795. *The Chlorostannates of Hydrazine and* 3 : 5 : 5-*Trimethylpyrazoline.*

By W. Pugh and A. M. Stephen.

Dihydrazinium chlorostannate has been prepared and shown to form compounds with simple aliphatic ketones. Monohydrazinium chlorostannate, although reported in the literature, appears not to exist. Condensation of acetone with stannic chloride and hydrazine dihydrochloride yields bis-3 : 5 : 5-trimethylpyrazolinium chlorostannate containing 1·5 mols. of acetone of crystallisation; the acetone-free salt is best prepared by a more direct method.

Druce (*Chem. News*, 1922, **124**, 310) prepared a series of diamine stannichlorides and reported a substance formulated as N_2H_4,H_2SnCl_6 (probably more correctly $N_2H_6SnCl_6$), this being the only chlorostannate of hydrazine in the literature. This formulation,

although in harmony with that of the chlorostannates of ethylenediamine and phenylenediamine, prepared also by Druce and confirmed in this laboratory, nevertheless appears to be an unusual one for a compound of hydrazine, which forms a well-known series of salts containing the univalent hydrazinium ion ($N_2H_5^+$); furthermore, the substance was made from stannic chloride and hydrazine monohydrochloride, a procedure which might be expected to yield dihydrazinium chlorostannate, $(N_2H_5)_2SnCl_6$.

This preparation has accordingly been repeated by use of stannic chloride and varying amounts of hydrazine mono- or di-hydrochloride, but the only product isolated is dihydrazinium chlorostannate. Furthermore, if such a compound as reported by Druce does exist, it might be expected to result from the direct union of hydrazine dihydrochloride and anhydrous stannic chloride; combination does not in fact take place when these substances are heated, whereas hydrazine monohydrochloride reacts vigorously with stannic chloride to give the expected dihydrazinium chlorostannate. In view of the catalytic decomposition of hydrazine salts, especially by platinum yielding ammonia (Audrieth and Ogg, "The Chemistry of Hydrazine," Wiley, 1951, p. 145), it is possible that Druce's product contained ammonium chlorostannate which contains tin and chloride in proportions very similar to the analytical figures given (the hydrazine content was not reported). Our preparations were made in glass vessels and none of them contained more than 0·1% of ammonia.

Dihydrazinium chlorostannate is not easy to obtain pure by crystallisation, for the hydrochlorides tend to separate with it, particularly from hydrochloric acid solution. Fractional crystallisation is usually necessary, though a reasonably pure product can be obtained from aqueous solutions containing less than the theoretical amount of hydrazine monohydrochloride. The best method is to crystallise from aqueous solutions containing small amounts of acetone, which seems to inhibit the separation of the hydrochlorides. Slow evaporation of a concentrated solution of dihydrazinium chlorostannate containing acetone of crystallisation, described below, yields flawless crystals suitable for *X*-ray crystallography.

Whereas the chlorostannate is obtained from water in the anhydrous condition, it is remarkable that it separates from aqueous ketones with ketone of crystallisation; *e.g.*, acetone–water solutions (1 : 1) yield particularly well-formed crystals, resembling Iceland spar, which contain 3 mols. of acetone per mol. of chlorostannate. The number of mols. of ketone accommodated by the crystal diminishes, however, as the molecular weight of the ketone rises; *e.g.*, the compounds with ethyl methyl ketone, diethyl ketone, and di-*n*-propyl ketone all contain 1·5 mols. of ketone per mol. of chlorostannate, and di*iso*propyl ketone does not form a compound at all. In the dry state these compounds are very stable, no loss in weight occurring when the acetone and diethyl ketone compounds are heated for several hours *in vacuo* at 112°. On the other hand, the ketones are liberated immediately the compounds are dissolved in water.

