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Further Studies in the Synthesis of Quaternary Hydrazinium and Aminophosphonium Salts

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The chloramination reaction has been extended to three additional tertiary phosphines, namely tribenzylphosphine, tris-(2-cyanoethyl)phosphine, and diallylphenylphosphine. The corresponding aminophosphonium chlorides were converted in each case to other aminophosphonium salts which were analyzed and found to correspond with the expected compositions. Triethylenediamine was chloraminated to give the monohydrazinium salt; and aniline was chloraminated to give phenylhydrazine in good yields. Triphenylaminophosphonium chloride was dehydrochlorinated by magnesium hydride in the absence of solvent, and the corresponding triphenylphosphineimine was isolated.

During recent years several communications concerning the chloramination of nitrogen-containing or phosphorus-containing Lewis bases have emanated from our laboratory formerly at the Ohio State University and more recently at the University of Florida. Among the more interesting results of these studies is the finding that chloramine combines smoothly with many tertiary amines to form 1,1,1-trisubstituted hydrazinium chlorides,[1] and with tertiary phosphines to form

$$R_3N: + NH_2Cl \longrightarrow [R_3N:NH_2]^+Cl^-$$

P-trisubstituted aminophosphonium chlorides.[2]

$$R_3P: + NH_2Cl \longrightarrow [R_3P:NH_2]^+Cl^-$$

Recent work in our laboratory has resulted in the synthesis of several new compounds which broaden significantly the range of these chloramination reactions. Furthermore, we have recently discovered a method for dehydrochlorinating triphenylaminophosphonium chloride to yield triphenylphosphine imine, which does not require the

$$[(C_6H_5)_3PNH_2]^+Cl^- \xrightarrow{-HCl} (C_6H_5)_3P{=}NH$$

use of liquid ammonia as does the recently published procedure of Appel.[3] Finally, as a corollary to these studies it was found that, contrary to prior experience in this laboratory, aniline may be directly chloraminated under anhydrous conditions to give phenylhydrazine in appreciable yields.

EXPERIMENTAL

Materials. Chloramine was produced as a gaseous mixture with excess ammonia in a reactor based upon the previously published design.[4] Triethylenediamine obtained from the Houdry Process Corporation was >99% pure and contained <1% water. Tris(2-cyanoethyl)phosphine was furnished by M. E. Castellion of the American Cyanamid Company. Tribenzylphosphine was prepared by the procedure of Hinton and Mann,[5] and melted at 92–95°, (lit., m.p. 92–95°). Diallylphenylphosphine, synthesized by the method of Jones, *et al.*,[6] boiled at 118° at 7–8 mm. (lit., b.p. 127° at 14 mm.) C.P. grade aniline was carefully fractionated to yield a product which boiled at 65–66° at 6.0 mm. and which had a refractive index of $1.5859^{20°}$ (lit. $1.5863^{20°}$). Melting points and boiling points are uncorrected. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn.

Chloramination of tribenzylphosphine. To a solution of 0.955 g. (3.14 mmoles) of tribenzylphosphine in 80 ml. of dry benzene at 25° was passed approximately 8.3 mmoles of chloramine in the form of the ammonia-chloramine gas mixture from the chloramine generator (rate of chloramine generation about 0.1 mole per hr.). The resultant crystalline product was filtered, washed with dry benzene, and dried under vacuum (weight, 0.745 g., 2.09 mmoles calcd. as $[(C_6H_5CH_2)_3PNH_2]Cl$). This, when recrystallized from hot chloroform, melted at 220–221° and gave analytical results in agreement with the formula $[(C_6H_5CH_2)_3PNH_2]Cl$. These results are presented in Table I. Evaporation of the liquid phase yielded 0.325 g. (1.06 mmoles) of unchanged tribenzylphosphine contaminated with the corresponding phosphine oxide. Thus it is apparent that the reaction is virtually quantitative in terms of the phosphine reacted. The tribenzylaminophosphonium ion was further confirmed by the preparation and analysis of the corresponding picrate and chloroplatinate salts. These salts were prepared by metathesis with alkali metal picrates or chloroplatinates in aqueous or ethanolic solutions. The physical and analytical data are summarized in Table I.

