[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORIES, THE OHIO STATE UNIVERSITY]

The Reaction of Chloramine with Tertiary Amines.[1] 1,1,1-Trisubstituted Hydrazinium Salts[2]

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It has been shown that chloramine reacts with a variety of tertiary amines to form the corresponding 1,1,1-trisubstituted hydrazinium chlorides in good yield. However, when the tertiary nitrogen is part of an aromatic ring as in pyridine, the corresponding N-amino compounds are not obtained. A series of 1,1,1-trisubstituted hydrazinium hexafluorophosphates has been prepared. The results have been discussed in terms of reaction mechanism, and their implications with respect to the chloramine–ammonia reaction.

1,1,1-Trisubstituted hydrazinium chlorides have been prepared by alkylating 1,1-disubstituted hydrazines with alkyl chlorides,[3] by alkylating hydrazine with alkyl chlorides,[4] by metathesis of the corresponding hydrazinium bromide[5] or iodide[6] with silver chloride, and by neutralizing the corresponding hydrazinium hydroxide with hydrochloric acid.[7] This study of the formation of 1,1,1-trisubstituted hydrazinium chlorides by the reaction of chloramine with tertiary amines is a continuation of the studies previously reported by this Laboratory on the reaction of chloramine with ammonia,[8] and unpublished data on the reaction of chloramine with primary and secondary amines.[9] The synthesis of trisubstituted hydrazinium chlorides by the reaction of chloramine with tertiary amines has not been reported previously.

TABLE I

1,1,1-TRISUBSTITUTED HYDRAZINIUM CHLORIDES

Hydrazinium chloride	Yield,[c] %	M.p., °C.	Empirical formula	Analyses, % Calcd. C	H	N	Cl⁻	Found C	H	N	Cl⁻	Recrystallized from[g]
1-Trimethyl-	95	(*ca.*) 245[a,b]	$C_3H_{11}ClN_2$	32.58	10.03	25.33	32.06	31.77	9.91	25.12	32.81	A-E
1-Triethyl-	99	177–178[b]	$C_6H_{17}ClN_2$	47.20	11.22	18.35	23.22	47.30	11.23	18.21	23.38	C-E
1-Tri-*n*-propyl-	85	154–155[d]	$C_9H_{23}ClN_2$	55.50	11.90	14.39	18.21	55.43	11.81	14.44	18.21	A-EA
1-Tri-*n*-heptyl-	..	65.5–66.5	$C_{21}H_{47}ClN_2$	69.47	13.05	7.71	9.76	69.56	13.11	7.71	9.68	PE-EA
1-Dimethyl-1-phenyl-	99	187–188[a,f]	$C_8H_{13}ClN_2$	55.65	7.59	16.23	20.54	55.78	7.69	16.08	20.60	A-E
1-Diethyl-1-phenyl-	65	197–198[a,e]	$C_{10}H_{17}ClN_2$	59.84	8.54	13.96	17.67	59.87	8.59	14.02	17.85	A-E
1-Dimethyl-1-(2-hydroxyethyl)-[h]	99	160–163[a]	$C_4H_{13}ClN_2O$	34.16	9.32	19.92	25.21	34.17	9.51	19.76	24.92	A-EA
1-Dimethyl-1-(*p*-tolyl)-	99	165–166[a]	$C_9H_{15}ClN_2$	57.90	8.10	15.01	18.99	57.76	8.33	14.96	19.15	A-E
1-Cyclohexyl-1-diethyl-	95	168–171[a,b]	$C_{10}H_{23}ClN_2$		11.21	13.55	17.15		11.42	13.40	17.41	A
1-Diethyl-1-(3-hydroxypropyl)-	99	115–116[b]	$C_7H_{19}ClN_2O$	46.02	10.48	15.33	19.41	46.02	10.71	15.21	19.24	A-E
4-Amino-4-methylmorpholinium chloride	80	235[a,b]	$C_5H_{13}ClN_2O$	39.34	8.58	18.36	23.24	39.16	8.54	18.26	23.20	A

[a] With decomposition. [b] Sealed capillary. [c] The yields are based upon the total chloramine reacted, as determined by the Cl^- in the reaction mixture. [d] Reported 156°: O. Westphal, *Ber.*, **74,** 769 (1941). [e] Heated rapidly. Reported 197–198°: B. Philips, *Ann.*, **252,** 273 (1889). [f] Reported 187–188°: B. K. Singh, *J. Chem. Soc.*, **105,** 1986 (1914). [g] A = alcohol, E = ether, C = chloroform, EA = ethyl acetate, and PE = petroleum ether (b.p. 30–60°). [h] 1-Diethyl-1-(2-hydroxyethyl)-hydrazinium chloride was also prepared but was not purified.

