The first step in the formation of enamines will be the addition of the amine to the carbonyl group. This addition will take place without the aid of an acid catalyst, which is in accordance with the mechanism of the addition of amines to carbonyl compounds, as proposed by Swain and Worosz.[15] The resulting zwitterion is rapidly converted to the α-amino alcohol.

The reaction of the amino alcohol to produce the immonium ion (the reverse of reaction 5) will be general acid catalyzed. It is in this reaction step that the catalytic influence of the frequently used p-toluenesulfonic acid will be found. Marchese[16] obtained evidence that in the formation of enamines the active catalyst is not p-toluenesulfonic acid but ammonium ions formed from the secondary amine and p-toluenesulfonic acid.

The observation of Marchese[16] that the morpholine enamine is formed faster than the piperidine enamine can be seen in this light. The greater electron-attracting power of the morpholine group as compared with the piperidine group would make the loss of a water molecule in the reverse reaction (5) for the morpholino intermediate more difficult if the same catalyst were active. However, the stronger acidity of the morpholinium ion than the piperidinium ion makes the former a more powerful catalyst, which effect obviously dominates.

Conclusion.—The hydrolysis of enamines and consequently also their formation takes place in a series of reactions all of which appear to be equilibria. A number of reactions may become rate determining each in a certain pH region. This picture is further complicated by the fact that changes in reactivity of the cyclic amine part cause appreciable shifts in the equilibria involved. However, considering well-known effects of inductive action and exocyclic double bond formation the seemingly large differences illustrated in Figure 2 are explained in a natural way. Extrapolation of the results obtained in this study to other compounds should take into careful consideration the shifts in a number of equilibria *and* the influence on rates caused by varying substituent effects.

Experimental Section

The enamines were synthesized from isobutyraldehyde and the secondary amines as described earlier.[2] The solvent water for the kinetic experiments was purified by demineralization and subsequent distillation in an all-silica apparatus. Proanalyse grade chemicals were used in preparing the solutions of the strong acids and the acetate buffer solutions.

The buffer solutions were prepared in the usual way, maintaining the ionic strength at 0.100 M by adding sodium chloride. The pH measurements were made on a Radiometer pH meter, Type TTT 1a, provided with a glass and a calomel electrode. The concentration of acid was determined by titration with an aqueous solution of sodium hydroxide using phenolphthalein as an indicator. The rate measurements were carried out following the decrease of the ultraviolet absorption in the range of 2000–2150 A using silica cells with a path length of 1 cm as described in a previous paper.[3] The instrument used was a Zeiss PMQ II spectrophotometer.

The first-order rate constants were determined graphically from plots of log ($E_t - E_\infty$) against time (t) except the rate constants for the hydrolysis of I in 6 M $\mathrm{HClO_4}$, II in 1 M $\mathrm{HClO_4}$, and III in 0.54 M $\mathrm{HClO_4}$. In these cases, since the reactions proceeded very slowly, the first-order rate constants were determined by the Guggenheim method.[12]

Nmr spectra were run on a Varian A-60 spectrophotometer. The spectra of I in 6 M aqueous perchloric acid and of isobutyraldehyde in 0.1 N aqueous hydrochloric acid were recorded from about 2% solutions of these compounds, using a solution of tetramethylsilane in carbon tetrachloride as an external reference.

Registry No.—I, 2403-55-6; II, 673-33-6; III, 2403-57-8.

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(15) C. G. Swain and J. C. Worosz, *Tetrahedron Letters*, 3199 (1965).

(16) J. S. Marchese, Ph.D. Thesis, University of Maryland, 1964.

The Reaction of Perchloryl Fluoride with Selected Amines

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Perchloryl fluoride reacts with piperidine in aqueous solution to give N-perchlorylpiperidine which decomposes slowly and can be hydrolyzed to the enamine, Δ^2-piperidine, isolated as the trimer tripiperideine. In contrast, the same oxidizer reacts with 2,6-dimethylpiperidine, 2,2,6,6-tetramethylpiperidine, and 2,2,6,6-tetramethylpiperidin-4-one in solution to form the corresponding N-fluoro derivatives. This, presumably, is due to steric effects of the α-methyl groups. Tertiary amines such as N-methylpiperidine and triethylamine are oxidized to the enamines, N-methyl-Δ^2-piperidine and diethylvinylamine, which were isolated, respectively, as condensation products with chloranil and 2,3-dichloronaphtho-1,4-quinone. Aqueous triethylenediamine, with perchloryl fluoride, undergoes an oxidative fragmentation reaction resulting in the formation of formaldehyde and piperazine.

