Hydrazine. Part IX. Condensation Products of Aldehydes and Ketones with Salts of Some Substituted Δ^2-Pyrazolines and Hydrazines.*

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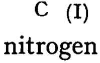
Chlorostannates and some other salts are described containing cations which are condensation products of carbonyl compounds and certain Δ^2-pyrazolines. They are chemically similar to the 3 : 5 : 5-trimethyl-1-*iso*propylidenepyrazolinium salts described in Part VIII.* *N*-Substituted pyrazolines do not form condensation products under the same conditions. Methylhydrazine in the presence of acetone and acids yields *N*-methyldimethylketazinium salts. It is concluded that condensation in all these cases occurs at the secondary amino-group. Phenylhydrazine with acids and acetone yields phenylhydrazonium salts, but these isomerise on long boiling, yielding salts of 3 : 5 : 5-trimethyl-1-phenylpyrazoline.

This paper presents the evidence for the suggestion made in Part VIII * that condensation of acetone with 3 : 5 : 5-trimethyl-Δ^2-pyrazoline in the presence of acids leads to the formation of 3 : 5 : 5-trimethyl-1-*iso*propylidenepyrazolinium salts. Such condensation is abundantly substantiated by using a number of aldehydes in place of acetone, whereby derivatives of the chlorostannate of 3 : 5 : 5-trimethylpyrazoline are readily prepared which are stable towards heating *in vacuo* but liberate the aldehyde when kept in aqueous acid or alkaline solution. In these derivatives the molar ratio of carbonyl compound to pyrazoline is always unity, and they are clearly of the same type as the salts described in Part VIII.

To determine the position of condensation, other substituted pyrazolinium chlorostannates were treated with acetone and certain aldehydes under similar conditions. Condensation occurred very readily with the chlorostannates of 5-methylpyrazoline and 4 : 5-dimethylpyrazoline, but not at all with the corresponding salts of 1 : 3 : 5 : 5-tetramethylpyrazoline, 3 : 5 : 5-trimethyl-1-phenylpyrazoline, 1 : 5-dimethylpyrazoline, and 1 : 1(?) : 5-trimethylpyrazoline. The revelant common feature of the pyrazoline bases whose salts condense is an unsubstituted secondary amino-grouping at position 1; replacement of hydrogen on this nitrogen atom by methyl or phenyl groups (*i.e.*, conversion into a tertiary amine) inhibits condensation under the mild conditions used. More vigorous treatment might cause condensation elsewhere in the pyrazoline nucleus (see p. 2430).

In the earlier stages of this work the 3-methyl group, activated as it is in 3 : 5 : 5-trimethylpyrazoline and its salts by the $N{:}C_{(3)}$ system, was considered a possible site of condensation. 3-*iso*Butenyl-5 : 5-dimethylpyrazoline was accordingly prepared and converted into a chlorostannate in the presence of acetone : the product, however, was not identical with the chlorostannate of 3 : 5 : 5-trimethyl-1-*iso*propylidenepyrazoline but contained an additional *iso*propylidene group attached to the base.

The view that the new cations contain the system (I) is supported by the preparation of the methochloride of cinnamylideneaniline by Zincke and Würker (*Annalen*, 1905, **338**, 133) and of salts of *iso*propylidene or cinnamylidene derivatives of a number of secondary amines (piperidine, diphenylamine, and methylaniline) by ourselves (forthcoming publication), all of which contain a positively charged nitrogen atom linked to three carbon atoms, one of them by a double bond. An even closer analogy is afforded by the condensation of methylhydrazine hydrochloride with acetone in the presence of stannic chloride to give a chlorostannate containing the *N*-methyldimethylketazinium ion; here the cation possesses the same atomic and electronic environment about a positively charged nitrogen atom as is depicted in (I), and it is in fact closely related in structure to the 3 : 5 : 5-trimethyl-1-*iso*propylidenepyrazolinium ion. It is noteworthy that this last experiment yielded an open-chain ion, in contrast to the pyrazolinium ions formed when phenylhydrazine and hydrazine hydrochlorides were used.