Experimental[10]

Materials.—All of the tertiary amines were commercially available. Eastman Kodak Co., white label, amines and Matheson trimethylamine (97%) were used without further purification. N-Methylmorpholine, N,N-diethylcyclohexylamine and α-picoline were dried over barium oxide and fractionated before use. The chloramine used in this study was produced by the gas phase reaction of ammonia and chlorine.[11]

Apparatus and Method.—The apparatus used was described previously.[12] The chloramine–ammonia stream was bubbled through the liquid tertiary amine[13] until a sufficient quantity of product separated from the reaction mixture or the products from several experiments were combined. The reaction mixture was filtered, the product was washed with ethyl ether, and recrystallized. The following examples will give more detail on the procedure used. The data on the hydrazinium chlorides are summarized in Table I.

1-Trimethylhydrazinium Chloride.—The gaseous chloramine–ammonia stream was bubbled through about 100 ml. of trimethylamine at about −30° for one hour. As the reaction proceeded the hydrazinium chloride contaminated with 1 or 2% ammonium chloride crystallized from the reaction mixture. The unreacted amine in the trap was allowed to evaporate and the solid residue was washed with ether and dried in an oven at 120°. The yield of crude product was 2.6 g. The crude product was treated with 25 ml. of absolute ethanol, and the undissolved residue filtered off. The residue (0.04 g.) gave qualitative tests for ammonium and chloride ions. Addition of ether to the alcoholic solution of the hydrazinium chloride and chilling in a Dry Ice-bath caused crystallization of the 1-trimethylhydrazinium chloride to occur. The crystals were very hygroscopic. The 1-trimethylhydrazinium chloride was converted to the iodide by treating a concentrated alcoholic solution of the chloride with hydroiodic acid (sp. gr. 1.5). The hydrazinium iodide crystallized from the solution in the form of glistening plates. The iodide was recrystallized from an alcohol–ethyl acetate mixture. It melted with decomposition at 235° (Fisher–Johns apparatus). The reported values are 235°[14] and 232–233°.[15] *Anal.* Calcd. for

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[1] Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy by George M. Omietanski.

[2] This nomenclature is based on the suggestions given in *C. A.*, **39,** 5926 (1945) and *Chem. Eng. News*, **33,** 547 (1955).

[3] E. Renouf, *Ber.*, **13,** 2172 (1880).

[4] O. Westphal, *ibid.*, **74,** 772 (1941).

[5] E. Fischer, *Ann.*, **190,** 105 (1878).

[6] E. Fischer, *ibid.*, **199,** 317 (1879).

[7] B. Philips, *ibid.*, **252,** 274 (1889).

[8] R. S. Drago and H. H. Sisler, THIS JOURNAL, **77,** 3191 (1955).

[9] A. D. Kelmers, Thesis, The Ohio State University, 1954.

[10] All melting points are uncorrected. The microanalyses are by Galbraith Laboratories, Knoxville, Tenn.

[11] R. Mattair and H. H. Sisler, THIS JOURNAL, **73,** 1619 (1951).

[12] H. H. Sisler, F. T. Neth, R. S. Drago and D. Yaney, *ibid.*, **76,** 3906 (1954).

[13] The reactions were carried out at room temperature (25°), except where noted in Table I.

[14] C. Harries and T. Haga, *Ber.*, **31,** 57 (1898).

[15] D. H. Meyer, Dissertation, University of Iowa, 1953, p. 38; *C. A.*, **48,** 3918 (1954).