Gaseous perchloryl fluoride ($\mathrm{ClO_3F}$) reacts strongly with most aliphatic and nonaromatic heterocyclic amines, and contacting the undiluted amines with perchloryl fluoride often results in violent, uncontrollable oxidations and/or explosions. However, these violent reactions can be moderated by either extreme dilution of the perchloryl fluoride with an inert gas or by dissolution of the amines in inert solvents, thereby permitting the isolation and identification of the products of the reactions.

Earlier studies[2] of the reactions of perchloryl fluoride with primary and secondary aliphatic amines indicate that the intermediate reaction products are extremely unstable and usually decompose to mixtures of unidentifiable dark tars. In our present work we have studied the reactions of perchloryl fluoride with piperidine, alkyl-substituted piperidines, and selected tertiary amines.

In general we found that the N-unsubstituted piperidines studied will form N-perchloryl and N-fluoro derivatives which are sufficiently stable for characteri-

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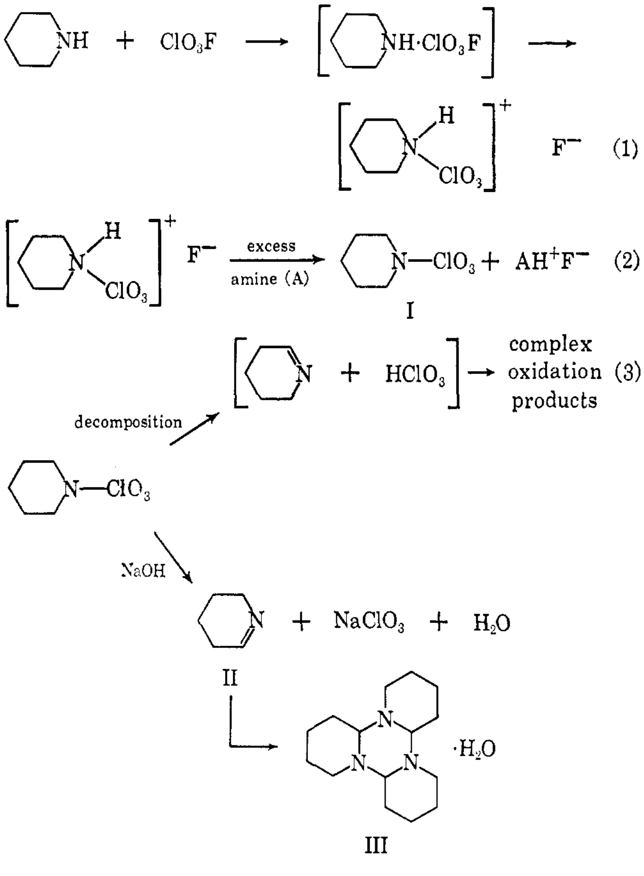
(1) Research Laboratories, U. S. Army Edgewood Arsenal, Edgewood Arsenal, Md.

(2) Unpublished observation at this laboratory.

zation. In contrast, tertiary amines, including N-methylpiperidine, eliminate protons from the α and β positions to form the reactive enamines.

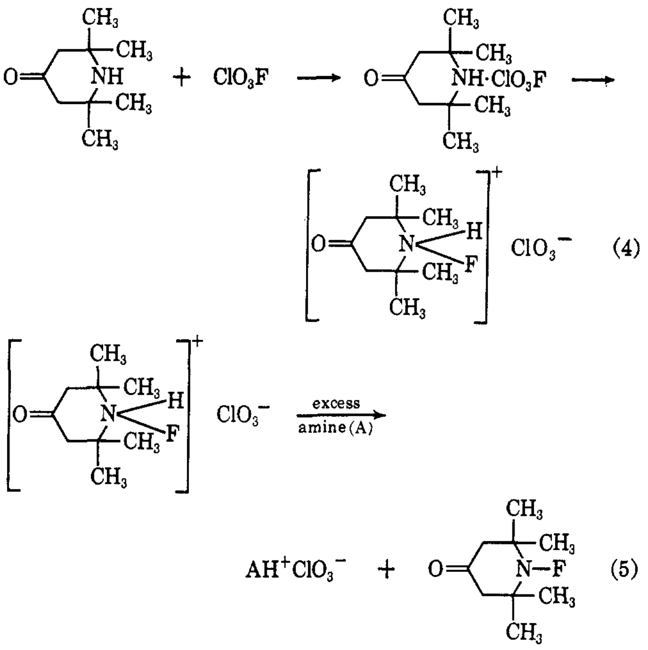
Reactions of Various Piperidines with Perchloryl Fluoride.—Aqueous piperidine is known to react with perchloryl fluoride to give N-perchlorylpiperidine (I).[3] This material slowly decomposes at ambient temperature to give a complex mixture of products similar to that obtained when undiluted piperidine is treated with perchloryl fluoride. Hydrolysis of N-perchlorylpiperidine results in the formation of Δ^1-piperidine (II), a Schiff base, which has been isolated in the form of its hydrated trimer, tripiperideine hydrate (III). In an analogous reaction the anhydrous tripiperideine (three isomers) is reported as the product of the hydrolysis of N-chloropiperidine.[4]