(I)

$$:N{\cdot}\overset{+}{\underset{\ddot{C}}{N}}_{(1)}{\cdot}C$$

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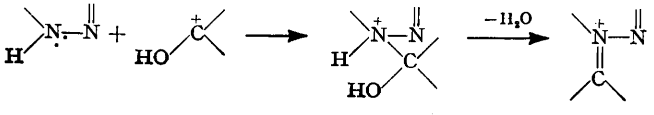
* Part VIII, preceding paper.

Whereas chlorostannates, chloroplatinates, and other complex salts containing condensed pyrazolinium ions are readily formed, considerable difficulty has been experienced in preparing corresponding chlorides. This may be due to the greater solubility and hygroscopic character of these salts; consequently, the reaction products of 3 : 5 : 5-trimethylpyrazoline hydrochloride and benzaldehyde or acetone have not been isolated pure. The product from cinnamaldehyde has, however, been obtained pure and shown to be readily convertible into the chlorostannate on treatment with alcoholic stannic chloride. Cinnamaldehyde has been found particularly suitable in this work because of its high reactivity and the insolubility of its condensation products. The main drawback is the possibility of its reacting in a different manner from that of aromatic or saturated aliphatic aldehydes, namely, by addition first to the double bond αβ to the carbonyl group. This is known to occur in reactions with piperidine and other secondary amines (Mannich, Handke, and Roth, *Ber.*, 1936, **69**, 2112; Mannich and Davidsen, *ibid.*, p. 2106), but the yellow colour of the compounds formed from pyrazolinium salts and αβ-unsaturated aldehydes (cinnamaldehyde, crotonaldehyde, and tiglic aldehyde) suggests that condensation occurs in these compounds through the aldehyde group to form a conjugated chain involving the pyrazoline double bond.

The reaction of carbonyl compounds with pyrazolinium salts, with or without the addition of excess of acid, is presumably of the normal acid-catalysed type, involving reaction between a carbonium ion and a molecule of the free base; it is unlikely that $N_{(1)}$ would bear a positive charge at the moment of addition. 3 : 5 : 5-Trimethylpyrazoline is a very weak base (K_b approx. 10^{-9}; unpublished work) and small amounts of free base would therefore be present in acid solution. A possible mechanism is as follows :



In processes of alkylation and benzoylation the free pyrazoline bases behave as secondary amines (Curtius and Wirsing, *J. pr. Chem.*, 1894, **50**, 546), and preliminary experiments have shown that if $N_{(1)}$ is unsubstituted, they react with aldehydes, in neutral or alkaline media, to form products in which the base and aldehyde residues are in the molar ratio of 2 to 1 (cf. Mannich and Davidsen, *loc. cit.*). If, on the other hand, the secondary amino-group is benzoylated, no reaction occurs under relatively mild conditions, *e.g.*, when 1-benzoyl-3 : 5 : 5-trimethylpyrazoline is heated for short periods with acetone, benzaldehyde, or cinnamaldehyde. Furthermore, the tertiary amines 1-phenyl- and 5-methyl-1-phenylpyrazoline are known to require long heating with benzaldehyde at a high temperature before condensation takes place, not on nitrogen, but at the 4-methylene group (Curtius and Wirsing, *loc. cit.*; Trener, *Monatsh.*, 1900, **21**, 1111). This type of condensation is clearly very different from those described in Part VIII and in this paper.

Experimental

Methods of analysis used were as reported in Parts I and VI (*J.*, 1952, 4138; 1953, 3445). Difficulties with the Volhard estimation of chloride, encountered with the yellow derivatives of cinnamaldehyde, were overcome by decomposing the sample in boiling sodium hydroxide (halogen-free) and extracting the liberated aldehyde and pyrazoline with ether. Chloroplatinates were destroyed with hydrazine before Volhard's method was applied (Pugh, *J. Appl. Chem.*, 1954, **4**, 47). As previously noted in work on ketazinium salts, carbon values are usually a little low, probably owing to surface hydrolysis by moist air.