Although acetone does not condense with dihydrazinium chlorostannate when heated under reflux, condensation does occur with hydrazine dihydrochloride and stannic chloride, colourless cubes being deposited from a deep maroon-coloured liquor in the course of 2—3 hours. The product (m. p. 218°), obtained in 90% yield, has been shown to be bis-3 : 5 : 5-trimethylpyrazolinium chlorostannate containing 1·5 mols. of acetone, the heterocyclic base, characterised as its hydrochloride, being isolated by decomposition with alkali and extraction with ether. This substituted pyrazoline is the expected product whether the reaction proceeds by condensation of hydrazine with mesityl oxide formed *in situ* from acetone or by the formation of dimethylketazine and subsequent isomerisation in presence of acid (Frey and Hoffmann, *Monatsh.*, 1901, **22**, 760). Diethyl ketone is insufficiently reactive to give a pyrazolinium derivative when substituted for acetone in this reaction.

Acetone is removed from this compound by dissolving it in alcohol and precipitation with ether, or by long storage in chloroform, though not by heating *in vacuo* at 100°. Bis-3 : 5 : 5-trimethylpyrazolinium chlorostannate is prepared more conveniently, however, by mixing 3 : 5 : 5-trimethylpyrazoline hydrochloride and excess of stannic chloride in alcohol and adding ether. The product readily adds 1·5 mols. of acetone per mol. of chlorostannate, but does not form compounds with ethyl methyl ketone or diethyl ketone under similar conditions.

It is hoped that an examination of the crystal structures of some of these compounds, at present in progress in the Physics Department of this University, will throw some light on the mode of linking of the ketone.

Experimental

M. p.s are uncorrected. Analyses were made by standard methods: hydrazine and chloride by Andrews's and Volhard's methods, respectively, tin by precipitation with ammonia (Hillebrand and Lundell, "Applied Inorganic Analysis," Wiley, 1929, p. 239), and ketones by precipitation with 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid (the chlorostannates of hydrazine and 3 : 5 : 5-trimethylpyrazoline were shown not to interfere).

Preparation of Dihydrazinium Chlorostannate.—(*a*) Stannic chloride pentahydrate (25·6 g.) and hydrazine monohydrochloride (9 g.) were dissolved in water (20 c.c.), and the clear solution was evaporated slowly over sulphuric acid. The first two crops of *dihydrazinium chlorostannate* (8 g.) were separated on a sintered-glass funnel, washed with ethanol and ether, and dried in air (Found: N_2H_4, 17·5; Cl′, 53·0; Sn, 27·2%). The next crop (12 g.) was washed instead with ice–water (considerable loss) and dried, first on filter-paper and then over sulphuric acid [Found: N_2H_4, 15·9; Cl′, 53·3; Sn, 29·5. $(N_2H_5)_2SnCl_6$ requires N_2H_4, 16·1; Cl′, 53·3; Sn, 29·85%]. Washing with ethanol and ether thus causes decomposition with the removal of a disproportionate amount of stannic chloride. When an excess of hydrazine monohydrochloride or when the dihydrochloride was used, or when hydrochloric acid was added, the chlorostannate crystals were contaminated with hydrochloride. Crystallisation from hot solutions had the same effect.

(*b*) Anhydrous stannic chloride (3 c.c.) was distilled on to hydrazine monohydrochloride (1 g.); there was a considerable heat of reaction. The mixture was refluxed for 5 minutes, and excess of stannic chloride was then removed in a current of dry air. The increase in weight and analysis of the product indicated 80% conversion of the monohydrochloride into chlorostannate. The product was finely ground and treated again in the same manner, yielding a white crystalline powder (Found: N_2H_4, 15·8; Cl′, 53·5%).

Properties of Dihydrazinium Chlorostannate.—The salt crystallises as transparent tetragonal needles. It sublimes with decomposition when heated gently in a current of nitrogen, the sublimate containing mostly ammonium salts and only a trace of hydrazine; rapid heating to a higher temperature affords a yellow oil just below red heat. The salt is insoluble in ether, benzene, chloroform, and carbon tetrachloride, but soluble in hot methanol and ethanol (from which hydrazine monohydrochloride is deposited on cooling) and exceedingly soluble in water. Concentrated aqueous solutions remain clear when kept, but dilution causes precipitation of gelatinous tin hydroxide. Solutions in simple aliphatic ketones or in ketone–water mixtures afford compounds containing ketone of crystallisation.

