Hydrazine. Part X. Salts of Some Aldazines and Ketazines.*

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[Reprint Order No. 5430.]

Simple and complex salts of a variety of aromatic aldazines and ketazines are described. No salts of aliphatic aldazines, and only a few of aliphatic ketazines, could be prepared by similar methods.

Parts II, IV, and VI * describe some complex salts of dimethyl ketazine and certain hydrazones. Shoesmith and Slater had previously reported a chlorostannate of anisaldazine (*J.*, 1925, **127**, 1490). The present work, undertaken to survey the salt-forming properties of azines in general, has resulted in the preparation of halides, sulphates, halogeno-antimonites, -bismuthites, -stannates, and -platinates of a variety of azines. The following points emerge: (1) Aromatic aldazines and ketazines yielded halides, sulphates, and complex salts. (2) Aliphatic ketazines gave salts less readily; no simple salts were obtained; dimethyl ketazine yielded complex salts but its homologues, under comparable conditions, formed salts of the corresponding hydrazones instead, thereby confirming observations made in Parts II, IV, and VI (*locc. cit.*). (3) Aliphatic aldazines have yielded no crystalline salts; in some cases, oily products were obtained at −50° or below (which decomposed rapidly at room temperature) and, in other cases, crystalline products of variable composition showing varying degrees of polymerisation. (4) "Mixed" azines, containing 1 mol. of each of aromatic aldehyde and acetone condensed per mol. of hydrazine, gave salts most readily. (That these were not salts of Mannich bases is shown on p. 1755.)

The halides and sulphates were obtained, with the single exception of salicylaldazine hydrobromide, only under strictly anhydrous conditions; they are readily hydrolysed in aqueous solution. The same was true of the chloro-complexes; the bromo- and iodo-complexes, on the other hand, are less soluble and more stable and were generally obtained by adding the concentrated acid to the azine and metal salt in nitrobenzene solution. The complex platinates undergo self-reduction in aqueous media and were also best prepared from non-aqueous media.

Experimental

Analytical Methods.—The methods of analysis employed were those previously reported (Part VI, *loc. cit.*; *J. Appl. Chem*, 1954, **4**, 47), but it was essential to remove aldehyde and ketone as a preliminary to analysis by boiling with 5N-hydrochloric acid (for hydrazine, sulphate, bismuth, and tin) or with 2N-sulphuric acid (for halogen and antimony). Tin was first separated as sulphide because direct precipitation of hydrated oxide gave low results.

General Methods of Preparation.—Although the ketazinium salts described in previous papers were made direct from the ketone, the salts now to be described were best prepared from the azine. The salts of salicylaldazine in particular were liable to contain free salicylaldazine, and fractional crystallisation or extraction with hot solvent was found necessary. The yields were in most cases 40—90%.

(*a*) Hydrochlorides and chloro-metallic complex salts: hydrogen chloride was passed through solutions of the azine, or of azine and metal halide, in nitrobenzene, ether, or xylene; in a few instances, nitrobenzene solutions of azine hydrochloride and metal chloride were mixed.

(*b*) Bromo- and iodo-metallic complex salts: the azine in nitrobenzene was mixed with the metal bromide or iodide in nitrobenzene, ether, or xylene, and excess of hydrobromic acid (48%) or hydriodic acid (57%) was added. Crystals separated at the interface.

(*c*) Complex platinates: chloroplatinic acid in ether, or bromoplatinic acid in *n*-butyl alcohol, was added to the azine and a small amount of the corresponding aldehyde or ketone in ether.

(*d*) Sulphates: an equivalent quantity of sulphuric acid (98%) in ether solution (2%) was added to the azine in ether or xylene.

(*e*) "Mixed" azines: molecular proportions of aromatic aldehyde and hydrazine hydrate (95%) were boiled with acetone and excess of hydrobromic or hydriodic acid; or the hydrazone was simply dissolved in acetone. The iodide (Table 3) was also made by adding hydriodic acid to dimethyl ketazine in benzaldehyde at 0°.

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* Parts II, IV, VI, IX, *J.*, 1953, 354, 2491, 3445; 1954, 2429.

