Some Salts of Secondary Amines and of their Condensation Products with Carbonyl Compounds.

By M. LAMCHEN, W. PUGH, and A. M. STEPHEN.

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Aldehydes and acetone are shown to condense with some salts of secondary amines, forming cations of the type $[R^1R^2N{:}CR^3R^4]^+$. Chlorostannates containing such cations have been obtained from 5 aldehydes and acetone, in conjunction with 10 secondary amines. Condensation occurs in the ratio of one mol. of carbonyl compound per mol. of amine, and the condensed salts have the properties expected of *N*-substituted salts, *e.g.*, they hydrolyse in acid and alkali solutions, liberating aldehyde or ketone. The chlorostannate of dimethylaniline does not form such compounds, condensation being limited to cases where the amino-group is not tertiary. A number of new halogenoantimonites and -bismuthites of dimethylamine and di-*n*-butylamine are described and some of these are shown to form similar condensation products.

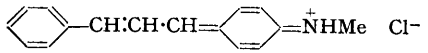
LAMCHEN, PUGH, and STEPHEN (*J.*, 1954, 2429) have shown that aldehydes and ketones condense readily with the chlorostannates of Δ^2-pyrazolines unless there is substitution on $N_{(1)}$ by an alkyl or acyl group, and it was noted that salts of piperidine, monomethylaniline, and diphenylamine react similarly. The products are ternary iminium salts containing the cation $[R^1R^2C{:}NR^3R^4]^+$, and this paper describes the preparation of a number of these compounds by interaction under mild conditions of carbonyl compounds and secondary amine salts.

A few salts of this type appear to have been reported, *e.g.*, the methochloride of cinnamylideneaniline (prepared from cinnamaldehyde and methylaniline in acid solution) and the derived chloroplatinate (Zincke and Würker, *Annalen*, 1905, **338**, 133); the instability of these products towards hydrolysis was noted. Glutacondialdehyde condensed similarly, forming a cyanine dye, but other aldehydes failed to react under the conditions used. On the other hand, it is well known that anhydro-salts containing the iminium ion, similar in nature to those described in this paper, are formed from *pseudo*-bases such as cotarnine and berberine in acid solution.

Although they have never been isolated, compounds of the type $R_2C{:}NR_2{}^+\}X^-$ have been suggested as intermediates in a number of reactions, notably that of Knoevenagel where secondary amine salts are employed as catalysts (Bergstrom, *Chem. Reviews*, 1944, **35**, 240), the catalytic decomposition of aldol by secondary amines wherein the dipolar immonium ion $^-CH_2{\cdot}C({:}NR_2{}^+){\cdot}CH_3$ is involved (Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, New York, 1953, p. 685), and an example of the Mannich reaction (Bergstrom, *loc. cit.*, p. 188) in which the existence of $CH_2{:}NEt_2{}^+$ has been tentatively postulated (cf., however, Alexander and Underhill, *J. Amer. Chem. Soc.*, 1949, **71**, 4014). In recent publications (Adams, "Organic Reactions," J. Wiley and Sons, Inc., New York, 1949, Vol. V, Chap. 7 by Moore; de Benneville and Macartney, *J. Amer. Chem. Soc.*, 1950, **72**, 3073) there is no suggestion that such cations take part in the Leuckart alkylation of secondary amines by carbonyl compounds in formic acid, but this reaction involves linkage of a carbonyl-carbon atom to nitrogen in much the same way as in the condensations described below.

Acetaldehyde, phenylacetaldehyde, butyraldehyde, benzaldehyde, crotonaldehyde, cinnamaldehyde, and acetone have now been used in reactions with the chlorostannates of the following secondary amines: dimethylamine (10·7), di-*n*-butylamine (11·2), piperidine (11·2), morpholine (8·7), (±)-ephedrine (*ca.* 10), 1 : 2 : 3 : 4-tetrahydro*iso*quinoline (*ca.* 11), 1 : 2 : 3 : 4-tetrahydroquinoline (5·0), 1 : 2 : 3 : 4-tetrahydro-6-methylquinoline, methylaniline (4·4), and diphenylamine (0·9). Figures in parentheses are pK_a values, an inverse relation being expected between the basic strength of an amine and its ability to condense at low pH; this has been qualitatively borne out, although steric factors and solubility relations affect the reaction and the ease of isolation of condensed salts. Warm ethanol, methanol, or water was the usual solvent but sometimes pure aldehyde or ketone served this purpose. Cinnamaldehyde, in keeping with its high reactivity towards ammonia and primary aromatic amines (Sprung, *Chem. Reviews*, 1940, **26**, 307, 325) and the stabilising effect of a conjugated system in the condensed products, was the most satisfactory of the aldehydes used and formed new compounds in alcohol with all the amine salts named except the first two; with some of the aromatic amines there is a possibility that reaction occurred at some other part of the molecule as well as at the amino-group. By contrast, salts of the relatively strong bases dimethylamine and di-*n*-butylamine gave condensation products with undiluted cinnamaldehyde only. Acetaldehyde and crotonaldehyde afforded numerous products, the less reactive benzaldehyde only few. Acetone condensed with salts of the very weak bases only. None of the secondary amine salts gives products with quite the same facility as pyrazolinium salts do (Lamchen, Pugh, and Stephen, *loc. cit.*), but their mode of reaction is probably the same as is suggested in the earlier paper.