TABLE II

1,1,1-TRISUBSTITUTED HYDRAZINIUM HEXAFLUOROPHOSPHATES

Hydrazinium hexafluorophosphate	M.p., °C.	Empirical formula	Analyses, % Calcd. C	 H	 N	 P	 Found C	 H	 N	 P
1-Trimethyl-	>300[a]	$C_3H_{11}F_6N_2P$	16.36	5.04	12.72	14.07	16.41	5.05	12.55	14.02
1-Diethyl-1-phenyl-	110–111	$C_{10}H_{17}F_6N_2P$	38.71	5.52	9.03	9.98	38.48	5.59	8.85	9.94
1-Dimethyl-1-phenyl-	165–166	$C_8H_{13}F_6N_2P$	34.05	4.64	9.93	10.98	34.29	4.76	9.80	10.78
1-Tri-*n*-propyl-[b]	202.5–203.5	$C_9H_{23}F_6N_2P$	35.52	7.62	9.21	10.17	35.50	7.77	9.34	9.97
1-Tri-*n*-butyl-[c]	87.5–88.5	$C_{12}H_{29}F_6N_2P$	41.67	8.44	8.09	8.94	41.77	8.54	8.26	9.02
1-Di-*n*-propyl-1-phenyl-	135–136[d]	$C_{12}H_{21}F_6N_2P$	42.60	6.26	8.28	9.15	42.54	6.41	8.29	9.22
1-Dimethyl-1-(*p*-tolyl)-	120–121	$C_9H_{15}F_6N_2P$	36.49	5.10	9.46	10.46	36.67	5.25	9.39	10.46
1-Tri-*n*-hexyl-[c]	80–81	$C_{18}H_{41}F_6N_2P$	50.22	9.60	6.51	7.19	50.22	9.65	6.44	7.26
1-Cyclohexyl-1-diethyl-[c]	128–129	$C_{10}H_{24}F_6N_2P$	37.97	7.33	8.86	9.79	38.21	7.44	8.82	9.76
4-Amino-4-methylmorpholinium hexafluorophosphate[e]	>300[a]	$C_5H_{13}F_6N_2P$	22.91	5.00	10.69	11.82	22.80	5.20	10.55	11.99
1-Tri-*n*-heptyl-[c,f]	98–99	$C_{23}H_{47}F_6N_2P$	53.37	10.02	5.93	6.55	53.32	9.98	5.88	6.62

[a] With decomposition. [b] Recrystallized from water–acetone. [c] Recrystallized from alcohol–water. [d] Pale green crystals. [e] Recrystallized from alcohol–acetone. [f] Prepared by treating a methanol–water solution of the hydrazinium chloride with aqueous KPF_6.

$[(CH_3)_3NNH_2]I$: C, 17.83; H, 5.48; N, 13.86; I, 62.81. Found: C, 17.75; H, 5.58; N, 13.86; I, 62.94.

1-Diethyl-1-phenylhydrazinium Chloride.—The chloramine–ammonia mixture was bubbled into 100 ml. of diethylaniline at about 25° for one hour. The yield of raw product was 1.9 g. Addition of ether to the filtrate caused the additional precipitation of 0.2 g. of raw product. The combined solids were treated with 25 ml. of absolute ethanol. The residue (0.3 g.) gave qualitative tests for ammonium and chloride ions. The yield of 1-diethyl-1-phenylhydrazinium chloride was 65%. When the reaction was run in a 50% by volume ether solution at about −10°, the yield of the hydrazinium chloride decreased to 18%. 1-Diethyl-1-phenylhydrazinium chloroplatinate, $[(C_2H_5)_2(C_6H_5)NNH_2]_2PtCl_6$, was prepared by adding a concentrated aqueous solution of chloroplatinic acid to a hot aqueous solution of the hydrazinium chloride. Upon cooling, the yellow-orange needles which had formed were filtered, washed with cold water and dried. They melted at 167–168° dec.

1-Dimethyl-1-(2-hydroxyethyl)-hydrazinium Chloride.—The chloramine–ammonia stream was bubbled through 25 ml. of N,N-dimethylaminoethanol for 45 minutes at 25°. Upon chilling the trap to about −30°, the hydrazinium chloride precipitated completely; yield 3 g. The raw solid was completely soluble in absolute ethanol. It was recrystallized from an ethanol–ethyl acetate mixture and was obtained in the form of hygroscopic, feathery needles. The yield was nearly quantitative.

1-Tri-*n*-heptylhydrazinium Chloride.—The reaction of chloroamine with tri-*n*-heptylamine was carried out in the usual manner with the amine itself at 40°, and with 50% by volume solution of the amine in petroleum ether (b.p. 30–60°) at about 0°. In both cases the hydrazinium chloride was formed in an exothermic reaction. The yield was not determined because of the difficulty of freeing the raw solid from the entrapped amine; however, the presence of considerable ammonium chloride in the raw solid suggests that the yield is quite low. The alcohol-insoluble portion of the solid was recrystallized from a water–ethanol mixture. *Anal.* Calcd. for NH_4Cl: Cl, 66.29. Found: Cl, 66.17.

