

Table IV. Synthetic Procedure

Metal Salt ^a	Step					Recovery of Product ^b
	1	2	3	4	5	
MgCl ₂	20 ml. NMF, stir until dissolved	10 ml. EOF, stir 1 hr.	Triturate 3-4 times with 50-ml. portions of ether	Add 5 ml. abs. alc., stir 10 min.	Add 10 ml. ether, stir until obtain fine powder	1
MnCl ₂	6 ml. NMF, dissolve	5 ml. EOF, stir 1 hr.	50 ml. ether, stir 1 hr., decant off, repeat	Add 5 ml. abs. alc., stir ½ hr., add 10 ml. ether, stir	Scrape solid off walls, crush, and stir until obtain fine powder	1
CoCl ₂	5 ml. NMF, dissolve	5 ml. EOF, stir 1 hr.	Add 50 ml. ether, stir ½ hr., decant off ether	Add 5 ml. abs. alc., stir 10-15 min.	Add 25 ml. ether, stir overnight	2
NiCl ₂	20 ml. EOF, heat, stir 1 hr.	Slowly add 20 ml. NMF, stir vigorously	Initially obtain green gelatinous solid, stir	After 1-2 hr., obtain fine yellow powder	Stir until no trace of green solid remains	2
CuCl ₂	10 ml. NMF, dissolve	5 ml. EOF, stir 1 hr.	Add 25 ml. ether, stir	Obtain green powder continue stirring 1-2 hr.		2
ZnCl ₂	5 ml. NMF, dissolve	5 ml. EOF, stir 1 hr.	Add 15 ml. ether, stir overnight	Filter, wash solid with ether, dry in vac.	Recrystallize from benzene	3
CdCl ₂	7 ml. NMF, 1 ml. H ₂ O, stir ½ hr.	Obtain thick paste, strong stirring needed	10 ml. EOF, stir ½ hr.	Add 10 ml. abs. alc. stir overnight		4
ZnI ₂	1 ml. NMF and 29 ml. ether	Stir overnight				2

^aUse 0.01 mole of appropriate hydrated metal salt. ^bFilter, wash, and dry in vacuum. 1. Wash with mixture of 5 ml. alc. + 10 ml. ether, then with ether. 2. Wash with ether. 3. Wash with benzene, then with ether. 4. Wash with alcohol, then with ether.

The synthesis of these complexes generally consisted of dissolution of the hydrated metal chloride in NMF and dehydration with ethyl orthoformate (EOF), followed by the recovery of the complex, usually by addition of ether. The procedures and quantities of reagents used are summarized in Table IV.

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 Elemental analyses performed by the Analytical Research Department, Chemical Research Laboratory, Edgewood Arsenal, Md. 21010.

Synthesis of Hydrazonium Salts

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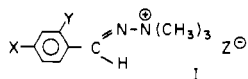
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The trimethylhydrazonium iodide, chloride, hexachlorostannate, tosylate, and fluoborate salts of benzaldehyde, 4'-nitrobenzaldehyde, anisaldehyde, and 2',4'-dichlorobenzaldehyde (I) have been prepared and characterized. Similarly, the iodide, chloride, hexachlorostannate, hexafluorophosphate, tetrafluoroborate, perchlorate, nitrate, and tosylate bistrimethylhydrazonium salts of glutaraldehyde (II) and trimethylhydrazonium salts of 4-cyano-2,2-dimethylbutyraldehyde (III) have been prepared and characterized. In addition, the bromide and hexafluoroarsenate salts of II are reported. Infrared and NMR data on these compounds are included.

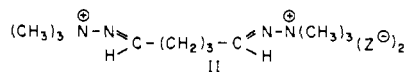
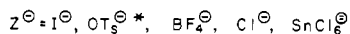
RECENT interest in the chemistry of hydrazonium salts (5, 6, 7) prompts this report. As a part of another study, various trimethylhydrazonium salts of benzaldehyde, 4'-nitrobenzaldehyde, anisaldehyde, 2',4'-dichlorobenzaldehyde (I), glutaraldehyde (II), and 4-cyano-2,2-dimethylbutyraldehyde (III) have been prepared by alkylation of the corresponding dimethylhydrazones (Figure 1). All of these are new compounds except Ia and Ic, *p*-toluenesulfonates (tosylates), and Ib, iodide (7).

The structures of these compounds were assigned on

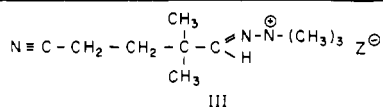
the basis of their accurate elemental analyses and infrared and nuclear magnetic resonance spectra (Table I). The chloride salts did not all analyze correctly because of their hygroscopic nature. Their structures are assigned on the basis of spectroscopic evidence (Table I) and the fact that they were readily converted to the corresponding hexachlorostannates. In the infrared, the $>C=N-$ absorption was independent of the anion, but in the aromatic salts it varied with the electronegativity of the ring substituent (Table I), the more electronegative groups shifting the



- I a: X = OCH₃, Y = H,
 I b: X = Y = H
 I c: X = NO₂, Y = H,
 I d: X = Cl, Y = Cl,



- II: Z[⊖] = I[⊖], Br[⊖], Cl[⊖], SnCl₆[⊖], OT_s[⊖], ClO₄[⊖],
 BF₄[⊖], PF₆[⊖], AsF₆[⊖], NO₃[⊖].