Reaction of Bis-(3 : 5 : *5-trimethylpyrazolinium) Hexachlorostannate with Carbonyl Compounds.*—The above salt, made as described in Part VIII (*loc. cit.*) from a mixture of the simple salts, was treated in ethanolic solution (approx. 30% w/v) with excess of the appropriate aldehyde or ketone. Immediate precipitation occurred in most cases, and in others crystallisation commenced within 1 hr. at 0°. The mixtures were kept at 0° for several days, after which the crystals were filtered off, washed with ethanol containing a little of the carbonyl compound and finally with dry ether, and dried at 100° *in vacuo*. All the condensation products described below are slowly hydrolysed in water, and all gave within a few minutes the characteristic test for the relevant aldehyde or ketone with cold 2 : 4-dinitrophenylhydrazine reagent in 2N-hydrochloric acid. The m. p.s tend to vary according to the mode of heating.

(a) *With acetaldehyde.* Colourless needles of *bis*-(1-*ethylidene*-3 : 5 : 5-*trimethylpyrazolinium*) *hexachlorostannate* were precipitated immediately, in good yield, m. p. 160—161° (decomp.) [Found : C, 31·6; H, 5·1; Cl, 35·0. $(C_8H_{15}N_2)_2SnCl_6$ requires C, 31·5; H, 4·9; Cl, 34·9%].

(b) *With propaldehyde.* The corresponding 1-*propylidene* derivative separated immediately as colourless plates, m. p. 220—221° (decomp.) [Found: C, 33·6; H, 5·4; Cl, 33·2. $(C_9H_{17}N_2)_2SnCl_6$ requires C, 33·8; H, 5·3; Cl, 33·4%].

(c) *With butaldehyde.* A plate-like mass of the 1-*butylidene* derivative separated immediately in very good yield, and had m. p. 190—195° (decomp.) [Found: C, 35·2; H, 5·7; Cl, 31·8; Sn, 17·9. $(C_{10}H_{19}N_2)_2SnCl_6$ requires C, 36·0; H, 5·7; Cl, 32·0; Sn, 17·8%].

(d) *With* isovaleraldehyde. An immediate white precipitate of the 1-3′-*methylbutylidene* derivative, m. p. 214° (decomp.), was formed in good yield [Found: C, 37·2; H, 6·0; Cl, 31·1. $(C_{11}H_{21}N_2)_2SnCl_6$ requires C, 38·1; H, 6·1; Cl, 30·8%]. (This specimen had been kept for several weeks before analysis for C and H, and had probably lost some aldehyde by hydrolysis in air.)

(e) *With crotonaldehyde.* Pale yellow crystals were formed in a few minutes, the ultimate yield of *bis*-(1-*but*-2′-*enylidene*-3 : 5 : 5-*trimethylpyrazolinium*) *hexachlorostannate*, m. p. 188° (decomp.), being good [Found : C, 35·9; H, 5·0; Cl, 32·1. $(C_{10}H_{17}N_2)_2SnCl_6$ requires C, 36·2; H, 5·1; Cl, 32·2%].

(f) *With tiglic aldehyde.* Clear yellow prisms of the 1-(2-*methylbut*-2-*enylidene*) derivative began to separate at room temperature within 1 hr. and the yield was good after 2 days at 0°; it had m. p. 176° (decomp. with earlier reddening) [Found : C, 38·2; H, 5·5; Cl, 30·8; Sn, 17·2. $(C_{11}H_{19}N_2)_2SnCl_6$ requires C, 38·3; H, 5·5; Cl, 30·9; Sn, 17·2%].

(g) *With benzaldehyde.* The 1-*benzylidene* derivative separated almost immediately as a colourless crystalline powder, m. p. 225° (decomp.) [Found: C, 41·8; H, 4·4; Cl, 28·9; Sn, 16·2. $(C_{13}H_{17}N_2)_2SnCl_6$ requires C, 42·5; H, 4·6; Cl, 29·0; Sn, 16·2%]. A portion of the product was shaken with a mixture of N-sodium hydroxide and ether, and the ether layer was washed with water. Small aliquot parts of the ether extract were then treated with 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid and with phenylhydrazine respectively, yielding the corresponding hydrazones of benzaldehyde, m. p.s 237° and 158°. The bulk of the ether extract was then treated with dry hydrogen chloride; an oily solid was formed, which, after recrystallisation, was shown to be the hydrochloride of 3 : 5 : 5-trimethylpyrazoline, m. p. 176°.

