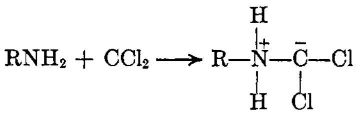
(formed in reaction 2 below) with the amine salt (formed in reaction 4 below) to produce chloroform and the free amine (reaction 5 below).[11] In one run utilizing approximately a 2:1 molar ratio of sodium trichloroacetate to *p*-chloroaniline, a 60% yield of chloroform (based on acetate) was obtained. In all runs black, tarlike material remained after distillation.

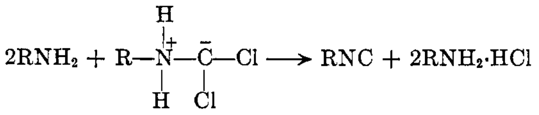
These observations are consistent with the mechanistic sequence of reactions depicted in the following steps:

$$\mathrm{CCl_3CO_2^- \longrightarrow CCl_3^- + CO_2} \qquad (1)$$

$$\mathrm{CCl_3^- \longrightarrow CCl_2 + Cl^-} \qquad (2)$$



$$\mathrm{RNH_2 + CCl_2 \longrightarrow R{-}\underset{H}{\overset{H}{\overset{+}{N}}}{-}\underset{Cl}{\overset{-}{C}}{-}Cl} \qquad (3)$$



$$\mathrm{2RNH_2 + R{-}\underset{H}{\overset{H}{\overset{+}{N}}}{-}\underset{Cl}{\overset{-}{C}}{-}Cl \longrightarrow RNC + 2RNH_2{\cdot}HCl} \qquad (4)$$

$$\mathrm{RNH_2{\cdot}HCl + CCl_3^- \longrightarrow CHCl_3 + RNH_2 + Cl^-} \qquad (5)$$

The over-all stoichiometry can be represented by the following equation:

$$\mathrm{RNH_2 + 3CCl_3CO_2Na \longrightarrow RNC + 2CHCl_3 + 3CO_2 + 3NaCl}$$

Further extensions of this reaction with other amines are currently under investigation and will be reported shortly.

EXPERIMENTAL

Preparation of isocyanides. (a) *p-Tolyl isocyanide.* To a solution of 5.4 g. (0.05 mole) of *p*-toluidine in 100 ml. of 1,2-dimethoxyethane (distilled from lithium aluminum hydride) was added 28 g. (0.15 mole) of sodium trichloroacetate. A slight exothermic reaction occurred and a fine pasty-white solid separated. On gentle warming, a clear solution resulted which was refluxed for 30 min. During this time a copious evolution of carbon dioxide occurred, and after refluxing for 15 min. a yellow solid separated. After 30 min. the solid settled to the bottom and the mixture was colored brown. The mixture was cooled, filtered, and the solid (weight 10 g.) washed with ether. The reddish-black filtrate was concentrated on a Rinco rotary evaporator. Near the end of the evaporation a solid separated. Ether was added to the pasty mass; the ethereal layer was washed twice with water and dried over sodium sulfate. The ether was removed by distillation and the residual red-black oil distilled under reduced pressure to yield 2.5 g. (43% based on amine) of a pale yellow liquid boiling at 38°/1 mm.; m.p. 19–20°. Reported:[12] b.p. 94°/25 mm.; m.p. 20°. The product exhibited a strong isocyanide infrared absorption band at 4.69 μ and contained no unchanged amine.

(b) *p-Methoxyphenyl isocyanide.* As in procedure (a) above using 6.2 g. (0.05 mole) of *p*-anisidine, 100 ml. of dry 1,2-dimethoxyethane and 29 g. (0.16 mole) of sodium trichloroacetate. The mixture was refluxed for 30 min. On work-up and distillation under reduced pressure there was obtained 2.5 g. (38% based on amine) of material boiling at 45°/1 mm. which solidified in the receiver. This material was crystallized from ether at low temperature; m.p. 28–30°. Reported:[12] m.p. 30°. The infrared absorption spectrum (20% solution in carbon tetrachloride) exhibited strong isocyanide absorption at 4.70 μ and the product contained no unreacted amine.

(c) *Phenyl isocyanide.* As in (a) above using 5.0 g. (0.05 mole) of aniline, 50 ml. of dry 1,2-dimethoxyethane, and 10.0 g. (0.05 mole) of sodium trichloroacetate. The mixture was refluxed for 15 hr. On work-up and distillation under reduced pressure there was obtained 2.8 g. of a pale yellow liquid boiling at 43–44°/1.5 mm. The product on examination in the infrared was contaminated with unchanged amine. From the intensity of the isocyanide band at 4.69 μ the product contained about 40% phenyl isocyanide. This constitutes a 20% yield of phenyl isocyanide based on amine.