While there is little doubt that condensation occurs on nitrogen in the aliphatic and alicyclic amine salts, there is some uncertainty in formulating the products from monomethylaniline, tetrahydroquinoline, and diphenylamine. These bases are known to combine with carbonyl compounds in the presence of acid catalysts to give substituted di- or tri-arylmethanes, through reaction at the *p*-position with respect to the amino-group. 1 : 2 : 3 : 4-Tetrahydroquinoline and its *N*-methyl derivative condense in this way with substituted benzaldehydes on heating for long periods in concentrated hydrochloric acid, there being no reaction if $C_{(6)}$ is blocked by a nitro-group (which, incidentally, deactivates the whole of the aromatic ring). Diphenylamine and *N*-methyldiphenylamine have been heated with formaldehyde–hydrochloric acid and benzaldehyde respectively to give similar products containing aldehyde and amine combined in the ratio 1 : 2 (Einhorn, *Ber.*, 1886, **19**, 1243; Sen and Sen, *J. Indian Chem. Soc.*, 1930, **7**, 965). In some instances the initial addition compound formed in this kind of reaction has been isolated, *e.g.*, monomethylaniline and chloral hydrate yielded *p*-$NHMe\cdot C_6H_4\cdot CH(OH)\cdot CCl_3$ (Boessneck, *Ber.*, 1888, **21**, 782). It follows that a plausible formulation of Zincke and Würker's compound (*loc. cit.*) is (I)



(I)

and analogous quinonoid structures could be written for our compounds derived from monomethylaniline, tetrahydroquinoline, and diphenylamine; these compounds could all arise by loss of a molecule of water from alcoholic addition products of the above type in the presence of acid. Such a possibility is, however, discounted on the following grounds : (i) the condensation products, described in this paper as iminium salts, are easily hydrolysed in acid and are clearly different in character from those just noted which are formed, by the linkage of carbon to carbon, on long boiling with acids; and (ii), whereas dimethylaniline fails to condense with cinnamaldehyde or acetone under acid conditions similar to those used in preparing derivatives from monomethylaniline, the chlorostannate of tetrahydro-6-methylquinoline reacts with cinnamaldehyde with very great ease to give a product similar in properties to the derivative made from tetrahydroquinoline. As found with the pyrazolines, it is conversion of the secondary into a tertiary amino-group that prevents the type of condensation noted in our experiments.

We have accordingly formulated all our condensation products as iminium salts. The presence of a C:N double bond introduces the possibility of geometrical isomerism where pairs of dissimilar groups are involved. Further, the salts named below as ethylidene

$$\text{(II}a\text{)}\quad CH_3\cdot CH{:}\overset{+}{N}R^1R^2\}X^- \qquad CH_2{:}CH\cdot\overset{+}{N}HR^1R^2\}X^-\quad \text{(II}b\text{)}$$

derivatives (II*a*) may in fact exist in the solid state as the tautomeric enamine salts (II*b*), which would be hydrolysed with similar ease to liberate acetaldehyde (Mannich and Davidsen, *Ber.*, 1936, **69**, 2106). Detailed hydrolysis studies and crystal-structural examination might distinguish between these formulæ.

With a single exception (the double salt of morpholine) all the chlorostannates prepared have been of the normal type containing 6-covalent tin (cf. Schaffer, *Acta Cryst.*, 1954, **7**, 242, who describes the crystal structure of dihydrazinium hexachlorostannate). In addition a number of complex halogeno-antimonites and -bismuthites of dimethylamine and di-*n*-butylamine have been made from aqueous-acetone solutions; in no case was condensation observed, but when certain of these salts were dissolved in cinnamaldehyde cinnamylidene derivatives were formed as from chlorostannates. The naming of the complex anions is without prejudice as to the actual existence of these ions (cf. Pugh, *J.*, 1954, 1385).

EXPERIMENTAL

Analytical Methods.—Metals were estimated by methods already reported (Pugh *et al.*, *J.*, 1952, 4138; 1953, 3445), and halogens by Volhard's method. Difficulties were, however, encountered in applying these methods to the cinnamylidene and benzylidene compounds, because they yielded insoluble products on boiling with acids or alkalis, and in some instances because the liberated aromatic amine was nitrated easily, giving yellow or brown colours which made it impossible to detect the end-point on Volhard titration. In these cases, the salts were dissolved by stirring the sample vigorously with 2N-sodium hydroxide (halogen-free; 5 c.c.) and acetone (5 c.c.); tin was precipitated as hydroxide, after dilution and boiling, by careful neutralisation with hydrochloric acid and ammonia (methyl-orange), and chloride was estimated in a separate sample, dissolved in the same way, after extraction with ether to remove aldehyde and free base. As previously reported, the carbon values for compounds containing tin and chlorine tend to be low.

General Methods of Preparation.—The salts of dimethylamine and di-*n*-butylamine were made by crystallisation from warm aqueous-acetone solutions containing the amine, metal halide, and the corresponding halogen acid. Stannic chloride pentahydrate and bismuth iodide were available as solids, antimony and bismuth chlorides and bromides as concentrated solutions obtained by dissolving the metal oxides in the minimum of concentrated acid. The complex salts crystallised readily from solutions containing 50—80% of acetone by volume. In a few cases, oils separated at first but these crystallised slowly at 0°, and the crude products were recrystallised from acetone, in which they are readily soluble. The chlorostannates of morpholine, ephedrine, tetrahydroquinoline, tetrahydro*iso*quinoline, tetrahydro-6-methylquinoline, and dimethylaniline were crystallised from hydrochloric acid solutions containing the amine (2 mols.) and stannic chloride (1 mol.).