TABLE 1. *Halogeno-antimonites and -bismuthites of benzaldazine, salicylaldazine, and anisaldazine,* (R:N·N:R)HMX$_4$

Compound * R	MX$_4$	M. p.	Formula	Found (%) C	H	N$_2$H$_4$	M	X	Required (%) C	H	N$_2$H$_4$	M	X	Method †
(1) C_6H_5·CH	$SbCl_4$	156—157°	$C_{14}H_{13}N_2SbCl_4$	35·2	2·7	6·8	26·1	30·7	35·5	2·7	6·8	25·8	30·2	*a* (nb)
(2) *o*-C_6H_4(OH)·CH	$SbCl_4$	175—182	$C_{14}H_{13}O_2N_2SbCl_4$	33·7	2·5	6·2	24·1	28·1	33·3	2·6	6·3	24·2	28·1	*a* (nb)
(3) *p*-C_6H_4(OMe)·CH	$SbCl_4$	198—200	$C_{16}H_{17}O_2N_2SbCl_4$	36·1	3·5	6·2	22·9	26·5	36·0	3·2	6·0	22·9	26·7	*a* (nb)
(4) C_6H_5·CH	$SbBr_4$	179—180	$C_{14}H_{13}N_2SbBr_4$	25·9	2·2	4·8	18·7	49·4	25·8	2·0	4·9	18·7	49·2	*a* (nb)
(5) *o*-C_6H_4(OH)·CH	$SbBr_4$	192—193	$C_{14}H_{13}O_2N_2SbBr_4$	24·7	1·9	4·8	17·9	47·0	24·6	1·9	4·7	17·9	46·9	*b* (nb)
(6) *p*-C_6H_4(OMe)·CH	$SbBr_4$	216—218	$C_{16}H_{17}O_2N_2SbBr_4$	27·6	2·7	4·5	17·1	45·0	27·0	2·4	4·5	17·2	45·0	*b* (nb)
(7) C_6H_5·CH	SbI_4	173—190	$C_{14}H_{13}N_2SbI_4$	20·8	1·6	3·6	15·0	60·7	20·1	1·6	3·8	14·6	60·5	*b* (ether and xylene)
(8) *o*-C_6H_4(OH)·CH	SbI_4	211—212	$C_{14}H_{13}O_2N_2SbI_4$	19·1	1·8	3·6	13·9	58·1	19·3	1·5	3·7	14·0	58·4	*b* (nb)
(9) *p*-C_6H_4(OMe)·CH	SbI_4	214—215	$C_{16}H_{17}O_2N_2SbI_4$	22·0	2·1	3·5	13·9	56·5	21·6	1·9	3·6	13·6	56·5	*b* (nb)
(10) C_6H_5·CH	$BiCl_4$	200—206	$C_{14}H_{13}N_2BiCl_4$	29·6	2·4	5·7	37·4	25·5	30·0	2·3	5·7	37·3	25·4	*a* (nb)
(11) *o*-C_6H_4(OH)·CH	$BiCl_4$	213—220	$C_{14}H_{13}O_2N_2BiCl_4$	28·0	2·6	5·5	35·2	24·3	28·4	2·2	5·4	35·3	24·0	*a* (nb)
(12) *p*-C_6H_4(OMe)·CH	$BiCl_4$	236—237	$C_{16}H_{17}O_2N_2BiCl_4$	30·9	3·1	5·2	33·6	22·9	31·0	2·7	5·2	33·7	22·9	*a* (nb)
(13) C_6H_5·CH	$BiBr_4$	229—234	$C_{14}H_{13}N_2BiBr_4$	22·4	1·7	4·3	27·7	43·8	22·8	1·8	4·3	28·3	43·4	*b* (nb)
(14) *o*-C_6H_4(OH)·CH ‡	$BiBr_4$	*ca.* 227	$C_{14}H_{13}O_2N_2BiBr_4$	—	—	4·6	—	40·3	—	—	4·2	—	41·6	*b* (nb)
(15) *p*-C_6H_4(OMe)·CH	$BiBr_4$	244—245	$C_{16}H_{17}O_2N_2BiBr_4$	25·3	2·4	4·2	26·2	40·6	24·3	2·2	4·1	26·2	40·5	*b* (xylene)
(16) C_6H_5·CH	BiI_4	228—230	$C_{14}H_{13}N_2BiI_4$	17·9	1·7	3·8	22·4	55·2	18·2	1·4	3·5	22·6	54·8	*b* (nb)
(17) *o*-C_6H_4(OH)·CH	BiI_4	246—253	$C_{14}H_{13}O_2N_2BiI_4$	17·4	1·6	3·3	21·6	—	17·5	1·4	3·3	21·8	—	*b* (nb)
(18) *p*-C_6H_4(OMe)·CH	BiI_4	235—238	$C_{16}H_{17}O_2N_2BiI_4$	19·6	1·6	3·1	20·8	51·0	19·5	1·7	3·2	21·2	51·5	*b* (nb)

* Colour (and form) of crystals: (1) pale yellow; (2) yellow; (3) orange; (4) yellow; (5) yellow; (6) orange; (7) orange-red; (8) orange-red; (9) orange-red; (10) yellow needles; (11) orange; (12) orange; (13) yellow; (14) orange; (15) orange; (16)—(18) red.