(d) *p-Chlorophenyl isocyanide.* As in (a) above using 6.4 g. (0.05 mole) of *p*-chloroaniline, 50 ml. of dry 1,2-dimethoxyethane and 17 g. (0.09 mole) of sodium trichloroacetate. The mixture was refluxed for 45 min., cooled, and poured into ice water. The dark bottom layer was separated and dried over sodium sulfate (weight 11 g.). On distillation there was obtained 7 g. (64% yield based on acetate) of chloroform and 4 g. of a dark black pot residue. The infrared spectrum of this undistilled material (in KBr window) showed the presence of an isocyanide band at 4.70 μ and also unreacted amine. No further work-up was effected.

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[11] F. H. Verhoek, *J. Am. Chem. Soc.*, **56**, 571 (1934) reports that the decomposition of anilinium trichloroacetate yields chloroform.

[12] D. Ll. Hammick, R. C. A. New, N. V. Sidgwick, and L. E. Sutton, *J. Chem. Soc.*, 1876 (1930).

Preparation of Heterocyclic Dihydroxyphosphonium Salts

Sheldon A. Buckler and Martin Epstein

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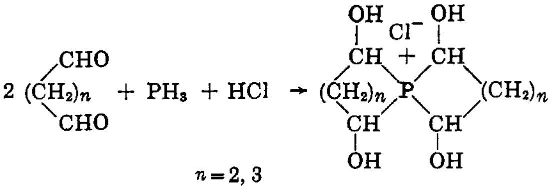
Previous reports from this laboratory described the preparation of *spiro*-tetrahydroxyphosphonium salts.[1]



We now report the preparation of a number of monocyclic dihydroxyphosphonium salts (I and II) by the reaction of secondary phosphines with succinaldehyde or glutaraldehyde in the presence of hydrochloric acid. The heterocycles III and IV,

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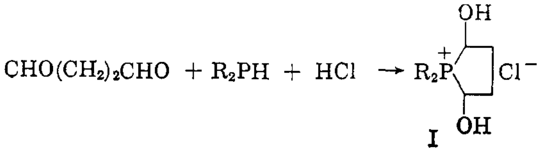
[1] S. A. Buckler and V. P. Wystrach, *J. Am. Chem. Soc.* **80**, 6454 (1958). *J. Am. Chem. Soc.*, **83**, 168 (1961).

TABLE I

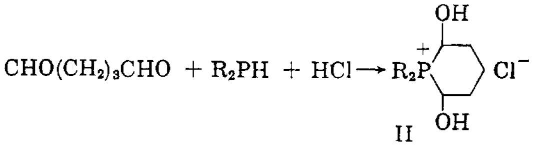
Heterocyclic Dihydroxyphosphonium Salts

Compound	M.P.	Yield, %	Recrystallization Solvent	NMR[a] Shift	Calcd.				Found				Molecular Weight			
					C	H	Cl	P	C	H	Cl	P	Calculated	Found[b]		
														H_2O	C_2H_5OH	$CHCl_3$
1,1-Diisobutyl-2,6-dihydroxyphosphoniacyclohexane chloride	150–152	34	Acetone	−23	55.21	9.98	12.54	10.95	54.85	9.91	12.39	10.99	282.8	163	231	293
1,1-Di-*n*-butyl-2,6-dihydroxyphosphoniacyclohexane chloride	115–117	42	Acetone	−20	55.21	9.98	12.54	10.95	55.23	10.12	12.03	11.01	282.8	164	232	257
1,1-Di-*n*-octyl-2,6-dihydroxyphosphoniacyclohexane chloride	100–105	36	Acetonitrile	−25	63.85	11.23	8.98	7.84	63.50	11.03	9.02	7.66	394.9	—	392	—
1,1-Dicyclohexyl-2,6-dihydroxyphosphoniacyclohexane chloride	160–164	32	Acetonitrile	−20	60.97	9.63	10.69	9.25	61.15	9.83	10.72	8.96	334.9	—	—	354
1,1,Diisobutyl-2,5-dihydroxyphosphoniacyclopentane chloride	149–150	32	Acetonitrile	−39	53.62	9.75	13.19	11.53	53.33	9.81	—	11.34	268.8	156	270	—
1,1-Di-*n*-butyl-2,5-dihydroxyphosphoniacyclopentane chloride	107–108	52	Acetone	−46	53.62	9.75	13.19	11.53	53.60	9.85	13.36	11.49	268.8	—	278	—
2,6-Dihydroxy-1′,3′,5′,7′-tetramethylspiro(phosphoniacyclohexane-1,6′-[2.4.8]trioxa[6]phosphaadamantane) chloride (IV)	168–170	51	Acetonitrile	—	51.06	7.43	10.05	8.78	51.14	7.60	9.89	8.70	352.8	173	368	—
2,5-Dihydroxy-1′,3′,5′,7′-tetramethylspiro(phosphoniacyclopentane-1,6′-[2.4.8]trioxa[6]phosphaadamantane) chloride (III)	170–171	30	Methanol-ether[c]	—	49.63	7.14	10.47	9.14	50.03	7.43	10.53	8.96	338.8	188	345	—

[a] NMR spectroscopy in the phosphorus region. The values are in p.p.m. relative to 85% H_3PO_4. [b] Ebullioscopic measurements. [c] Precipitated from methanol solution with ether.