Condensation products of salts of dimethylamine and di-*n*-butylamine were obtained from solutions of these salts in undiluted aldehyde only, but chlorostannates derived from the other amines were generally obtained from warm ethanolic, methanolic, or aqueous solutions of the salts, after addition of aldehyde or ketone. Some of the products crystallised on cooling, others were precipitated with ether. The solids were collected by filtration and washed first with ether containing a little of the carbonyl compound and then with ether.

General Properties of the Condensation Products.—These products are similar to the corresponding pyrazolinium and ketazinium salts described earlier (Lamchen, Pugh, and Stephen, *loc. cit.*). The chlorostannates are crystalline and colourless. except those derived from αβ-unsaturated aldehydes which are yellow to red. The latter also seem to be more stable, for, while the salts derived from saturated aldehydes and acetone dissolve easily, with decomposition, in water, dilute acids, and alkalis, the cinnamylidene derivatives are difficult to bring into solution. All the iminium salts, however, yield precipitates of the expected aldehyde or ketone 2 : 4-dinitrophenylhydrazone within a few minutes of their being added to a cold solution of the reagent in 2N-hydrochloric acid. They are hydrolysed slowly even in moist air, often smelling of aldehyde, but they do not lose weight (unless solvated as well) on being heated in a dry atmosphere to 100°.

*Some Complex Salts of Dimethylamine and Di-*n*-butylamine and their Reactions with Carbonyl Compounds.*—Bisdimethylammonium hexachlorostannate has been described by Ries (*Z. Krist.*, 1882, **36**, 332); it was made (m. p. 297°) for the present purpose by crystallisation from a mixture of dimethylamine (2 mols.) and stannic chloride (1 mol.) in hydrochloric acid. Bisdi-*n*-butylammonium hexachlorostannate, as a monohydrate, has also been described (Berg, *Compt. rend.*, 1891, **112**, 437), but without an analysis. The salt made in the same way in these laboratories, however, has always been the dihydrate. Neither of these salts, nor any of the the other salts of these bases described below, condensed with acetone when they were crystallised from acetone (cf. salts of methylaniline and diphenylamine, p. 4424; pyrazolinium salts, Lamchen, Pugh, and Stephen, *loc. cit.*).

Bisethylidenedimethyliminium hexachlorostannate. To bisdimethylammonium hexachlorostannate (1 g.), dissolved in a few drops of hot water, was added acetaldehyde (15 c.c.). The mixture boiled vigorously and on cooling yielded colourless crystals of the very hygroscopic *ethylidenedimethyliminium* salt, m. p. indefinite from 140° [Found: Cl, 44·6; Sn, 24·8. $(C_4H_{10}N)_2SnCl_6$ requires Cl, 44·7; Sn, 25·0%]. A solution of the salt treated with 2 : 4-dinitrophenylhydrazine gave the characteristic 2 : 4-dinitrophenylhydrazone, m. p. 146°, of acetaldehyde.

Biscinnamylidenedimethyliminium hexachlorostannate. Bisdimethylammonium hexachlorostannate (1 g.) was dissolved in hot cinnamaldehyde (4 c.c.), and the cooled solution was treated with ether. The yellow crystalline *salt*, washed with ether and dried *in vacuo* at 100°, had m. p. 245—250° (decomp.) [Found: C, 40·8; H, 4·6; Cl, 32·9; Sn, 18·2. $(C_{11}H_{14}N)_2SnCl_6$ requires C, 40·6; H, 4·3; Cl, 32·7; Sn, 18·3%].

Pentakisdimethylammonium tetradecabromotriantimonite. This salt separated as the *dihydrate*, yellow needles, m. p. 267°, from dimethylamine (3 mols.) and antimony tribromide (1 mol.) in acetone–hydrobromic acid [Found, in material dried in air: Br, 64·2; Sb, 20·9. $(C_2H_8N)_5Sb_3Br_{14},2H_2O$ requires Br, 64·2; Sb, 20·9%]. Desiccation (H_2SO_4) *in vacuo* at 20° (Found: loss, 2·3. Required: loss, 2·1%) yielded the anhydrous *salt*, m. p. 267° (partial sublimation) [Found: Br, 65·6; Sb, 21·5. $(C_2H_8N)_5Sb_3Br_{14}$ requires Br, 65·4; Sb, 21·4%]. This may be a double salt, *e.g.*, $(C_2H_8N)_3SbBr_6,2C_2H_8NSbBr_4$.

Trisdimethylammonium hexabromobismuthite. Dimethylamine (3 mols.) and bismuth tribromide (1 mol.) in acetone–hydrobromic acid gave creamy-yellow needles of the *hexabromo*-salt, m. p. 265—267° [Found: Br, 58·1; Bi, 25·2. $(C_2H_8N)_3BiBr_6$ requires Br, 58·0; Bi, 25·3%].