Gas Phase Reaction of Chloramine–Trimethylamine.—The gaseous chloramine–ammonia stream was treated with an excess of gaseous trimethylamine at 25° by allowing the gases to mix in a glass reactor tube 21 cm. in length and 5.5 cm. in diameter. The exit end of the tube contained a glass wool plug filter. It was evident that reaction does not occur in the gas phase, but does occur slowly at the glass surface. A 50-minute experiment yielded 1.3 g. of raw solid. The percentage yield of 1-trimethylhydrazinium chloride was identical to that obtained in the reaction of chloramine with liquid trimethylamine. The hydrazinium chloride was converted to the iodide by the method mentioned previously. *Anal.* Calcd. for $[(CH_3)_3NNH_2]I$: C, 17.83; H, 5.48; N, 13.86; I, 62.81. Found: C, 17.83; H, 5.52; N, 13.69; I, 62.99.

Trisubstituted Hydrazinium Hexafluorophosphates.—These salts were prepared by treating a concentrated aqueous solution of the corresponding hydrazinium chloride with a saturated aqueous solution of potassium hexafluorophosphate (Matheson, Coleman and Bell; recrystallized). The precipitates were filtered, washed with cold water and recrystallized from hot water except where indicated in Table II. Many of the hydrazinium hexafluorophosphates were prepared directly from the raw reaction products. The ammonium chloride impurity did not interfere. The data on the hydrazinium hexafluorophosphates are summarized in Table II.

Miscellaneous Hydrazinium Salts.—The nitrates and the perchlorate were made by simple metathesis of the hydrazinium chlorides with the calculated amount of silver nitrate or silver perchlorate.[16] The picrates were prepared by two methods.

Method A.—The corresponding hydrazinium chloride was converted to the hydroxide with moist silver oxide, and a warm aqueous solution of the hydrazinium hydroxide was neutralized with picric acid. Upon cooling or concentrating the solution, the picrate crystallized. **Method B.** A saturated alcoholic solution of picric acid was added to a concentrated alcoholic solution of the corresponding hydrazinium chloride, and the picrate crystallized spontaneously upon stirring. The data on the miscellaneous hydrazinium salts are summarized in Table III.

Reactions of Chloramine with Some Other Bases.—Using methods analogous to those outlined above, the reactions of chloramine with pyridine, α-picoline and *n*-propyl sulfide were carried out. In all these instances the sole crystalline product isolated was ammonium chloride. In the pyridine reaction there was evident decomposition of the heterocyclic base.

Chloramine was likewise treated with N,N-diethyl-1-naphthylamine at 20°, 80–90° and at about −25° in a 50% by volume solution of the amine in low boiling petroleum ether (b.p. 30–60°). The resulting solids were combined, washed with petroleum ether and absolute alcohol and dried. The solids were analyzed and found to be ammonium chloride. *Anal.* Calcd. for NH_4Cl: Cl, 66.29. Found: Cl, 66.12.

Discussion

Trisubstituted Hydrazinium Hexafluophosphates.—Many quaternary ammonium hexafluophosphates are known.[17,18] Since substituted hydrazinium salts are quite similar in many of their properties to their quaternary ammonium analogs,[19-21] it was believed that the hydrazinium hexafluorophosphates should be formed readily in

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(16) Obtained from Bios Laboratories, Inc., New York, N. Y.

(17) W. Lange and E. Muller, *Ber.*, **63B**, 1067 (1930).

(18) Ozark-Mahoning F P Salts January, 1955, Ozark-Mahoning Co., Tulsa, Oklahoma.

(19) O. Westphal, *Ber.*, **74B**, 1366 (1941).

(20) E. Fischer, *ibid.*, **9**, 885 (1876).

(21) B. K. Singh and M. Lal, *J. Chem. Soc.*, **119**, 210 (1921).