(h) *With cinnamaldehyde.* Addition of this aldehyde gave a reddish-yellow solution which rapidly deposited bright yellow crystals of the 1-*cinnamylidene* derivative, m. p. 238° (decomp.) [Found : C, 45·6; H, 4·9; Cl, 27·0. $(C_{15}H_{19}N_2)_2SnCl_6$ requires C, 45·8; H, 4·8; Cl, 27·1%].

(i) *With acetone.* The *iso*propylidene derivative was described in Parts I and VIII (*locc. cit.*) as cubes. Prepared as here described, however, the crystals were unlike cubes but the composition and m. p. were identical. The difference in crystal habit may be due to the presence, in the liquors of the previous preparations, of hydrochloric acid, which would cause formation of some mesityl oxide. Mesityl oxide itself does not form a condensation product with the chlorostannate of 3 : 5 : 5-trimethylpyrazoline in alcoholic solution, but if it contains a little acetone it yields crystals which appear to be cubes visually but are not truly cubic when examined under the polarising microscope. They yield the 2 : 4-dinitrophenylhydrazone of acetone.

(j) *With other carbonyl compounds.* Similar products, which, however, were not analysed, were obtained with glyoxal (deep-red hygroscopic mass), *m*- and *p*-nitrobenzaldehyde and vanillin (yellow solids), acetylacetone (colourless), terephthalaldehyde (very insoluble, deep yellow solid), and furfuraldehyde (colourless solid which decomposed rapidly in a desiccator).

Reaction of Bis-(5-methylpyrazolinium) Hexachlorostannate with Carbonyl Compounds.—5-Methylpyrazoline (b. p. 91°/97 mm.; 4·4 c.c.), prepared from crotonaldehyde and hydrazine hydrate (von Rothenburg, *J. pr. Chem.*, 1895, **52**, 52), was added to a solution of stannic chloride pentahydrate (8·5 g.) in concentrated hydrochloric acid (5 c.c.), but it was not possible to crystallise a pure specimen of the chlorostannate of the above base. Evaporation *in vacuo* yielded a hygroscopic mass from a syrupy liquor. This was therefore dissolved in ethanol (30 c.c.), a small residue of hydrazine dihydrochloride being filtered off, and aliquot parts of the ethanolic solution were then added to approx. equal volumes of aldehyde or ketone. The precipitates were washed and dried as described in the previous section. They were all tested for the presence of hydrazine salts (iodate titration) and found to be free from contamination. All gave characteristic tests with 2 : 4-dinitrophenylhydrazine.

(a) *With acetone.* Immediate crystallisation of *bis*-(5-*methyl*-1-iso*propylidenepyrazolinium*) *hexachlorostannate* occurred, m. p. 196° [Found: C, 28·5; H, 4·5; Cl, 36·6; Sn, 20·4. $(C_7H_{13}N_2)_2SnCl_6$ requires C, 28·9; H, 4·6; Cl, 36·6; Sn, 20·4%].

(b) *With ethyl methyl ketone.* An oil separated immediately, which solidified to a white powder when shaken with ethanol; this 1-sec.-*butylidene* derivative had m. p. 155—157° [Found: C, 31·7; H, 4·8; Cl, 35·0. $(C_8H_{15}N_2)_2SnCl_6$ requires C, 31·5; H, 4·9; Cl, 34·9%].

(c) *With crotonaldehyde.* Yellow prisms of the 1-*but-2'-enylidene* derivative separated rapidly, m. p. 128—130° (decomp.) [Found: C, 32·1; H, 4·2; Cl, 35·1; Sn, 19·5. $(C_8H_{13}N_2)_2SnCl_6$ requires C, 31·7; H, 4·3; Cl, 35·1; Sn, 19·6%].

(d) *With benzaldehyde.* The 1-*benzylidene* derivative was precipitated immediately, m. p. 203° (decomp.) [Found: C, 38·3; H, 3·9; Cl, 31·2; Sn, 17·6. $(C_{11}H_{13}N_2)_2SnCl_6$ requires C, 38·9; H, 3·8; Cl, 31·4; Sn, 17·6%].