Bisdi-n-*butylammonium hexachlorostannate.* Di-*n*-butylamine (2 mols.), treated with a small excess of concentrated hydrochloric acid and stannic chloride pentahydrate (1 mol.), gave an oil which crystallised after several days at 0°. The crude salt was recrystallised from 90% acetone, yielding colourless needles of the *dihydrate*, m. p. 72° [Found, in material dried in air: C, 30·4; H, 6·9; Cl, 34·0; Sn, 18·8; loss at 110°, 5·9. $(C_8H_{20}N)_2SnCl_6,2H_2O$ requires C, 30·6; H, 7·0; Cl, 33·9; Sn, 18·9; H_2O, 5·7%]. Desiccation (H_2SO_4) *in vacuo* at 20° gave the anhydrous *salt*, m. p. 156—157° [Found: Cl, 36·2; Sn, 20·1. $(C_8H_{20}N)_2SnCl_6$ requires Cl, 36·0; Sn, 20·1%].

Bisdi-n-*butylcinnamylideneiminium hexachlorostannate.* Bisdi-*n*-butylammonium hexachlorostannate (1 g.) was dissolved in hot redistilled cinnamaldehyde (4 c.c.) and to the cooled solution dry ether was added; the reddish oil which separated was then rubbed vigorously with ether, yielding the yellow *cinnamylidene* derivative, m. p. 140—147° after drying *in vacuo* at 20° [Found: C, 48·6; H, 6·8; Cl, 26·0; Sn, 14·4. $(C_{17}H_{26}N)_2SnCl_6$ requires C, 49·8; H, 6·4; Cl, 26·0; Sn, 14·5%].

Bisdi-n-*butylammonium hexabromostannate.* Stannic chloride pentahydrate (4 g.) was evaporated repeatedly to small bulk with concentrated hydrobromic acid, and di-*n*-butylamine (3 g.) and acetone (10 c.c.) were then added. The clear yellow solution separated on cooling into two layers, and the lower layer gave soft yellow crystals after several days at 0°. The crude *salt* was recrystallised from dilute hydrobromic acid containing a little acetone, and then had m. p. 100° [Found: Br, 55·8; Sn, 13·6. $(C_8H_{20}N)_2SnBr_6$ requires Br, 55·9; Sn, 13·8%]. It is exceedingly soluble in water and in aqueous acetone and, like the hexachlorostannate, it crystallises unchanged from ethanol containing cinnamaldehyde.

Bisdi-n-*butylammonium pentachloroantimonite.* Di-*n*-butylamine (3 mols.) and antimony trichloride (1 mol.) were dissolved in the minimum of warm concentrated hydrochloric acid–acetone (1 : 2 v/v); colourless platelets, m. p. 127—128°, of the *pentachloroantimonite* separated on cooling [Found: C, 35·0; H, 7·2; Cl, 31·8; Sb, 21·8. $(C_8H_{20}N)_2SbCl_5$ requires C, 34·3; H, 7·2; Cl, 31·7; Sb, 21·8%]. It is readily soluble in ethanol and when a warm solution was treated with cinnamaldehyde the salt crystallised unchanged; on addition of ether to a solution in the aldhyde, however, an impure cinnamylidene derivative separated.

Trisdi-n-*butylammonium hexabromoantimonite.* Warm solutions of mixtures of di-*n*-butylamine (3 mols.) and antimony tribromide (1 mol.) in hydrobromic acid gave two phases; the lower oily layer crystallised slowly at 0°. The pure *salt* was obtained as soft yellow crystals by recrystallisation from acetone, in which it is very soluble [Found: Br, 48·4; Sb, 12·3.

$(C_8H_{20}N)_3SbBr_6$ requires Br, 48·4; Sb, 12·3%]. It melts over the range 120—200°, possibly because it decomposes into a mixture of simpler salts.

Di-n-*butylammonium tetrabromoantimonite.* Mixtures of di-*n*-butylamine (1 mol.) and antimony tribromide (1 mol.) in hydrobromic acid behaved in the same way as the above, and the pure salt obtained by recrystallisation from acetone and drying in air was the *monohydrate.* It forms soft, yellow crystals, m. p. 159—160° [Found: Br, 53·9; Sb, 20·4. $C_8H_{20}NSbBr_4,H_2O$ requires Br, 54·2; Sb, 20·6%]. Desiccation (H_2SO_4) *in vacuo* at 20° (Found: loss, 3·0. Required: loss, 3·0%) gave the anhydrous *tetrabromoantimonite* (Found: Br, 56·2; Sb, 21·4. $C_8H_{20}NSbBr_4$ requires Br, 56·0; Sb, 21·4%).

Trisdi-n-*butylammonium hexachlorobismuthite.* Mixtures of di-*n*-butylamine (1 mol). and bismuth chloride (1 mol.) in acetone–hydrochloric acid yielded, not the expected tetrachlorobismuthite, but the *hexachlorobismuthite,* as white granular crystals, m. p. 161—163° [Found: C, 35·9; H, 7·4; Cl, 26·1; Bi, 25·7. $(C_8H_{20}N)_3BiCl_6$ requires C, 35·6; H, 7·4; Cl, 26·2; Bi, 25·8%]. Addition of ether to a solution of this salt in cinnamaldehyde caused an oil to separate which crystallised as a yellow solid on rubbing with ether. Although it could not be obtained analytically pure, this substance was undoubtedly a cinnamylidene derivative of the pentachlorobismuthite, *i.e.*, $(C_{17}H_{26}N)_2BiCl_5$.