These results suggest the following sequence of reactions (eq 1–3).



The substitution of methyl groups at the 2 and 6 positions in the piperidine ring has a pronounced effect on the course of reaction with perchloryl fluoride. When the reactions are carried out in an inert solvent, only the insoluble amine hydrochlorate salts precipitate, resulting in the formation of the N-fluoro derivatives. N-fluoro-2,2,6,6-tetramethylpiperidin-4-one, N-fluoro-2,2,6,6-tetramethylpiperidine, and N-fluoro-2,6-dimethylpiperidine have been prepared in this manner, although the dimethyl derivative proved to be so unstable that conclusive analytical data in support of the proposed structure could not be obtained. This instability is presumably a result of the presence of α protons and the ready elimination of hydrogen fluoride.

The reactions leading to the N-fluoro derivatives can be summarized as follows using 2,2,6,6-tetramethylpiperidin-4-one as an example (eq 4 and 5).



Reaction of Tertiary Amines with Perchloryl Fluoride.—The reaction of triethylamine with perchloryl fluoride in both aqueous and nonaqueous solvent systems gave complex mixtures of products resulting from degradative oxidation. In aqueous solution chlorate and fluoride ions, tars, and traces of acetaldehyde were identified. In nonaqueous solvents the precipitation of chlorate and fluoride salts of the amine was noted as well as the slow formation of tars and other products and a darkening of the initially clear solutions.

It has been reported by Buckley and co-workers[5] that the oxidation of triethylamine results in the formation of diethylvinylamine which was isolated by condensation reactions with certain chlorinated quinones. By applying this technique to our investigation we were able to isolate the blue condensation product of 2,3-dichloronaphtho-1,4-quinone and diethylvinylamine, which was formed *in situ* when perchloryl fluoride was passed into a solution of triethylamine in ethyl acetate in the presence of the quinone. The identity of this condensation product was verified by comparing the infrared spectrum with that of the known condensation product prepared independently by oxidizing triethylamine with benzoyl peroxide in the presence of 2,3-dichloronaphtho-1,4-quinone.

The reaction of triethylamine with perchloryl fluoride can be summarized by the following equations. The

$$(C_2H_5)_3N + ClO_3F \longrightarrow (C_2H_5)_3N\cdot ClO_3F \tag{6}$$

$$(C_2H_5)_3N\cdot ClO_3F \longrightarrow [(C_2H_5)_3NClO_3]^+F^- \tag{7}$$

$$[(C_2H_5)_3NClO_3]^+F^- \xrightarrow[\text{amine (A)}]{\text{excess}} [(C_2H_5)_2N{=}CHCH_3]^+ClO_3^- + AH^+F^- \tag{8}$$

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(3) D. M. Gardner, R. Helitzer, and C. J. Mackley, *J. Org. Chem.*, **29**, 3738 (1964).

(4) C. Schöpf, A. Komzak, F. Braun, and E. Jacobi, *Ann.*, **559**, 1 (1948).

