by ebullioscopic measurements in acetone and in carbon tetrachloride.

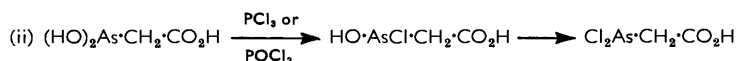
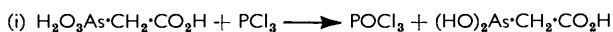
The infrared spectra examined are tabulated. The dichloroarsine has the characteristic

Compound	ν_{OH} (cm. ⁻¹)	ν_{CO} (cm. ⁻¹)	ν_{OH} (cm. ⁻¹)
Cl ₂ As·CH ₂ ·CO ₂ H ^a	2660, 2560	1685	890
" ^b	2600, 2540	1675	885—915
(HO) ₂ AsO·CH ₂ ·CO ₂ H ^c	2400	1690	885
AcOH ^d	2660, 2570	1712 ± 5	930
Cl·CH ₂ ·CO ₂ H ^a	2700, 2590, 2540	1713	933
Cl·CH ₂ ·CH ₂ ·CO ₂ H ^d	2640, 2580	1715	910
Ph·AsCl·CH ₂ ·CO ₂ H ^a	2640, 2540	1683	945, 920

^a Hexachlorobutadiene mull. ^b KBr disc. ^c Nujol mull. ^d Flett, *J.*, 1951, 962.

O-H and C=O bands associated with carboxylic acids though the inductive effect of the arsenic and chlorine atoms influences the position of the maxima. The existence of hydrogen bonding often encountered in structures such as carboxylic acids, which are capable of dimerisation, was demonstrated. The strong vibrational C-O band in the region 1770—1815 cm.⁻¹, usually present in the spectra of acid halides, was absent.

It is not possible to offer any evidence to support any particular path for the reduction of the quinquevalent arsenic in the arsonic acid into the trivalent state by the phosphorus trichloride. Consideration of the following reaction scheme, using available bond-energy data,⁵ suggests that the reactions could take place and that reaction (i) would indeed be exothermic.



By essentially the same method two new acids, dibromocarboxymethylarsine and 2-carboxyethylchloroarsine were prepared, the former less stable than the corresponding dichloro-acid. The new acid where the arsenic atom was separated from the carboxyl group by two methylene units was more stable, in accord with Braunholtz and Mann's observations³ on the stabilities of di-(2-carboxyethyl)phenylarsine and related compounds. Attempts to isolate pure 1-carboxyethylchloroarsine were unsuccessful; the product seemed very unstable, though this may have been due to impurities.

EXPERIMENTAL

Carboxymethylarsonic Acid.—The following modification of Palmer's method⁴ was used. Arsenic trioxide (99 g.) and sodium hydroxide (160 g.) were dissolved in water (300 ml.), and

⁴ Palmer, *J. Amer. Chem. Soc.*, 1923, **45**, 3023.

⁵ Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 2nd edn., 1958.

the solution was cooled to 30°. Monochloroacetic acid (47.3 g.) was added and the mixture stirred for 2 hr. The solution was then carefully neutralised with glacial acetic acid, the addition of acid being controlled potentiometrically. The mixture was set aside for 12 hr. at 20°, filtered, and added to aqueous barium chloride (185 g. in 500 ml.). The barium salt was washed, dried at 130° (yield 185 g., 83%), and decomposed at room temperature by addition of 10% less than the equivalent of 2N-sulphuric acid. The arsonic acid was isolated from the aqueous solution by lyophilising, as solutions of the free acid decomposed readily when warmed. It recrystallised from glacial acetic acid (yield 55 g., 74%) and had m. p. 152° (Found: As, 40.65. Calc. for $C_2H_5AsO_5$: As, 40.7%).

2-Carboxyethylarsonic acid, made from β -chloropropionic acid by the same method, had m. p. 146° (Found: As, 37.95. Calc. for $C_3H_7O_5As$: As, 37.85%).

Carboxymethyldichloroarsine.—This compound was prepared by the route used by Steinkopf and Schmidt¹ but all operations were carried out under nitrogen. Reactants and solvents were freshly dried and distilled. Carboxymethylarsonic acid (15 g.) was suspended in carbon tetrachloride (25 ml.) and to this was added slowly phosphorus trichloride (35 g.) in the same solvent (50 ml.). The reaction is exothermic and the vessel must be kept below 30°. After 1½ hr. the mixture was cooled to -5°, and the product washed with cold carbon tetrachloride and then extracted in ether. This extract was evaporated at once and the acid recrystallised from carbon tetrachloride. Finally the white crystalline product was dried under reduced pressure at 56°. The yield was 4.5 g. (27%), and the m. p. 122° (Found: As, 36.2; Cl, 34.7. Calc. for $C_2H_3AsCl_2O_2$: As, 36.6; Cl, 34.6%).

Dibromocarboxymethylarsine.—This method was similar to that used for the dichloro-compound, with phosphorus tribromide (69 g.) instead of the trichloride. Reaction was rapid and exothermic and it was important to keep the temperature at 15°. At higher temperatures the product decomposed to a brown oil. Rapid recrystallisation was also necessary, otherwise the white crystals decomposed. However, once the acid was dry and free from phosphorus contaminants it seemed stable. The yield of crystalline *dibromocarboxymethylarsine*, m. p. 108—112°, was 4 g. (24%) (Found: As, 24.4; Br, 53.3. $C_2H_3AsBr_2O_2$ requires As, 25.5; Br, 54.4%).

2-Carboxyethyldichloroarsine.—2-Carboxyethylarsonic acid (16 g.) was suspended in carbon tetrachloride (25 ml.), and phosphorus trichloride (35 g.) in the same solvent (50 ml.) was added, after initial cooling in a freezing mixture. Vigorous stirring was necessary and the temperature had to be kept below 15°. The acid was extracted and purified as before. After a second recrystallisation from carbon tetrachloride, it had m. p. 90° (2 g., 12%) (Found: As, 34.1; Cl, 32.4. $C_3H_5AsCl_2O_2$ requires As, 34.2; Cl, 32.4%).