Di-n-*butylammonium tetrachlorobismuthite.* Partial evaporation of the mother-liquors from the preparation of the hexachlorobismuthite described above, followed by small additions of acetone, yielded white crystals of the *tetrachlorobismuthite,* m. p. 209—211° (decomp.) (Found: Cl, 29·6; Bi, 43·3. $C_8H_{20}NBiCl_4$ requires Cl, 29·5; Bi, 43·5%).

Trisdi-n-*butylammonium hexabromobismuthite.* In this case also, mixtures of di-*n*-butylamine (1 mol.) and bismuth bromide (1 mol.) in hydrobromic acid–acetone yielded the *hexabromobismuthite,* not the expected tetrabromo-salt, as pale yellow granular crystals, m. p. 160—162° [Found: Br, 44·6; Bi, 19·4. $(C_8H_{20}N)_3BiBr_6$ requires Br, 44·5; Bi, 19·4%]. An attempt to condense this salt with cinnamaldehyde by boiling a portion with ethanol and excess of the aldehyde led to separation of the original salt.

Pentakisdi-n-*butylammonium tetradecaiodotribismuthite.* Di-*n*-butylamine (1 mol.) and bismuth tri-iodide (1 mol.) were dissolved in warm acetone containing a small excess of hydriodic acid; the resulting deep red solution yielded well-formed scarlet granules, m. p. 161—162° [Found: I, 58·3; Bi, 20·6. $(C_8H_{20}N)_5Bi_3I_{14}$ requires I, 58·2; Bi, 20·5%]. This *salt* may also be a double salt, *e.g.*, $(C_8H_{20}N)_3BiI_6,2C_8H_{20}NBiI_4$.

Condensation of Dipiperidinium Hexachlorostannate with Aldehydes.—Piperidinium chlorostannate has been described by Hjörtdahl (*Z. Krist.*, 1878, **3**, 300). A pure sample, m. p. 241°, was made from piperidine (2 mols.), hydrochloric acid, and stannic chloride pentahydrate (1 mol.) and the following condensation products were obtained.

Bis-(1-*ethylidenepiperidinium*) *hexachlorostannate.* To piperidinium chlorostannate in the minimum of hot water was added a large excess of acetaldehyde, and the clear solution was kept for 1 day at −5°. Colourless elongated prisms separated, m. p. 185° (darkening)—195° (red melt) [Found, in material dried *in vacuo*: Cl, 38·3; Sn, 21·2. $(C_7H_{14}N)_2SnCl_6$ requires Cl, 38·4; Sn, 21·4%]. From a specimen of this *salt* the 2 : 4-dinitrophenylhydrazone of acetaldehyde was prepared.

Bis-(1-*but*-2′-*enylidenepiperidinium*) *hexachlorostannate.* Piperidinium chlorostannate, treated in ethanol with an excess of crotonaldehyde, yielded pale yellow prisms, m. p. 193° (decomp.), of the *crotonylidene* derivative [Found: C, 34·8; H, 4·8; Cl, 35·2; Sn, 19·3. $(C_9H_{16}N)_2SnCl_6$ requires C, 35·5; H, 5·2; Cl, 35·1; Sn, 19·5%].

Bis-(1-*cinnamylidenepiperidinium*) *hexachlorostannate.* On adding cinnamaldehyde (2 c.c.) to a solution of dipiperidinium hexachlorostannate (1 g.) in ethanol (5 c.c.) containing a drop of water, a deep yellow solution was obtained which crystallised only after several weeks at 0°. Subsequent preparations, however, took only a few hours after seeding, yielding yellow crystals of the *cinnamylidene* derivative, m. p. 233° (decomp.) after being dried at 100° *in vacuo* [Found: C, 46·2; H, 4·9; Cl, 29·1; Sn, 16·3. $(C_{14}H_{18}N)_2SnCl_6$ requires C, 45·9; H, 4·9; Cl, 29·1; Sn, 16·2%].

These were the only pure condensed salts obtained from piperidinium chlorostannate. When acetone and butyraldehyde were used, the original salt was recovered. Phenylacetaldehyde in ethanol gave a product which was probably a mixture of the condensed and uncondensed salts from which a pure specimen of the condensed salt could not be separated.

Dimorpholinium Hexachlorostannate and its Condensation Products with Aldehydes.—*Dimorpholinium hexachlorostannate* was obtained by partial evaporation of a solution containing concentrated hydrochloric acid (12 cc.), stannic chloride pentahydrate (20 g.), and morpholine

(10 g.); it forms colourless prisms, m. p. 240° (decomp.) [Found, in air-dried material: Cl, 42·0; Sn, 23·3. $(C_4H_{10}ON)_2SnCl_6$ requires Cl, 42·0; Sn, 23·4%]. It is partly decomposed in solution: aqueous-acetone solutions deposit crystals of morpholinium chloride, but solutions in aqueous ethanol, in acetone–ethanol (1 : 1), in butyraldehyde–ethanol, and in benzaldehyde, deposit large rhombic plates and needles of a *double salt*, m. p. 223—225° [Found, in air-dried material: C, 24·6; H, 5·8; Cl, 37·7; Sn, 15·8. $(C_4H_{10}ON)_2SnCl_6,2C_4H_{10}ONCl$ requires C, 25·4; H, 5·3; Cl, 37·6; Sn, 15·8%]. There was no evidence of condensation with acetone, butyraldehyde, or benzaldehyde in the processes described above, or when the chlorostannate in ethanol was treated with phenylacetaldehyde.