(e) *With cinnamaldehyde.* The 1-*cinnamylidene* derivative, formed immediately, was deep yellow, m. p. 210° (decomp.) [Found: C, 43·4; H, 4·2; Cl, 29·0. $(C_{13}H_{15}N_2)_2SnCl_6$ requires C, 42·8; H, 4·1; Cl, 29·2%].

No satisfactory solid products could be isolated when acetaldehyde and butaldehyde were used; terephthalaldehyde, on the other hand, gave an immediate deep-yellow precipitate.

Reaction of Bis-(4 : 5-*dimethylpyrazolinium*) *Hexachlorostannate with Carbonyl Compounds.*—A mixture of hydrazine (95%; 1 g.) and tiglic aldehyde (2·2 g.) in dry methanol (10 c.c.) was heated under reflux for 2 hr., and to the cooled product was added a solution of stannic chloride pentahydrate (4·4 g.) in dilute hydrochloric acid. Evaporation of the resulting solution, first on the steam-bath and then *in vacuo*, furnished a pale yellow syrup; this was diluted with ethanol, and the solution, after having been filtered from some hydrazine dihydrochloride, was added in portions to the aldehydes and ketones noted below. Immediate precipitation of crystalline solids occurred. The products were washed and dried as previously described, and shown to be free from hydrazine salts; all were shown to contain aldehyde or ketone residues.

(a) *With acetone. Bis-*(4 : 5-*dimethyl*-1-iso*propylidenepyrazolinium*) *hexachlorostannate* separated as colourless crystals, m. p. 210—211° [Found: C, 32·3; H, 4·9; Cl, 34·8; Sn, 19·5. $(C_8H_{15}N_2)_2SnCl_6$ requires C, 31·5; H, 4·9; Cl, 34·9; Sn, 19·5%].

(b) *With ethyl methyl ketone.* The 1-sec.-*butylidene* derivative separated as a crystalline solid, m. p. 198—199° [Found: C, 33·8; H, 5·3; Cl, 33·7; Sn, 18·8. $(C_9H_{17}N_2)_2SnCl_6$ requires C, 33·8; H, 5·3; Cl, 33·4; Sn, 18·7%]: this ketone could not be condensed with the chlorostannate of 3 : 5 : 5-trimethylpyrazoline, possibly because of steric influences.

(c) *With benzaldehyde.* The 1-*benzylidene* derivative separated at first as an oil which, when scratched and cooled, gave a very pale buff-coloured solid, m. p. 185° (decomp.) [Found: C, 40·4; H, 4·4; Cl, 30·2. $(C_{12}H_{15}N_2)_2SnCl_6$ requires C, 40·8; H, 4·3; Cl, 30·2%].

(d) *With cinnamaldehyde.* The deep-yellow 1-*cinnamylidene* derivative had m. p. 193° (decomp.) [Found: C, 44·4; H, 4·5; Cl, 28·0; Sn, 15·8. $(C_{14}H_{17}N_2)_2SnCl_6$ requires C, 44·4; H, 4·5; Cl, 28·1; Sn, 15·7%].

Bis-(1 : 3 : 5 : 5-*tetramethylpyrazolinium*) *Hexachlorostannate.*—1 : 3 : 5 : 5-Tetramethylpyrazolinium iodide, prepared according to Curtius and Wirsing (*loc. cit.*), was dissolved in sodium hydroxide solution, and the free base was extracted with ether. The ether extract, washed with water and acidified with concentrated hydrochloric acid, was evaporated, finally to dryness, *in vacuo* over sulphuric acid and sodium hydroxide. The resulting hygroscopic, crystalline chloride, on treatment with the calculated quantity of stannic chloride in acetone solution, yielded the crude *hexachlorostannate*; it was recrystallised from acetone by addition of dry ether, forming colourless needles, m. p. 196° [Found: C, 28·2; H, 5·1; Cl, 36·5; Sn, 20·2. $(C_7H_{15}N_2)_2SnCl_6$ requires C, 28·7; H, 5·1; Cl, 36·4; Sn, 20·3%]. It gave no precipitate, even after long standing, when mixed in concentrated alcoholic solution with cinnamaldehyde, and the chlorostannate was recovered unchanged on adding ether.