Chloramination of tris(2-cyanoethyl)phosphine. The gaseous effluent of the chloramine generator (approx. 5 mmoles chloramine) was passed into a solution of 0.533 g. (2.76 mmoles) of tris(2-cyanoethyl)phosphine in 80 ml. of dry methylene chloride at room temperature. The resultant crystalline solid was washed with dry methylene chloride and vacuum dried at room temperature (weight 0.581 g.) Volhard chloride analysis gave 16.21 Cl (Calcd. for $[(NCCH_2CH_2)_3PNH_2]Cl$, 14.49 Cl). These analytical data would indicate about 3.3% ammonium chloride contamination of the aminophosphonium salt. The yield of crude product was approximately 85% based on the phosphine reacted. A convenient method for removing this contamination was not found but the identity of the principal constituent of the product was established by conversion, through metathesis, to the tris(2-cyanoethyl)aminophosphonium picrate and the hexachloroplatinate, both of which were purified and analysed. These data are presented in Table II.

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[1] G. Omietanski and H. Sisler, *J. Am. Chem. Soc.*, **78**, 1211 (1956).

[2] H. Sisler, A. Sarkis, H. S. Ahuja, R. S. Drago, and N. L. Smith, *J. Am. Chem. Soc.*, **81**, 2982 (1959).

[3] R. Appel and E. Guth, *Z. Naturforsch.*, **15b**, 57 (1960); R. Appel and A. Hauss, *Angew. Chem.*, **71**, 626 (1959).

[4] H. Sisler, F. Neth, R. Drago, and D. Yaney, *J. Am. Chem. Soc.*, 76, 3906 (1954).

[5] R. Hinton and F. Mann, *J. Chem. Soc.*, 2835 (1959).

[6] W. Jones, W. Davis, S. Bowden, C. Edwards, V. Davis, and L. Thomas, *J. Chem. Soc.*, 1448 (1947).

TABLE I

TRIBENZYLAMINOPHOSPHONIUM SALTS $[(C_6H_5CH_2)_3PNH_2]^+X^-$

Salt	M.P.	Empirical Formula	C Calcd. Found	H Calcd. Found	N Calcd. Found	P Calcd. Found	Cl Calcd. Found
Chloride	220–221	$C_{21}H_{23}ClNP$	70.88	6.51	3.94	8.71	9.97
			70.76	7.01	3.82	8.90	10.10
Picrate	179.5–180.5	$C_{27}H_{25}N_4O_7P$	59.12	4.59	10.22	5.65	—
			58.74	4.91	10.54	5.97	—
Hexachloroplatinate	190–191	$C_{42}H_{46}Cl_6N_2P_2Pt$	48.10	4.42	2.67	5.91	20.29
			45.64	4.43	2.49	5.71	22.96

TABLE II

TRIS(2-CYANOETHYL)AMINOPHOSPHONIUM SALTS $[(NCCH_2CH_2)_3PNH_2]^+X^-$

Salt	M.P.	Empirical Formula	C Calcd. Found	H Calcd. Found	N Calcd. Found	P Calcd. Found	Cl Calcd. Found
Picrate	154	$C_{15}H_{16}N_7O_7P$	41.19	3.68	22.42	7.08	—
			40.03	3.75	22.35	6.85	—
Hexachloroplatinate	210 dec.	$C_{18}H_{28}Cl_6N_8P_2Pt$	26.16	3.41	13.56	7.50	25.75
			26.55	3.88	12.98	7.71	25.33