Bis-(4-ethylidenemorpholinium) hexachlorostannate. On addition of excess of acetaldehyde to morpholine chlorostannate in the minimum of water an oil separated which solidified slowly at −5°. The colourless condensed *salt*, obtained by rubbing the solid with dry ether containing acetaldehyde, was dried *in vacuo* at room temperature; it had m. p. 138—140° (decomp.) [Found: Cl, 37·9; Sn, 21·2. $(C_6H_{12}ON)_2SnCl_6$ requires Cl, 38·0; Sn, 21·3%].

Bis-(4-but-2′-enylidenemorpholinium) hexachlorostannate. Cooling a warm ethanolic solution of morpholinium chlorostannate containing crotonaldehyde gave yellow prisms, m. p. 188—189° [Found: C, 30·6; H, 4·8; Cl, 34·3; Sn, 19·2. $(C_8H_{14}ON)_2SnCl_6$ requires C, 31·4; H, 4·6; Cl, 34·8; Sn, 19·4%]. This *salt* smells of crotonaldehyde in moist air and decomposes readily in dilute sodium hydroxide solution.

Bis-(4-cinnamylidenemorpholinium) hexachlorostannate. Morpholinium chlorostannate (1 g.) in ethanol (5 c.c.), containing sufficient hydrochloric acid to give a clear solution, was treated with cinnamaldehyde (2 c.c.). The yellow precipitate which formed was washed with ether–cinnamaldehyde and then ether, and dried at 20° *in vacuo* [Found: C, 41·1; H, 4·2; Cl, 28·7; Sn, 16·2. $(C_{13}H_{16}ON)_2SnCl_6$ requires C, 42·4; H, 4·3; Cl, 28·9; Sn, 16·1%]. This *salt*, m. p. 222°, dissolves with difficulty in acids and alkalis.

Bisephedrinium Hexachlorostannate and its Condensation Product with Acetaldehyde.—Crystallisation of mixtures of (±)-ephedrine (2 mols.) and stannic chloride (1 mol.) from hydrochloric acid, followed by washing with concentrated hydrochloric acid, yielded colourless needles of *bisephedrinium hexachlorostannate*, m. p. 187—188° [Found, in material dried at 100° *in vacuo*: Cl, 32·0; Sn, 17·9. $(C_{10}H_{16}ON)_2SnCl_6$ requires Cl, 32·0; Sn, 17·9%]. When ether was added to a solution of this salt in warm cinnamaldehyde an oil was obtained which yielded a yellow powder on being rubbed with several changes of ether. This product contained tin and chlorine in the ratio 1 : 6·0, and 1·5 mols. (approx.) of aldehyde per mol. of amine; it had properties in common with other cinnamylidene derivatives described here. It was possibly a condensation product of normal type (1 : 1) with additional aldehyde condensed or present as solvate.

*Bis-(*N*-ethylidene-ephedrinium) hexachlorostannate.* When ephedrinium chlorostannate was dissolved in pure acetaldehyde, the solution almost immediately deposited colourless needles, m. p. 175°, of the *ethylidene* derivative. This was washed with dry ether and dried at 56° *in vacuo* [Found: Cl, 29·8; Sn, 16·8. $(C_{12}H_{18}ON)_2SnCl_6$ requires Cl, 29·8; Sn, 16·6%]. The salt smells of acetaldehyde and dissolves readily in water. The 2 : 4-dinitrophenylhydrazone of acetaldehyde was prepared from a sample of the salt.

*Bis-(1 : 2 : 3 : 4-tetrahydro*iso*quinolinium) Hexachlorostannate and Some Condensation Products.*—Colourless needles, m. p. 258—259°, of this *hexachlorostannate* were obtained from a hydrochloric acid solution of the hydrochloride of the base (2 mols.) and stannic chloride (1 mol.); the salt was recrystallised from dilute hydrochloric acid and dried at 100° *in vacuo* [Found: Cl, 35·1; Sn, 20·0. $(C_9H_{12}N)_2SnCl_6$ requires Cl, 35·5; Sn, 19·8%]. When this salt was refluxed with ethanol–benzaldehyde (1 : 5) for 3 hr. and the solution cooled to 0°, white crystals, m. p. 226—230°, were obtained which, washed with ether and dried at 100° *in vacuo*, smelled of benzaldehyde in moist air and gave a strong positive test for the aldehyde in acid solution. A benzylidene derivative was evidently formed, but the sample was somewhat contaminated [Found: Cl, 28·4. Calc. for $(C_{16}H_{16}N)_2SnCl_6$: Cl, 27·5%].

*Bis-(2-ethylidene-1 : 2 : 3 : 4-tetrahydro*iso*quinolinium) hexachlorostannate.* When bis-(1 : 2 : 3 : 4-tetrahydro*iso*quinolinium) hexachlorostannate (1 g.) was dissolved in acetaldehyde (25 c.c.), the solution crystallised almost immediately; the pale yellow *salt*, washed with dry ether and dried at 100° *in vacuo*, had m. p. 126° [Found: C, 40·0; H, 4·3; Cl, 32·5; Sn, 18·4. $(C_{11}H_{14}N)_2SnCl_6$ requires C, 40·3; H, 4·3; Cl, 32·7; Sn, 18·3%].