Bis-(1 : 5-*dimethylpyrazolinium*) *Hexachlorostannate.*—This *salt* was obtained as colourless crystals, m. p. 207° (decomp.), when 1 : 5-dimethylpyrazoline, prepared according to von Auwers and Broche (*Ber.*, 1922, **55**, 3880), was added to a dry ethanol solution of stannic chloride containing excess of hydrogen chloride [Found, in material dried *in vacuo* at 56°: C, 22·3; H, 4·2; Cl, 40·2; Sn, 22·3. $(C_5H_{11}N_2)_2SnCl_6$ requires C, 22·6; H, 4·2; Cl, 40·2; Sn, 22·4%]. It was freely soluble in acetone from which it was recovered unchanged on addition of ether. Its solutions in ethanol yielded no precipitate with cinnamaldehyde, even on long standing at 0°.

Bis-[1 : 1(?) : 5-*trimethylpyrazolinium*] *Hexachlorostannate.*—A vigorous reaction occurred on mixing of 5-methylpyrazoline (9 c.c.) with methyl iodide (6 c.c.), the product being soluble in ethanol, from which 1 : 5-*dimethylpyrazoline methiodide* crystallised as colourless plates, m. p. 171—172° (Found: C, 29·5; H, 5·4; I, 53·0. $C_6H_{13}N_2I$ requires C, 30·0; H, 5·4; I, 53·0%).

This compound (0·65 g.) was heated under reflux for 8 hr. with ethanol and freshly-precipitated silver chloride (1 g.), the mixture being then stored for 2 days. After filtration to remove silver salts, the solution was evaporated *in vacuo*, yielding colourless needles (0·25 g.) which, on treatment with excess of stannic chloride in ethanol, gave the corresponding *hexachlorostannate*, m. p. 228—230° [Found: C, 26·1; H, 4·6; Cl, 38·1; Sn, 21·4. $(C_6H_{13}N_2)_2SnCl_6$ requires C, 25·8; H, 4·7; Cl, 38·2; Sn, 21·3%]; this is only sparingly soluble in ethanol, and was unchanged on treatment with acetone or cinnamaldehyde.

These two compounds presumably contain the 1 : 1 : 5-trimethylpyrazolinium ion. The secondary amino-group in pyrazolines is more basic than $N_{(2)}$ (Curtius and Wirsing, *loc. cit.*; von Auwers and Heimke, *Annalen*, 1927, **458**, 186) and substitution of a methyl group for a hydrogen atom at $N_{(1)}$ should further increase the basic character. 1 : 5-Dimethylpyrazoline would accordingly be methylated at $N_{(1)}$, not at $N_{(2)}$. This view is supported by the work of Theilacker and Leichtle (*Annalen*, 1951, **572**, 121).

1-*Cinnamylidene*-3 : 5 : 5-*trimethylpyrazolinium Chloride*.—3 : 5 : 5-Trimethylpyrazolinium chloride (1 g.), dissolved in dry ethanol (2 c.c.), was treated with cinnamaldehyde (2 c.c.), and the solution was boiled for a few minutes, and set aside for 1 hr.; addition of dry ether (10 c.c.) then gave yellow needles of the *chloride* of the 1-cinnamylidene derivative, m. p. 162° (decomp.). It was necessary to wash it with dry ether containing cinnamaldehyde, and finally with dry ether [Found, in material dried *in vacuo* at 100°: C, 66·8; H, 7·2; Cl, 13·4. $C_{15}H_{19}N_2Cl$ requires C, 68·8; H, 7·3; Cl, 13·5%]. (The low C value may be due to slight loss of aldehyde during the weighing.) The salt gave the characteristic phenylhydrazone of cinnamaldehyde, m. p. 168°, and on treatment with stannic chloride in ethanol yielded an immediate precipitate of yellow bis-(1-cinnamylidene-3 : 5 : 5-trimethylpyrazolinium) hexachlorostannate, m. p. 238°, identical with the product described on p. 2431.