- III: Z[⊖] = I[⊖], Cl[⊖], SnCl₆[⊖], OT_s[⊖], PF₆[⊖], ClO₄[⊖], BF₄[⊖], NO₃[⊖]

* OT_s[⊖] = p-TOLUENESULFONYL

Figure 1. Trimethylhydrazonium salts

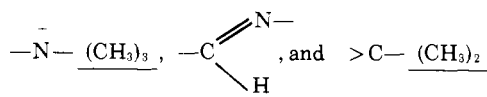
Table I. Spectroscopic Data^a

NMR Chemical Shift, τ

Com- pounds	N—		> C(CH ₃) ₂	Infrared Wavelength, μ , > C=N—
	+ —N—(CH ₃) ₃	—C—H		
Ia	6.31–6.48	0.32–1.00	...	6.20–6.25
Ib	6.35–6.46	0.36–0.84	...	6.20
Ic	6.37–6.43	0.32–0.72	...	6.10
Id	6.28–6.42	0.60–0.83	...	6.15–6.20
II	6.50–6.60	1.15–1.60 ^b	...	6.10
III	6.49–6.70	1.23–1.70	8.87–8.95	6.10

^a Lower and upper limits of range in which series of compounds absorbed. ^b Range of center peaks of triplets.

absorption to shorter wavelength (I). These structure assignments were confirmed by the NMR spectra. For simplicity, only the easily identified singlets are reported



in Table I. The aromatic protons in Ia–d and aliphatic protons of II and III are not included in the table because of the complexity of their absorptions.

EXPERIMENTAL

Melting points (Table II) were determined in open capillaries and are in degrees centigrade and uncorrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and National Bureau of Standards, Gaithersburg, Md. Infrared spectra were determined in mineral oil on a Beckman IR 5 spectrophotometer. NMR spectra were determined in d₆ DMSO on a Varian A-60 instrument. All of the compounds reported decomposed exothermically above 220°C., but compound II-ClO₄[⊖] should be handled with care, as it decomposed violently on heating to 250°C. Analytical data, yields, and recrystal-

Table II. Melting Points

Compound	Melting Point, ° C.	Compound	Melting Point, ° C.
Ia	I [⊖]	II	OT _s [⊖]
	OT _s [⊖]	I	155–58
	BF ₄ [⊖]	ClO ₄ [⊖]	189–90
	Cl [⊖]	BF ₄ [⊖]	196–97
	SnCl ₆ [⊖]	Cl [⊖]	158–59
Ib	I [⊖]	160–63	Br [⊖]
	OT _s [⊖]	165d	SnCl ₆ [⊖]
	BF ₄ [⊖]	225–27	PF ₆ [⊖]
	Cl [⊖]	204–06	NO ₃ [⊖]
	SnCl ₆ [⊖]	127–28	AsF ₆ [⊖]
Ic	I [⊖]	208–09	I [⊖]
	OT _s [⊖]	149–50	OT _s [⊖]
	BF ₄ [⊖]	114–16	ClO ₄ [⊖]
	Cl [⊖]	78–79	BF ₄ [⊖]
	SnCl ₆ [⊖]	64–65	PF ₆ [⊖]
Id	I [⊖]	100–01	NO ₃
	OT _s [⊖]	107–08	Cl [⊖]
	BF ₄ [⊖]	51–52	SnCl ₆ [⊖]
	Cl [⊖]	211–12	
	SnCl ₆ [⊖]	168	
	229–30		

^a Ultimate analyses (C, H, N, halogen) for all these compounds agree, within usually accepted limits, with theoretical values. These data, yields, and recrystallization solvents are recorded in a supplementary table, deposited with ASIS National Auxiliary Publications Service.

lization solvents can be obtained from the ASIS National Auxiliary Publications Service.

Preparation of Hydrazones. The dimethylhydrazones of the aromatic aldehydes and of 4-cyano-2,2-dimethylbutyraldehyde were prepared by refluxing a mixture of the aldehyde and one equivalent of 1,1-dimethylhydrazine in benzene under a Dean-Stark trap until the theoretical quantity of water was obtained. The hydrazones were not isolated but were alkylated directly.

Since pure glutaraldehyde is not commercially available, glutaraldehyde-bisdimethylhydrazone was prepared by refluxing a suspension of 0.1 mole of the dibisulfite addition compound of glutaraldehyde with 0.4 mole of 1,1-dimethylhydrazine for 16 hours. Excess hydrazine was removed in vacuo, and 125 ml. of benzene was added. The mixture was then refluxed under a Dean-Stark trap with vigorous stirring until no more water was obtained. The solution was filtered, the filtrate reduced in volume in vacuo, and the residue distilled in vacuo (b.p. 116°C./3 mm., γ = 94%). It was identified by comparison of its infrared spectrum with published data (9).