Reactions of Dihydrazinium Chlorostannate.—(*a*) *With acetone.* Crystallisation of the chlorostannate (or a mixture of hydrazine monohydrochloride and stannic chloride in equivalent quantities) from water–acetone (1 : 1) yielded large clear rhombs, m. p. 137—138°, of solvated *chlorostannate* [Found: N_2H_4, 11·25; Cl′, 37·2; Sn, 20·8. $(N_2H_5)_2SnCl_6,3C_3H_6O$ requires N_2H_4, 11·2; Cl′, 37·2; Sn, 20·8%]. The presence of the acetone was established by formation of its 2 : 4-dinitrophenylhydrazone (m. p. and mixed m. p. 127°) in 96% of the theoretical yield.

(*b*) *With ethyl methyl ketone.* This *compound* could only be prepared in the absence of water. Dihydrazinium chlorostannate (3 g.) dissolved in the ketone (3 c.c.) with evolution of heat, forming a viscous liquid which failed to crystallise. When this was shaken with ether (10 vols.) two phases separated and crystallisation then occurred during several days at 0°, yielding large clear tetragonal prisms, m. p. 90° [Found: N_2H_4, 12·7; Cl′, 42·1; Sn, 23·3; C_4H_8O, 21·2. $(N_2H_5)_2SnCl_6,1{\cdot}5C_4H_8O$ requires N_2H_4, 12·65; Cl′, 42·0; Sn, 23·5; C_4H_8O, 21·45%]. The ethyl methyl ketone 2 : 4-dinitrophenylhydrazone formed from it had m. p. 112—113°, raised to 114° on admixture with an authentic specimen.

(*c*) *With diethyl ketone.* A solution containing stannic chloride pentahydrate (10·5 g.) and hydrazine monohydrochloride (4·1 g.) in water (10 c.c.) and diethyl ketone (5 c.c.) gave rectangular prisms, m. p. 155° (recrystallised from ethanol containing diethyl ketone) [Found: N_2H_4, 12·2; Cl′, 40·5; Sn, 22·4; $C_5H_{10}O$, 25·2. $(N_2H_5)_2SnCl_6,1{\cdot}5C_5H_{10}O$ requires N_2H_4, 12·15; Cl′, 40·4; Sn, 22·5; $C_5H_{10}O$, 24·5%]. The 2 : 4-dinitrophenylhydrazone of diethyl ketone, prepared from this *compound*, had m. p. and mixed m. p. 153°. Refluxing hydrazine dihydrochloride (2 g.) and stannic chloride (1 c.c.) in diethyl ketone (8 c.c.) for 6 hours gave as the major product, precipitated in the cold by ether, the above chlorostannate, m. p. 155°, and not a pyrazoline derivative (see below).

(*d*) *With di-*n*-propyl ketone.* Dihydrazinium chlorostannate (2 g.) was boiled with di-*n*-propyl ketone (3 c.c.). Most of it dissolved, leaving a small oily layer which crystallised on cooling (hydrazine monohydrochloride). When the solution was shaken with ether (6 vols.) the liquid separated into two layers and crystallised slowly at 0°, forming the *complex* in clear rhombs, m. p. 87—89° (decomp.) [Found: N_2H_4, 11·3; Cl′, 37·2; Sn, 20·7. $(N_2H_5)_2SnCl_6,1{\cdot}5C_7H_{14}O$ requires N_2H_4, 11·25; Cl′, 37·4; Sn, 20·9%]. The 2 : 4-dinitrophenylhydrazone prepared from this had m. p. 72°, undepressed by a specimen obtained from di-*n*-propyl ketone.