TABLE III

DIALLYLPHENYLPHOSPHINIUM SALTS $[(CH_2{=}CHCH_2)_2(C_6H_5)PNH_2]^+X^-$

Salt	M.P.	Empirical Formula	C Calcd. Found	H Calcd. Found	N Calcd. Found	P Calcd. Found	Cl Calcd. Found	S Calcd. Found
Anthraquinone β-sulfonate	181–183	$C_{26}H_{24}NO_5PS$	63.27	4.90	2.84	6.28		6.50
			63.68	5.02	2.91	6.41		6.85
Hexachloroplatinate	192–193	$C_{24}H_{34}Cl_6N_2P_2Pt$	35.14	4.18	3.42	7.55	25.94	
			36.73	4.54	3.36	7.57	24.86	

It is interesting to note that when an attempt was made to chloraminate tris(2-cyanoethyl)phosphine in solution in c.p. methanol the white, crystalline solid obtained proved to be the corresponding phosphine oxide.

Chloramination of diallylphenylphosphine. To a solution of 2.91 g. (15.1 mmoles) diallylphenylphosphine dissolved in 80 ml. of dry ethyl ether, 25 mmoles of chloramine in the form of the gaseous ammonia-chloramine mixture from the chloramine generator was added at 25°. A light yellow, sticky solid formed on the sides of the tube. The reaction mixture was chilled to about −65° and the mother liquor decanted. The solid residue was washed with two 30-ml. portions of ethyl ether by decantation. The reaction tube and solid was kept cold and the solid scraped from the sides of the container (weight, 2.94 g. or 12.16 mmoles calcd. as $[(CH_2{=}CHCH_2)_2(C_6H_5)PNH_2]Cl$.) About 3.0 g. (1.56 mmoles) of unchanged phosphine was recovered from the ether filtrate and washings. The solid product contained 15.72 % Cl as determined by the Volhard method (calcd. for $[(CH_2{=}CHCH_2)_2(C_6H_5)PNH_2]Cl$: 14.67 Cl). The product is, therefore, slightly contaminated with traces of ammonium chloride. The yield of this product is about 90% based upon phosphine reacted. To confirm the presence of the diallylphenylaminophosphonium ion the chloride product was converted by metathesis to the anthraquinone-β-sulfonate and the hexachloroplatinate. The physical and analytical data are summarized in Table III.

Dehydrochlorination of triphenylaminophosphonium chloride to triphenylphosphine Imine. Appel and Hauss[3] have recently reported the dehydrochlorination of triphenylaminophosphonium chloride by reaction with sodium amide suspended in liquid ammonia. In order to avoid the inconvenience of the utilization of liquid ammonia as a solvent we have carried out this dehydrochlorination with magnesium hydride. A mixture of 0.30 g. (11.4 mmoles) of magnesium hydride (Dow Chemical Co., 95.2% magnesium hydride) and 0.50 g. (1.6 mmoles) of triphenylaminophosphonium chloride was heated for 0.5 hr. at 250° and the system allowed to cool. The pressure in the system was then reduced to 0.5 mm. and the temperature raised to 285° and maintained at these values for 1 hr. During this period about 0.15 g. of product condensed on the surface of a cold finger suspended in the reaction chamber. The product, a white, crystalline solid, was removed in an inert atmosphere in a dry box. The yield was 30% based on the aminophsphonium chloride originally placed in the mixture. It is probable that reaction is not complete.

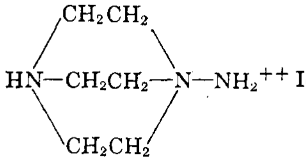
Anal. Calcd. for $(C_6H_5)_3P{=}NH$: N, 5.05 P, 11.17. Found N, 4.86 P, 11.04.

The product melted at 122.5–123.5° (sealed tube). This substance changes rapidly in air to the phosphine oxide but may be stored under nitrogen. Triphenylphosphine imine has also been prepared in our laboratory by the dehydrochlorination of triphenylaminophosphonium chloride with cyclohexylamine but the difficulty in separating the triphenylphosphineimine from the excess cyclohexylamine almost invariably results in the partial conversion of the product to triphenylphosphine oxide. Our experience leads us to the conclusion that the presence of appreciable triphenylphosphine oxide impurity in the triphenylphosphine imine results in the considerable elevation of the melting point of the product. Therefore, as the product become contaminated by conversion to the oxide, its melting point rises.