† See " General Methods of Preparation " (p. 1753); nb = nitrobenzene.

‡ After repeated crystallisation, and washing with hot nitrobenzene, still contained some salicylaldazine.

TABLE 2. *Halogeno-stannates and -platinates of some azines and hydrazones,* (R:N·N:R′)$_2$H$_2$MX$_6$.

Compound * R	R′	MX$_6$	M. p.	Formula	Found (%) C	H	N$_2$H$_4$	M	X	Required (%) C	H	N$_2$H$_4$	M	X	Method †
(1) C_6H_5·CH		$SnCl_6$	217—225°	$(C_{14}H_{13}N_2)_2SnCl_6$	45·3	3·9	8·6	15·4	27·9	44·8	3·5	8·6	15·8	28·4	*a* (ether)
(2) *o*-C_6H_4(OH)·CH		$SnCl_6$	212—220	$(C_{14}H_{13}O_2N_2)_2SnCl_6$	40·7	3·1	7·9	15·0	26·5	41·4	3·2	7·9	14·7	26·2	*a* (xylene)
(3) C_6H_5·CH		$SnBr_6$	218—225	$(C_{14}H_{13}N_2)_2SnBr_6$	32·4	2·6	6·3	11·6	46·7	33·1	2·6	6·3	11·6	47·2	*b* (nb)
(4) *p*-C_6H_4(OMe)·CH		$SnBr_6$	240—242	$(C_{16}H_{17}O_2N_2)_2SnBr_6$	33·9	2·9	5·6	10·5	42·2	33·9	3·0	5·6	10·4	42·3	*b* (nb)
(5) C_6H_5·CH		$PtBr_6$	188—189	$(C_{14}H_{13}N_2)_2PtBr_6$	—	—	5·9	18·7	44·1	—	—	5·9	17·9	43·8	*c*
(6) CMePh		$PtBr_6$	190—191	$(C_{16}H_{17}N_2)_2PtBr_6$	—	—	5·6	17·1	42·5	—	—	5·7	17·3	42·5	*c*
(7) C_6H_5·CH	CMePh	$PtBr_6$	214—216	$(C_{15}H_{15}N_2)_2PtBr_6$	—	—	5·0	15·1	37·4	—	—	5·0	15·2	37·4	*c*
(8) CMe$_2$		$PtBr_6$	82—84	$(C_6H_{13}N_2)_2PtBr_6$	—	—	6·9	22·9	54·5	—	—	7·1	21·7	53·3	*c*
(9) CMe$_2$		$PtCl_6$	157—158 (decomp.)	$(C_6H_{13}N_2)_2PtCl_6$	—	—	10·5	31·4	33·6	—	—	10·1	32·2	35·1	*c*
(10) CEt$_2$	H	$PtBr_6$	decomp.	$(C_5H_{13}N_2)_2PtBr_6$	—	—	7·3	21·7	56	—	—	7·3	22·3	54·7	*c*
(11) CEt$_2$	H	$PtCl_6$	187—188	$(C_5H_{13}N_2)_2PtCl_6$	—	—	10·4	34·5	34·8	—	—	10·5	32·1	35·1	*c*

* Colour, etc., of crystals: (1) pale yellow powder; (2)—(4) yellow crystalline powder; (5) orange powder; (6) and (7) red, birefracting straight extinction; (8) red, birefracting; (9) orange, birefracting; (10) red powder; (11) orange powder.

† See " General Methods of Preparation " (p. 1753); (nb) = nitrobenzene.

(*f*) Hydrobromic acid (48%) was added to a hot saturated solution of the azine in nitrobenzene.

General Properties of the Salts.—Apart from the complex platinates, which are red, the aldazinium salts show the expected gradation in colour and m. p. The chloro-salts are lightly coloured, the bromo-salts yellow or orange, and the iodo-salts red; the m. p. rises with increasing complexity of the base for any one anion, with increasing atomic weight of the halogen for the same base and metal, and with increasing atomic weight of the metal for the same base and halogen. The simple salts and the chloro-complexes are readily hydrolysed in water, smelling of aldehyde or ketone in moist air, but the bromo- and the iodo-complexes, especially, are decomposed with difficulty by boiling hydrochloric acid. The complex platinates undergo self-reduction, slowly in water and rapidly in alkali, to platinum and nitrogen. They are insoluble in *cyclo*hexane, ether, and xylene, and sparingly soluble in nitrobenzene, dioxan, and pyridine.