TABLE III

MISCELLANEOUS HYDRAZINIUM SALTS

Name	M.p., °C.	Empirical formula	Analyses, % Calcd. C	H	N	Found C	H	N
1-Triethylhydrazinium picrate[b,f]	214–215[a]	$C_{12}H_{19}N_5O_7$	41.73	5.54	20.28	41.80	5.39	20.23
1-Dimethyl-1-phenylhydrazinium chloroplatinate	156–157[a,c]	$C_{16}H_{26}Cl_6N_4Pt$	28.16	3.84	28.61[k]	28.26	3.95	28.49[k]
1-Diethyl-1-(2-hydroxyethyl)-hydrazinium picrate[d,g]	179.5–180.5	$C_{12}H_{19}N_5O_8$	39.88	5.30	19.38	39.89	5.25	19.39
1-Dimethyl-1-(2-hydroxyethyl)-hydrazinium picrate[d,f]	170	$C_{10}H_{15}N_5O_8$	36.03	4.54	21.01	36.09	4.61	21.10
4-Amino-4-methylmorpholinium picrate[b,h]	248–249	$C_{11}H_{15}N_5O_8$	38.26	4.38	20.28	38.38	4.32	20.48
1-Triethylhydrazinium nitrate[i]	71–75[e]	$C_6H_{17}N_3O_3$	40.21	9.56	23.45	39.97	9.85	23.43
1-Tri-*n*-heptylhydrazinium perchlorate[j]	77.5–78.5[a]	$C_{21}H_{47}ClN_2O_4$	59.06	11.09	6.56 8.30[l]	59.02	11.26	6.78 8.37[l]
1-Tri-*n*-heptylhydrazinium nitrate[j]	77–78	$C_{21}H_{47}N_3O_3$	64.73	12.16	10.79	64.84	12.22	10.73

[a] With decomposition. [b] Method B. [c] Reported 158–159°. B. K. Singh, *J. Chem. Soc.*, **105**, 1986 (1914). [d] Method A. [e] Sealed capillary. [f] Recrystallized from alcohol. [g] Recrystallized from hot water. [h] Recrystallized from water–acetone. [i] Recrystallized from alcohol–ethyl acetate. [j] Recrystallized from alcohol–ether. [k] Pt. [l] Cl.

aqueous solution and be useful as derivatives. This was found to be the case.[22]

A Suggested Mechanism.—On the basis of the studies in this Laboratory on the reaction of chloramine with ammonia,[23] primary,[9] secondary[9] and tertiary amines in non-aqueous media, it is believed that the reaction of chloramine with any amine is an acid–base reaction in the Lewis sense with chloramine being the electrophilic reagent. The mechanism is pictured as being analogous to the mechanism for the chloramine–ammonia reaction proposed by Cahn and Powell[24] and affirmed by Drago and Sisler[8]

$$R'R''R'''N + NH_2Cl \longrightarrow [R'R''R'''NNH_2]^+, Cl^-$$

where R′, R″ and R‴ may represent alkyl or aryl radicals or hydrogen atoms. Thus, the first step in a chloramine–ammonia reaction or a chloramine–amine reaction is a bimolecular displacement reaction in which an hydrazinium ion is formed.[8] If the quaternary nitrogen contains a hydrogen atom attached to it, then the hydrazinium ion will be subjected to a protolysis reaction with the strongest base present. With ammonia or with primary or secondary amines, hydrazine or substituted hydrazines would be formed

$$[NH_3NH_2]^+ + B \longrightarrow NH_2NH_2 + BH^+$$
$$[RNH_2NH_2]^+ + B \longrightarrow RNHNH_2 + BH^+$$
$$[RR'NHNH_2]^+ + B \longrightarrow RR'NNH_2 + BH^+$$

With tertiary amines the reaction does not proceed beyond the hydrazinium ion stage because the quaternary nitrogen does not contain an available proton

$$R'R''R'''N + NH_2Cl \longrightarrow [R'R''R'''NNH_2]^+, Cl^-$$

3. **Acknowledgments.**—This research has been supported in large part by the Davison Chemical Co., a Division of W. R. Grace and Co., through a contract with the Ohio State University Research Foundation. The crystallization of the hydrazinium nitrates and perchlorate was carried out by Mrs. Sandra Simonaitis.

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[22] 1-Triethyl-, 1-dimethyl-1-(2-hydroxyethyl)-, 1-diethyl-1-(2-hydroxyethyl)- and 1-diethyl-1-(3-hydroxypropyl)-hydrazinium hexafluorophosphates could not be prepared in the usual manner.

[23] H. H. Sisler, F. T. Neth and F. R. Hurley, THIS JOURNAL, **76**, 3909 (1954).

[24] J. W. Cahn and R. E. Powell, *ibid.*, **76**, 2565 (1954).