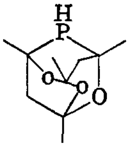


R = n-C_4H_9, i-C_4H_9

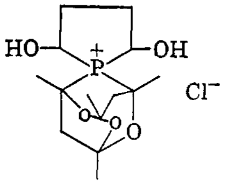


R = n-C_4H_9, i-C_4H_9, $cyclo$-C_6H_{11}, n-C_8H_{17}

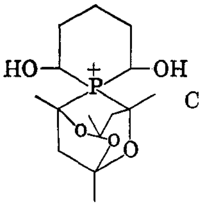
in which the phosphorus atoms are parts of spiran as well as adamantane ring systems were also obtained readily by this method. The secondary phosphine (V) used in these cases is produced by the reaction of phosphine with 2,4-pentanedione.[2]



V



III



IV

In carrying out this heterocycle synthesis, the order of addition of reagents proved to be critical. The general method adopted after detailed study of the reactions of di-n-butylphosphine and di-i-butylphosphine with glutaraldehyde, was to add concentrated hydrochloric acid to an alcoholic solution of the phosphine and aldehyde reactants. This technique produced 30–50% yields of the crystalline heterocyclic phosphonium salts. Other modes of addition resulted in lower yields or complex mixtures of products.

Aside from correct analyses and reasonable infrared data, support for the proposed cyclic structures was obtained from molecular weight measurements (Table I). The results show that the salts are dissociated in aqueous solution. On the other hand, values obtained in the less polar solvents ethanol and chloroform are generally in good agreement with those calculated for the formula weight.

EXPERIMENTAL[3]

Materials. Di-n-octylphosphine, diisobutylphosphine and dicyclohexylphosphine were prepared by the method of Stiles, Rust and Vaughan.[4] Di-n-butylphosphine was obtained from Food Machinery and Chemical Corp. Glutaraldehyde and succinaldehyde (2,5-diethoxytetrahydrofuran) were Carbide and Carbon Chemicals Co. materials.

1,1-Diisobutyl-2,6-dihydroxyphosphoniacylcyclohexane chloride. To a solution of 9.0 g. (0.062 mole) of diisobutylphosphine, 24.7 g. (0.062 mole) of 25% aqueous glutaraldehyde, 50 ml. of methanol and 25 ml. of tetrahydrofuran under a nitrogen atmosphere was added dropwise 7 ml. of concentrated hydrochloric acid. The solution was heated under reflux for 2 hr. and then evaporated under reduced pressure. The residue was recrystallized from acetone to give 6.0 g. (34%) of product, m.p. 150–152°.

Other Heterocyclic Dihydroxy Phosphonium Salts. These were prepared using minor variations of the above procedure. The pertinent information is given in Table I.

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[2] M. Epstein and S. A. Buckler, *J. Am. Chem. Soc.*, **83**, 3279 (1961).

[3] Melting points are uncorrected. Analyses and molecular weight measurements were carried out under the supervision of Dr. J. A. Kuck.

[4] A. R. Stiles, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **74**, 3282 (1952).

Isomeric Hydroxyacetanilides by Reductive Acylation of Nitrophenols

MORRIS FREIFELDER

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The need for some pure hydroxyacetanilides in this laboratory prompted an investigation into reductive acetylation of the isomeric nitrophenols. While aminophenols are readily acylated their well known propensity for darkening on storage leads to colored reaction products unless the starting materials are freshly prepared. It was thought therefore that reduction of the nitrophenols in the presence of acetic anhydride might lead to better products.

This procedure has been used for the *para* derivative employing platinum oxide catalyst.[1] In our hands the same reduction with this catalyst led to a colored product. The use of palladium-on-carbon, on the other hand, gave not only good yield, but also a product that required little purification. Similarly, excellent quality o- and m-hydroxyacetanilides were prepared from the corresponding nitrophenols.

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[1] J. H. Burckhalter *et al.*, *J. Am. Chem. Soc.*, **70**, 1363 (1948) obtained a 58% yield. Obviously since it was an intermediate in synthesis the authors reported no attempt to increase yield.