Iodide and Tosylate Salts. The benzene solution of the hydrazone was treated with one equivalent of either methyl iodide or methyl tosylate, and the solution was heated to reflux for 3 hours (the 4'-nitrobenzaldehyde dimethylhydrazone required 16 hours at reflux before alkylation was complete), then allowed to cool, and stirred overnight. The precipitated salt was removed by filtration and recrystallized from the appropriate solvent.

Chloride Salts. The chloride salts, with the exception of Ic and Id, were prepared by placing a benzene solution of the hydrazone in a pressure bottle and bubbling in methyl chloride until one equivalent had been absorbed. The bottle was then sealed, and the solution was stirred at room temperature for 2 days. The precipitated solid was then removed by filtration and recrystallized.

The chloride salts of Ic and Id did not readily form under the above conditions, either at room temperature or at 60°C. This is presumably due to the low nucleophilicity of the methylated nitrogen atom of the hydrazone, caused by the electron-withdrawing effect of the 4'-nitro

and 2',4'-dichloro substituents. These salts were therefore prepared by slowly passing a methanol solution of the corresponding iodide salt through a chromatographic column containing a large excess of Amberlite IRA-400 (chloride) ion exchange resin. The column effluent was evaporated to dryness in vacuo and the residue was recrystallized.

Bromide Salt of II was prepared in the same manner as the chloride salts, but utilizing methyl bromide.

Hexachlorostannate Salts were prepared by a modification of the method of Goyal *et al.* (3). One equivalent of the corresponding chloride salt was dissolved in a small amount of acetyl chloride, and one equivalent of stannic chloride (anhydrous-fuming) was added. The hexachlorostannate precipitated immediately and was removed by filtration and recrystallized. In some cases, the hexachlorostannate did not precipitate, and crystallization was induced by diluting the solution with a large volume of ether.

Fluoborate Salts. Attempts at preparing Ib fluoborate from Ib iodide by the aqueous sodium fluoborate method of Fishel and Newkome (2) were unsuccessful and the boron trifluoride etherate method of Wheeler and Sandstedt (8) was found to be less convenient than the method described below.

Fluoborate, Perchlorate, Hexafluorophosphate, Hexafluoroarsenate, and Nitrate Salts. The most general method for the preparation of hydrazone salts is treatment of the iodide salt with the silver salt of the desired anion. This method is limited only by the availability of the silver salt, the finding of a suitable solvent (one in which the iodide and the silver salt are soluble but which does not dissolve silver iodide), and the stability of the product. The following procedure was used.

A concentrated solution of the iodide salt in methanol was treated with a solution of the desired silver salt in a minimum amount of methanol. The resulting suspension was stirred for 2 hours and the precipitated silver iodide removed by filtration. The filtrate was then diluted with a large volume of ether, and the precipitated salt was filtered and recrystallized.

Attempted Preparation of Glutaraldehyde-bis(trimethylhydrazone) Acetate and Phenoxide. An attempt at preparing the acetate salt by treating the iodide salt with silver acetate failed. The odor of trimethylamine could be detected over the reaction mixture, and glutaronitrile was isolated. Likewise, treatment of the iodide salt with phenol and freshly prepared silver oxide according to the method of Lepley and Brodof (4) resulted in immediate amine evolution. Again, glutaronitrile was isolated. It appears that both acetate ion and silver oxide and/or phenoxide ion are sufficiently basic to cause decomposition of the hydrazone salt. This is not surprising, since Smith and Walker (7) have reported the preparation of nitriles by treating hydrazone salts with sodium methoxide.

ACKNOWLEDGMENT

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α -Aminophosphinic Acids and α -Aminophosphine Oxides

Carbamyl(methyl)phosphinic Acid, Carbamyl(phenyl)phosphinic Acid, and Carbamyl(diphenyl)phosphine Oxide

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Carbamyl(diphenyl)phosphine oxide, carbamyl(phenyl)phosphinic acid, and carbamyl(methyl)phosphinic acid were prepared in good yields by ammonolysis of carbethoxy(diphenyl)phosphine oxide, ethyl and methyl carbethoxy(phenyl)phosphinates, and ethyl carbethoxy(methyl)phosphinate, respectively.

OUR study of α -aminoalkylphosphinic acids and α -aminoalkylphosphine oxides (6) was extended to carbamylphosphinic acids and carbamylphosphine oxides. Arbuzov and Rizpolozhensky (2) described some dialkyl *N,N*-diethylcarbamyl phosphonates. *N*-Monosubstituted carbamylphosphines were obtained by the reaction of iso-

cyanates with phosphines (3). Recently Papp and Buckler (5) used cyanic acid instead of isocyanates with phosphines to synthesize carbamylphosphines which are unsubstituted in the carbamyl group and upon oxidation resulted in carbamylphosphine oxides; they prepared carbamyl(diphenyl)phosphinic oxide (II) in 15% yield. Nylen (4) used