Bis-(N-*methyldimethylketazinium*) *Hexachlorostannate*.—[This salt was isolated in an attempt to prepare 1 : 3 : 5 : 5-tetramethylpyrazolinium chlorostannate and, further, to determine whether this would condense with acetone to give an *iso*propylidene derivative (cf. 3 : 5 : 5-trimethyl*iso*propylidenepyrazolinium chlorostannate from hydrazine hydrochloride, Part VIII, *loc. cit.*). With methylhydrazine hydrochloride, however, there was no ring closure, or isomerisation, to a pyrazoline.] Methylhydrazine hydrochloride (2 g.; prepared as hygroscopic needles from the sulphate by addition of the calculated quantity of aqueous barium chloride solution, and evaporation of the filtrate to which a little hydrochloric acid had been added) and anhydrous stannic chloride (2·6 g.) were mixed in dry acetone. A white precipitate appeared in a few minutes, whereupon the mixture was boiled under reflux. After 2 hr. there appeared, on cooling, a mixture of large clear rhombs and a microcrystalline powder, but further heating caused all the solid to crystallise as rhombs. After 20 hr. the mixture was cooled in ice, and the solid *salt* was filtered off and washed with dry acetone; the yield was 5·0 g., and the m. p. 200—203° (decomp.) [Found, in material dried at 100° *in vacuo*: C, 27·5; H, 4·9; Cl, 36·8; Sn, 20·4; CH_6N_2, 15·9; C_3H_6O, 39·1. $(C_7H_{15}N_2)_2SnCl_6$ requires C, 28·7; H, 5·1; Cl, 36·4; Sn, 20·3; CH_6N_2, 15·7; C_3H_6O, 39·6%]. The methylhydrazine determination was by Andrews's method, the acetone by Messinger's. The low carbon value is typical of those found for ketazinium salts owing to surface decomposition by hydrolysis. Treatment with 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid gave an instantaneous dense yellow precipitate.

Reactions of Phenylhydrazinium Salts with Acetone.—(a) *Bis*(*acetone-phenylhydrazonium*) *hexachlorostannate*. Though mixtures of stannic chloride and phenylhydrazine hydrochloride are very soluble in water, all attempts to crystallise phenylhydrazinium chlorostannate failed because phenylhydrazine hydrochloride, being less soluble, crystallised continuously on evaporation and cooling. However, *bis*(*acetone-phenylhydrazonium*) *hexachlorostannate* was readily obtained from concentrated aqueous solutions of the mixed salts (mol. ratio, 1 : 2) and acetone (3—4 vols.) at 0°, and further crops of similar crystals were obtained by adding small amounts of concentrated hydrochloric acid to the mother-liquor. Recrystallisation from warm acetone containing hydrochloric acid (5 : 1) yielded colourless needles and prisms, m. p. 155° (decomp.) [Found: C, 33·7; H, 4·0; $C_6H_8N_2$, 34·4; Cl, 33·8; Sn, 18·8. $(C_9H_{13}N_2)_2SnCl_6$ requires C, 34·3; H, 4·1; $C_6H_8N_2$, 34·3; Cl, 33·8; Sn, 18·9%].

(b) *Bis*(*acetone-phenylhydrazonium*) *hexabromostannate*. Clear reddish solutions of stannic bromide and phenylhydrazine hydrobromide (mol. ratio, 1 : 2) in acetone–hydrobromic acid yielded yellowish needles of the above-named *salt*, m. p. 158° (vigorous decomp.) [Found: C, 23·1; H, 2·7; $C_6H_8N_2$, 24·6; Br, 53·6; Sn, 13·1. $(C_9H_{13}N_2)_2SnBr_6$ requires C, 24·1; H, 2·9; $C_6H_8N_2$, 24·5; Br, 53·5; Sn, 13·3%]. A solution of this salt in dilute hydrobromic acid, on exposure to air for a few days, deposited yellowish plates of *bisphenylhydrazinium hexabromostannate*

[Found: $C_6H_8N_2$, 26·3; Br, 59·1; Sn, 14·5. $(C_6H_9N_2)_2SnBr_6$ requires $C_6H_8N_2$, 26·5; Br, 58·8; Sn, 14·6%].