*Bis-(2-cinnamylidene-1 : 2 : 3 : 4-tetrahydro*iso*quinolinium) hexachlorostannate.* This *salt* was obtained initially as a sticky yellow solid on addition of ether to a solution of the chlorostannate of 1 : 2 : 3 : 4-tetrahydro*iso*quinoline (1 g.) in warm cinnamaldehyde (4 c.c.); after recrystallisation from ethanol containing cinnamaldehyde and being washed with dry ether, it formed a yellow powder [Found, in material dried at 80° *in vacuo*: C, 51·1; H, 4·4; Cl, 26·0; Sn, 14·3. $(C_{18}H_{18}N)_2SnCl_6$ requires C, 52·1; H, 4·3; Cl, 25·7; Sn, 14·4%]. The sample had no sharp m. p., forming a viscous mass at *ca.* 136°.

Bis-(1 : 2 : 3 : 4-*tetrahydroquinolinium*) *hexachlorostannate.* By mixing the hydrochloride of the base (2 mols.) with stannic chloride (1 mol.) in dilute aqueous hydrochloric acid and recrystallising the colourless product from dilute hydrochloric acid containing a little stannic chloride, this *salt* was prepared as colourless prisms, m. p. *ca.* 250° (decomp.) [Found: Cl, 35·1; Sn, 20·0. $(C_9H_{12}N)_2SnCl_6$ requires Cl, 35·5; Sn, 19·8%].

The above chlorostannate was kept at 0° in methanol solution with excess of cinnamaldehyde, whereupon a reddish-yellow substance separated, having m. p. 157—158° (decomp.) and giving a strong positive reaction for cinnamaldehyde in acid silution [Found: Cl, 25·0. Calc. for $(C_{18}H_{18}N)_2SnCl_6$: 25·7%].

No condensation products could be isolated on treating a solution of the chlorostannate in ethanol–methanol mixtures with butyraldehyde, crotonaldehyde, benzaldehyde, or acetone. With phenylacetaldehyde, the mother-liquor was green but there crystallised a nearly colourless product which gave a positive test for aldehyde. The chloride content was 1·7% low for the pure phenylethylidene derivative.

Bis-(1 : 2 : 3 : 4-*tetrahydro-*6-*methylquinolinium*) *hexachlorostannate.* Reduction of 6-methylquinoline with sodium and boiling ethanol (cf. Oldham and Johns, *J. Amer. Chem. Soc.*, 1939, **61**, 3289) yielded 1 : 2 : 3 : 4-tetrahydro-6-methylquinoline, n_D^{25} 1·5870, which solidified on storage. The hydrochloride, m. p. 186° (lit., m. p. 189°), was converted into the *hexachlorostannate*, m. p. 245—247°, in the usual way (Found, in material dried at 80° *in vacuo*: Cl, 34·2. $(C_{10}H_{14}N)_2SnCl_6$ requires Cl, 33·9%].

Bis-(1-*cinnamylidene-*1 : 2 : 3 : 4-*tetrahydro-*6-*methylquinolinium*) *hexachlorostannate.* Addition of cinnamaldehyde to the chlorostannate (prepared as above), dissolved in a large excess of cold methanol, gave a deep red solution from which a vermilion *cinnamylidene* derivative separated within 2 min. After being washed with dry ether and dried *in vacuo* at 100° to constant weight (5 hr.), the orange-brown product had m. p. 175—176° (decomp.) [Found: C, 52·4; H, 4·6; Cl, 24·8; Sn, 13·9. $(C_{19}H_{20}N)_2SnCl_6$ requires C, 53·2; H, 4·7; Cl, 24·9; Sn, 13·9%].

Condensation of Bismethylanilinium Hexachlorostannate with Carbonyl Compounds.—Hydrogen chloride gas was passed into a solution containing monomethylaniline (2 mols.) and stannic chloride (1 mol.) in boiling dry acetone under reflux. The solution was cooled, and the solid which separated was recrystallised by careful addition of ether to its solution in warm acetone–ethanol, yielding *bis(methyl*iso*propylideneanilinium) hexachlorostannate* as colourless crystals, m. p. 227—229° (decomp.) [Found, in material dried at 80°: C, 37·5; H, 4·6; Cl, 34·0; Sn, 18·9; C_3H_6O, 18·6. $(C_{10}H_{14}N)_2SnCl_6$ requires C, 38·2; H, 4·5; Cl, 33·9; Sn, 18·9; C_3H_6O, 18·5%]. Acetone was determined by Messinger's method (Goodwin, *J. Amer. Chem. Soc.*, 1920, **42**, 39). When aqueous hydrochloric acid was used instead of hydrogen chloride gas, the product was contaminated by the chlorostannate and chloride of monomethylaniline, and in an attempt to increase the yield of the desired condensation product, a quantity of zinc chloride equal to the weight of stannic chloride present was added to the reagents; in this case, however, the chlorostannate of monomethylaniline (m. p. 250°) crystallised.

