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 hydrazonium 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-bistrimethylhydrazonium 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 hydrazonium salt. This is not surprising, since Smith and Walker (*7*) have reported the preparation of nitriles by treating hydrazonium salts with sodium methoxide.

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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 isocyanates 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

Table I. Detailed Results

Product	M.P., °C., Dec.[a] (B.P., °C./Mm.)	Recryst. Solvent	Yield	Analyses				
$Ph_2P(O)CONH_2$, II	186–87[b]	EtOH-$(Me)_2CO$	71[c]	c.	63.66	4.94	5.72	16.62
				f.	63.48	4.84	5.61	12.26
$Ph(MeO)P(O)CO_2Et$, III	(121–23/0.3)	...	80	c.	52.70	5.70	...	13.60
				f.	52.51	5.67	...	13.32
$Ph(EtO)P(O)CO_2Et$, IV	(116–18/0.1)	...	84	c.	54.54	6.24	...	12.79
				f.	54.60	6.39	...	12.34
$Ph(NH_4O)P(O)CONH_2$ V	232–35	50% EtOH	66[c]	c.	41.58	5.52	13.86	15.31
				f.	41.60	5.54	14.20	15.20
$Ph(HO)P(O)CONH_2$, VI	187–89	EtOH	70	c.	45.41	4.35	7.56	16.74
				f.	45.41	3.88	7.87	16.37
$Me(EtO)P(O)CO_2Et$, VII	(72–74/0.6)	...	86	c.	40.00	7.27	...	17.20
				f.	40.40	7.33	...	16.83
$Me(NH_4O)P(O)CONH_2$, VIII	210	10% EtOH	70[c]	c.	17.16	6.47	20.00	21.12
				f.	17.01	6.24	19.70	21.50
$Me(HO)P(O)CONH_2$, IX	161–62	EtOH	60	c.	18.52	4.91	11.38	25.17
				f.	18.18	4.74	11.53	25.22

[a] All m.p.'s with decomposition. [b] Lit. m.p. 190–91 (from C_6H_{14}-PhH). [c] Crude.

anhydrous ammonia to obtain $H_2NC(O)P(O)(OEt)_2$ from $EtOC(O)P(O)(OEt)_2$. We modified Nylen's method for the preparation of carbamyl(phenyl)phosphinic acid (VI), carbamyl(methyl)phosphinic acid (IX), their ammonium salts (V and VIII, respectively), and carbamyl(diphenyl)phosphine oxide (II). The ammonolysis was carried out in aqueous-alcoholic ammonia instead of in anhydrous ammonia.

The known carbethoxy(diphenyl)phosphine oxide (I) was prepared as described in the literature (*1*). The other three intermediates—i.e., the phosphinates (III, IV, and VII)—were obtained in very good yields by the reaction of freshly distilled ethyl chloroformate with pure dimethyl phenylphosphonite, diethyl phenylphosphonite, and diethyl methylphosphonite, respectively, following Arbuzov and Nikinorov's procedure (*1*). They are colorless liquids distilling without any significant decomposition in vacuo, soluble in acetone, benzene, ethanol, and ether, and slightly soluble in *n*-hexane. As expected, the ammonolysis of III, IV, and VII caused not only amidation of the carbethoxy group, but also hydrolysis of RO-P. The intermediate ammonium salts (V and VIII) were isolated without difficulty, since they are soluble in water and insoluble in ethanol. Their 0.01*N* aqueous solutions had a pH of 5.2. The carbamylphosphinic acids (VI and IX) are also soluble in water, slightly soluble in ethanol, and insoluble in benzene and *n*-hexane. The 0.01*N* aqueous solutions of VI and IX had pH's of 2.1 and 2.0, respectively.

EXPERIMENTAL

Ethanol solutions of the carbethoxy compounds were stirred for 5 to 6 hours at 35–40° with an excess of concentrated NH_4OH and then evaporated to dryness in vacuo. The distillation residues were stirred in ethanol and filtered to obtain the crude ammonium salts, which were recrystallized. Phosphinates III and IV gave equal yields of V. The phosphine oxide (II) precipitated out of the ammonolysis reaction mixture and was recovered by filtration, rather than evaporation.

The aqueous solutions of the ammonium salts (V and VIII) were converted to the free phosphinic acids (VI and IX), respectively, by ion exchange on IR-120 Amberlite. The acidic aqueous eluents were evaporated to dryness and the combined residues were recrystallized.

Detailed results are listed in Table I.

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