Chloramination of Triethylenediamine. The gaseous chloramine-ammonia effluent of the chloramine generator was passed into a solution of 7.0 g. (62.4 mmoles) of triethylene-

TABLE IV

Salts Containing the



Ion

Salt	M.P.	C Calcd. Found	H Calcd. Found	N Calcd. Found
$[HN(CH_2CH_2)_3NNH_2]^{++}$	247–248	36.93	3.27	21.53
$[OC_6H_2(NO_2)_3]^{-}{}_2$		36.16	3.09	21.10
$[HN(CH_2CH_2)_3NNH_2]^{++}$	—	13.41	2.82	7.82
$[PtCl_6]^{=}$		13.62	3.11	7.55

diamine in 100 ml. of benzene at room temperature until an estimated 20 mmoles of chloramine had been introduced. The resulting white, crystalline, highly hydroscopic precipitate was rapidly filtered, washed with benzene and dried under vacuum (weight 3.4 g.)

Anal. Calcd. for $[N(CH_2CH_2)_3NNH_2]^+Cl^-$: Cl, 21.67. Found: Cl, 20.84. (Volhard method).

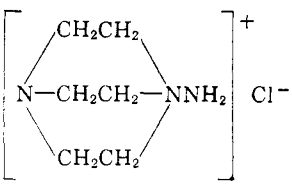
In order to establish the hydrazinium ion, portions of the product were converted to the corresponding picrate and hexachloroplatinate by aqueous metathetical reactions. The data on these products are summarized in Table IV.

Chloramination of aniline. Approximately 50 mmoles of chloramine in the form the ammonia-chloramine effluent of the chloramine generator was passed, over a period of 75 min., into 43.0 g. (0.46 mole) of freshly purified and distilled aniline at a temperature of 15 to 20°. The solid precipitate (1.4 g. identified as ammonium chloride) was removed by filtration and the filtrate distilled into two fractions: (a) b.p. 71° at 9 mm. (39.9 g.), unchanged aniline, and (b) b.p. 108° at 9 mm. (1.1 g.), crude phenylhydrazine (yield 46% based on aniline reacted). The phenylhydrazine fraction was redistilled yielding a yellow oil, b.p. 88° at 1.7 mm. n^{25}_D 1.6080 (literature values for phenylhydrazine, b.p. 137–138 at 18 mm., n^{18}_D 1.6030). The identity of the phenylhydrazine was further confirmed by its infrared spectrum and by forming the phenylhydrazone of benzaldehyde (m.p. 153.5–155°; lit., m.p. 154–155°). A mixed melting point with a known sample of benzaldehyde phenylhydrazone showed no melting point depression.

DISCUSSION

The chloramination of three new phosphines, two of which include functional groups in the side chains of the hydrocarbon radicals, indicates that the chloramination reaction can be used even more broadly in the synthesis of organic phosphorus and nitrogen compounds than had previously been demonstrated. The incorporation of nitrile and olefinic double bonds into aminophosphonium salts offers some particularly interesting synthetic possibilities.

The formation of the monochloramination product of triethylenediamine, is interesting and probably results from the low solubility of this salt in the reaction medium which removes it from the reaction zone and prevents dichloramination. However, this situation needs to be studied under conditions where an excess of chloramine is present. The chloramination of this and other diacid phosphorus and nitrogen bases is presently undergoing further examination in this laboratory.



The synthesis in approximately 50% yield of phenylhydrazine by the direct introduction of the gaseous ammonia-chloramine mixture into pure, anhydrous aniline represents the basis for a possible new path to the production of phenylhydrazine. There is little doubt that intensive study of this reaction would considerably increase the yield.

It should be noted that in two or three instances the carbon analyses for a derivative do not agree with the calculated values as closely as might normally be desired. However, experience, not only in our laboratory but in others also, has demonstrated that carbon analyses on organo-phosphorus-nitrogen salts tend to be erratic.

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