Unsuccessful Attempts to make Salts.—Attempts to make simple salts of acetaldazine, dimethyl ketazine, di-*n*-propyl ketazine, and di-*n*-butyl ketazine failed. Impure chlorides and sulphates were obtained from *n*-butaldazine and *n*-propaldazine. Propaldazine and butaldazine gave no salts with the complex acids used, but acetaldazine and crotonaldazine gave crystalline halogeno-stannates, -antimonites, and -bismuthites of variable composition; the equivalent weight of the base in these products was high, indicating polymerisation.

N-*o-Nitrobenzylidene*-N′-iso*propylidenehydrazinium Bromide.*—This *salt* separated as creamy white crystals, darkening with age, m. p. 156—158°, when hydrobromic acid (48%) was added to *o*-nitrobenzaldehyde hydrazone in acetone (Found: C, 41·9; H, 3·8; N_2H_4, 11·0; Br, 27·6. $C_{10}H_{12}O_2N_3Br$ requires C, 42·0; H, 4·2; N_2H_4, 11·0; Br, 27·4%). A sample of this salt was made into a paste with potassium carbonate and water and extracted with ether. The free base, isolated in the usual way, had m. p. 67°, undepressed on mixing with an authentic specimen. (This proved that it was not a salt of a Mannich base.)

Bis-(NN-*di-o-nitrobenzylidenehydrazinium*) *Hexachlorostannate.*—A greyish crystalline powder, m. p. 183—190° (blackening at 180), of the above-named *salt* was precipitated on treating *o*-nitrobenzaldazine (2 mols., in hot, dry xylene) with stannic chloride (1 mol., in nitrobenzene) and hydrogen chloride [Found: C, 37·0; H, 3·0; N_2H_4, 6·7; Cl, 22·7; Sn, 12·8. $(C_{14}H_{11}O_4N_2)_2SnCl_6$ requires C, 36·2; H, 2·4; N_2H_4, 6·9; Cl, 22·9; Sn, 12·8%].

Tables 1, 2, and 3 give the other salts that have been characterised.

TABLE 3. *Halides and sulphates of some aldazines and ketazines,* (R:N·N:R′)HX.

	Compound *					Found (%)			Required (%)			
	R	R′	X	M. p.	Formula	C	N_2H_4	X †	C	N_2H_4	X †	Method
(1)	C_6H_5·CH		HSO_4	160—161°	$C_{14}H_{13}N_2HSO_4$	53·4	10·5	31·7	54·8	10·5	31·4	*d* (ether)
(2)	*o*-C_6H_4(OH)·CH		Br	211—213	$C_{14}H_{13}O_2N_2Br$	50·9	9·9	24·9	52·3	10·0	24·9	*f*
(3)	*o*-C_6H_4(OH)·CH		HSO_4	178—179	$C_{14}H_{13}O_2N_2HSO_4$	49·7	9·5	28·3	49·7	9·5	28·4	*d* (xylene)
(4)	*p*-C_6H_4(OMe)·CH		HSO_4	202—203	$C_{16}H_{17}O_2N_2HSO_4$	52·1	8·7	26·3	52·5	8·7	26·2	*d* (ether)
(5)	CMePh		Cl	132—134	$C_{16}H_{17}N_2Cl$	—	11·8	13·4	—	11·7	13·0	*a* (ether)
(6)	CMePh		HSO_4	125—126	$C_{16}H_{17}N_2HSO_4$	—	9·8	29·4	—	9·6	28·8	*d* (ether)
(7)	CPh_2		Cl	166—168	$C_{26}H_{21}N_2Cl$	—	8·1	9·0	—	8·1	9·2	*a* (ether)
(8)	*o*-C_6H_4(OH)·CH	CMe_2	Br	177—178	$C_{10}H_{13}ON_2Br$	46·8	12·5	31·2	46·7	12·5	31·1	*e* (acetone)
(9)	C_6H_5·CH	CMe_2	Br	135—136	$C_{10}H_{13}N_2Br$	49·6	13·2	33·2	49·8	13·3	33·2	*e* (acetone)
(10)	C_6H_5CH	CMe_2	I	107—108	$C_{10}H_{13}N_2I,H_2O$ ‡	38·8	10·3	41·3	39·2	10·5	41·5	*e* (acetone)

* Colour, etc., of crystals: (1) yellow; (2)—(3) yellow plates; (4) yellow powder; (5)—(7) white; (8) pink, monoclinic; (9) white; (10) yellow. † Here, X = halogen or SO_4 (not HSO_4).

‡ Found: Loss at 56°/15 mm., 5·5. Required: H_2O, 5·9%.

Acknowledgment is made to R. von Holdt, B.Sc., for the combustion analyses, and to the Director of the National Chemical Laboratories of the C.S.I.R. for some microanalyses.

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[*Received, May* 31*st*, 1954.
Revised, January 6*th*, 1955.]