Cinnamaldehyde (1 c.c.) was added to a solution of monomethylaniline hydrochloride (1 g.) and stannic chloride (1 c.c.) in hot ethanol (30 c.c.) containing a few drops of water, whereupon an oil separated. When the aldehyde was added slowly in ethanol solution, however, a sticky yellow solid was precipitated which, after recrystallisation from hot ethanol containing a little cinnamaldehyde, afforded *bis(cinnamylidenemethylanilinium) hexachlorostannate* as a yellow powder, m. p. 195—198° (decomp.) [Found: C, 48·6; H, 4·4; Cl, 27·4; Sn, 15·3; C_9H_8O, 32·0. $(C_{16}H_{16}N)_2SnCl_6$ requires C, 49·6; H, 4·2; Cl, 27·5; Sn, 15·3; C_9H_8O, 34·0%]. Cinnamaldehyde was estimated gravimetrically as 2 : 4-dinitrophenylhydrazone.

Addition of ether to the dark orange solution obtained by heating monomethylaniline hydrochloride (2 g.), stannic chloride (2 c.c.), dry ethanol (10 c.c.), and benzaldehyde (3 c.c.) under reflux for 1 hr. caused the separation of lemon-yellow crystals, m. p. 240° after having been washed with ethanol–ether and dried *in vacuo*. The product was a hexachlorostannate containing benzaldehyde residues and monomethylaniline in the ratio 3 : 2. A fraction only of the benzaldehyde residues could be liberated by warming with dilute acid.

Considerable heat was evolved when acetaldehyde was added to the chlorostannate of monomethylaniline dissolved in cold methanol, and treatment of the resulting solution with ether gave an impure ethylidene derivative.

Condensation of Bisdiphenylammonium Hexachlorostannate with Acetone and with Cinnamaldehyde.—When a warm solution containing diphenylamine (2 g.), stannic chloride pentahydrate (4 g.), concentrated hydrochloric acid (1 c.c.), and acetone (20 c.c.) was cooled, there separated colourless needles of *bis(diphenyl*iso*propylideneiminium) hexachlorostannate*, m. p. 270° (vigorous decomp.) [Found, in material dried at 20° *in vacuo*: C, 47·0; H, 4·3; Cl, 28·3; Sn, 15·8; C_3H_6O, 16·2. $(C_{15}H_{16}N)_2SnCl_6$ requires C, 48·0; H, 4·3; Cl, 28·3; Sn, 15·8; C_3H_6O, 15·5%]. The same product was obtained by passing hydrogen chloride into dry acetone containing diphenylamine and anhydrous stannic chloride. It suffers no loss in weight at 100° *in vacuo*, is readily soluble (liberating acetone) in water, and is decomposed by aqueous sodium hydroxide with separation of diphenylamine.

Addition of cinnamaldehyde to solutions of diphenylamine hydrochloride (2 mols.) and stannic chloride (1 mol). in methanol, ethanol, or aqueous ethanol caused darkening and separation of yellow-brown or orange powders or oils. Despite the extreme difficulty in working up the products, m. p. *ca* 202° (decomp.), their composition was remarkably constant, indicating the presence of tin and chloride in the ratio 1 : 5·3 together with aldehyde residues and diphenylamine in the ratio 5 : 2.

Of all the products described here, the above derivative, the corresponding compound from ephedrine, and the benzylidene derivative of methylaniline are the only ones which are of uncertain constitution. Further work on these compounds is in progress.

Bisdimethylanilinium Hexachlorostannate.—Attempts to make condensation products with carbonyl compounds. Druce (*Chem. News*, 1919, **118**, 89) has described a chlorostannate of dimethylaniline, m. p. 116°. In our preparations, this salt has been obtained from aqueous media as the *monohydrate*, which loses its water of hydration below 100° (without melting) and then melts at 170—171° [Found: Cl, 35·8; Sn, 19·9; loss at 100°, 3·0. $(C_8H_{12}N)_2SnCl_6,H_2O$ requires Cl, 35·8; Sn, 20·0; H_2O, 3·0%]. The anhydrous salt (m. p. 170—171°) was obtained by mixing solutions of dimethylaniline hydrochloride and stannic chloride in anhydrous ethanol, and also by passing dry hydrogen chloride into a dry ethanol solution of the free base and stannic chloride [Found: Cl, 36·9; Sn, 20·7. Calc. for $(C_8H_{12}N)_2SnCl_6$: Cl, 37·0; Sn, 20·7%].

With cinnamaldehyde in warm aqueous ethanol it forms deep red solutions which deposit dark red, water-soluble crystals; on being heated in a m. p. tube they become colourless at *ca.* 130° and melt at 169—171°, the residue being free from cinnamaldehyde. Analysis shows the red crystals to be the above-described monohydrate contaminated with traces of cinnamaldehyde, probably adsorbed, as much of the impurity is removed by washing with ethanol.

When ethanol solutions of the chlorostannate of dimethylaniline, or of mixtures of the simple salts, or of dimethylaniline, stannic chloride, and hydrogen chloride, were treated with acetone, flat platelets were obtained which varied in colour from cream to yellow or orange. All samples prepared dissolved readily in water, contained acetone, and had identical composition; all became colourless at *ca.* 120° and melted at 169—171°. Heating *in vacuo* for several hours resulted in loss of weight (9%), and the product was then free from acetone and had m. p. 170—171°, unchanged by admixture with the *chlorostannate* of dimethylaniline. It is clear, therefore, that acetone is not present in condensed form but probably as solvate [Found: C, 34·6; H, 4·7; Cl, 33·8; Sn, 18·8; C_3H_6O, 8·8. $(C_8H_{12}N)_2SnCl_6,C_3H_6O$ requires C, 36·0; H, 4·7; Cl, 33·6; Sn, 18·8; C_3H_6O, 8·5%].

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