Bis-3 : 5 : 5-*trimethylpyrazolinium Chlorostannate.*—(*a*) Acetone (50 c.c.) containing hydrazine dihydrochloride (9 g., 0·086 mol.) and stannic chloride (5 c.c., 0·042 mol.) was heated under reflux for 3 hours, whereupon the hydrazine salt passed slowly into solution and the deep red liquid deposited yellowish cubic crystals (20 g.). Recrystallisation from hot ethanol containing acetone yielded *bis*-3 : 5 : 5-*trimethylpyrazolinium chlorostannate* with 1·5 mols. acetone of crystallisation, colourless cubes, m. p. 215—218° (decomp.) [Found, in material dried in air: N_2H_4, nil; N, 8·9; Cl′, 33·0; Sn, 18·5; C_3H_6O, 13·3. $(C_6H_{13}N_2)_2SnCl_6,1{\cdot}5C_3H_6O$ requires N, 8·7; Cl′, 33·0; Sn, 18·4; C_3H_6O, 13·5%]; the identification of this substance is described below.

When dihydrazinium chlorostannate was refluxed with acetone for 3 hours, the pyrazolinium compound was not formed. Instead, the product was dihydrazinium chlorostannate with acetone of crystallisation.

(*b*) 3 : 5 : 5-Trimethylpyrazoline, prepared by Kishner's method (*Chem. Zentr.*, 1912, I, 2025), was characterised as its *N*-benzoyl derivative, m. p. 238° (Frey and Hoffmann, *loc. cit.*, give 236°), hydrochloride, m. p. 175° (lit., 176°), and chloroplatinate, m. p. 185° (lit., 186°). The oxalate, needles, m. p. 131·5°, from ethanol–light petroleum (b. p. 75—90°), was analysed by Turrentine's method (*J. Amer. Chem. Soc.*, 1910, **32**, 577) (Found: N, 14·3; $H_2C_2O_4$, 44·1. Calc. for $C_6H_{12}N_2,H_2C_2O_4$: N, 13·9; $H_2C_2O_4$, 44·5%). Harries (*Annalen*, 1901, **319**, 233) gives m. p 148°. When acetone was added to 3 : 5 : 5-trimethylpyrazoline hydrochloride (0·7 g.) and stannic chloride (0·3 c.c.) in absolute ethanol (10 c.c.) acidified with hydrochloric acid, the chlorostannate separated with acetone of crystallisation as glistening, well-formed cubes, identical with the product, m. p. 215—218°, described above; the m. p. was raised to 221° (decomp.) by recrystallisation from methanol–acetone containing hydrochloric acid. When a large volume of ether was added to the pyrazoline hydrochloride (0·3 g.) and stannic chloride (0·16 c.c.) in ethanol, a colourless oil separated which when scratched afforded *bis*-3 : 5 : 5-*trimethylpyrazolinium chlorostannate* as microscopic prisms, m. p. 198° (decomp.) [Found, in material dried at 100° *in vacuo*: N, 10·0; Cl′, 38·0; Sn, 21·1. $(C_6H_{13}N_2)_2SnCl_6$ requires N, 10·0; Cl′, 38·2; Sn, 21·4%]. Addition of acetone to a concentrated solution of this compound in ethanol afforded the characteristic cubes, m. p. 221°, containing acetone of crystallisation, but no precipitate was obtained when ethyl methyl ketone or diethyl ketone was used in place of acetone.

Decomposition of the Chlorostannate (m. p. 218°) with Alkali.—The above compound (10 g.) was mixed into a paste with barium oxide (large excess) and water (10 c.c.), and solid potassium hydroxide (5 g.) was then added. After 30 minutes the mixture was extracted thoroughly with ether, and the ethereal extract dried (KOH) and distilled through a short column. The fraction, b. p. 156° (1·5 c.c.), was identified as 3 : 5 : 5-trimethylpyrazoline by formation of the hydrochloride, m. p. and mixed m. p. 177° (Found: N, 19·2. Calc. for $C_6H_{13}N_2Cl$; N, 18·9%).

The substance of this paper is to be read before Section A of the South African Association for the Advancement of Science at its meeting in Cape Town, July, 1952.

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