(c) *Bis(acetone-phenylhydrazonium) hexachloroplatinate.* Phenylhydrazine hydrochloride (1·5 g.) was dissolved in a warm mixture of acetone (3 c.c.) and water (1 c.c.), and chloroplatinic acid (1·5 g.) was added to the cooled solution. The mixture effervesced slightly (nitrogen), rapidly if warmed, and deposited orange crystals of the above-named *hexachloroplatinate*, m. p. 152° (vigorous decomp. with earlier darkening) [Found: Cl, 30·1; Pt, 27·8. $(C_9H_{13}N_2)_2PtCl_6$ requires Cl, 30·1; Pt, 27·6%].

(d) *Bis-*(3 : 5 : 5-*trimethyl-*1-*phenylpyrazolinium) hexachlorostannate.* A solution containing stannic chloride pentahydrate (15 g.), phenylhydrazine hydrochloride (12 g.), concentrated hydrochloric acid (2 c.c.), and acetone (40 c.c.) was boiled under reflux for 20 hr., the dark liquid depositing yellowish crystals (5 g.). Another crop (6 g.) was obtained from the mother-liquor by continuing the refluxing, with addition of a little more hydrochloric acid, for a further 20 hr. The crude products contained traces of acetone-phenylhydrazonium chlorostannate, described above (iodate titration), and were accordingly recrystallised from acetone–dilute hydrochloric acid (4 : 1), yielding colourless cubes of *bis-*(3 : 5 : 5-*trimethyl-*1-*phenylpyrazolinium) hexachlorostannate*, m. p. 230—231° (decomp.) [Found: C, 39·1; H, 4·7; Cl, 29·9; Sn, 16·7. $(C_{12}H_{17}N_2)_2SnCl_6$ requires C, 40·6; H, 4·8; Cl, 30·0; Sn, 16·8%]. Although this was produced in acetone solution no trace of acetone could be detected on testing with the usual reagent and, moreover, attempts to prepare condensation products, by treating its cold alcoholic solutions with aldehydes, failed. A sample of the salt in aqueous acetone, on treatment with chloroplatinic acid, gave orange crystals of bis-(3 : 5 : 5-trimethyl-1-phenylpyrazolinium) hexachloroplatinate, m. p. 180° (decomp.) [Found: Cl, 27·3; Pt, 24·8. Calc. for $(C_{12}H_{17}N_2)_2PtCl_6$: Cl, 27·1; Pt, 24·8%].

Condensation of Acetone and Bis-(3-iso*butenyl-*5 : 5-*dimethylpyrazolinium) Hexachlorostannate.*—Hydrazine (95%; 0·45 c.c.) was added slowly to well-cooled phorone (1·83 g.). A violent reaction occurred, and after some hours at 20° the mixture was warmed to 60° and treated with dry acetone (20 c.c.), anhydrous stannic chloride (0·8 c.c.), and hydrogen chloride (0·5 g.) in methanol (1·2 c.c.). Crystals separated after the mixture had stood for a week at 0°; they were washed with dry acetone followed by dry ether and were dried *in vacuo* at 100° (loss in wt. at 100°, 1·5%); m. p. 189—191° (decomp.) [Found: C, 38·6; H, 6·4; Cl, 29·2; C_3H_6O, 25·4. $(C_{12}H_{21}N_2)_2SnCl_6,H_2O$ requires C, 39·1; H, 6·0; Cl, 28·9; C_3H_6O, 31·6%]. Except for the acetone value, the experimental figures agree reasonably with those required for *bis-*(3-iso*butenyl-*5 : 5-*dimethyl-*1-iso*propylidenepyrazolinium) hexachlorostannate*; the low acetone value may be due to incomplete liberation of acetone from the 3-*iso*butenyl group which has been shown to be resistant to hydrolysis (von Auwers and Kreuder, *Ber.*, 1925, **58**, 1982; cf. Kishner, *Chem. Zentr.*, 1913, ii, 2130). These values nevertheless indicate that acetone does condense with the chlorostannate of 3-*iso*butenyl-5 : 5-dimethylpyrazoline (which requires acetone, 18%, assuming complete hydrolysis of the *iso*butenyl group).

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