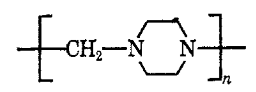
(5) (a) D. Buckley, S. Dunstan, and H. B. Henbest, *J. Chem. Soc.*, 4880 (1957); (b) D. Buckley, H. B. Henbest, and P. Slade, *ibid.*, 4891 (1957); (c) D. Buckley, S. Dunstant, and H. B. Henbest, *ibid.*, 4901 (1957).

$$[(C_2H_5)_2N{=}CHCH_3]^+ClO_3^- \xrightarrow[\text{amine (A)}]{\text{excess}} \underset{\text{diethylvinylamine}}{(C_2H_5)_2NCH{=}CH_2} + AH^+ClO_3^- \quad (9)$$

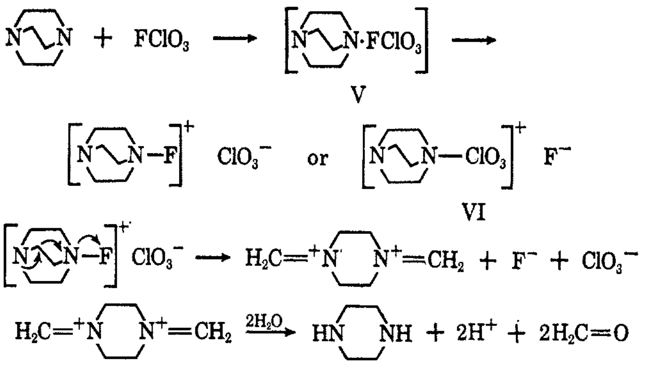
polymerization of diethylvinylamine and/or its subsequent reaction with more perchloryl fluoride leads to the tars found.

The reaction of N-methylpiperidine with perchloryl fluoride gave results similar to those obtained with triethylamine and the reaction product 1-methyl-Δ^2-piperidine was isolated by adding chloranil to a solution of N-methylpiperidine in benzene and passing perchloryl fluoride through the solution. The dark blue condensation product formed immediately and was identified by comparison of the infrared spectrum with that for the known condensation product prepared independently by treating N-methylpiperidine with benzoyl peroxide in the presence of chloranil.

The Reaction of Triethylenediamine with Perchloryl Fluoride.—Gaseous perchloryl fluoride reacted vigorously with triethylenediamine (*i.e.*, 1,4-diazabicyclo[2.2.2]octane) dissolved in 1,1,2-trifluoro-2,2,1-trichloroethane to produce the insoluble chlorate and fluoride salts of the amine as well as unidentifiable, tar-like residues. Triethylenediamine, dissolved in water, reacted with perchloryl fluoride with no visual change but with a definite temperature rise. On passing the product solution through an anion-exchange resin to remove chlorate and fluoride ions and evaporating the eluate, a fine, white solid was obtained which was identified as polymeric methylene piperazine (IV). Poly(methylenepiperazine) has been reported as a product of the reaction of aqueous formaldehyde with piperazine.[6]


IV

Reactions involving the breakage of carbon–carbon bonds α,β to a heteroatom have been given attention in the recent literature. Thus, in the most closely related example to be found, Huisgen and Kolbeck[7] observed the degradation of triethylenediamine N-oxide on treatment with benzoyl chloride to produce an intermediate easily hydrolyzed to piperazine, formaldehyde, hydrogen chloride, and benzoic acid. These authors recognized the similarity between this reaction and the solvolytic "fragmentation reaction" of 4-bromoquinuclidine described by Grob and co-workers.[8] The oxidation state of this mono-N-oxide is the same as that of the cations of the adduct VI postulated as the product of reaction between triethylenediamine and perchloryl fluoride. The poly(methylenepiperazine) that was isolated is formed by combination of the formaldehyde and piperazine during the evaporation of the reaction mixture after it was passed through the anion-exchange resin.


V

VI

This reaction of triethylenediamine which we would term "oxidative fragmentation" occurs with oxidants other than perchloryl fluoride.[9]

Experimental Section

The perchloryl fluoride gas was used as supplied by the Pennsalt Chemicals Corp. The purity was better than 97% with the principal contaminant being chlorine.

Preparation and Hydrolysis of N-Perchlorylpiperidine.—The compound was prepared by the procedure described in the literature.[3] The pure N-perchlorylpiperidine was added to 2% aqueous sodium hydroxide and the mixture was stirred until a homogeneous solution was obtained. The aqueous solution was extracted with ether, and the ether extract was dried over sodium sulfate and evaporated to give a brownish yellow, viscous oil with a stale, musty odor. The oil was identified as being principally the monohydrate of tripiperidine containing some of the anhydrous material.

Anal. Calcd for $C_{15}H_{29}N_3O$: C, 67.37; H, 10.93; N, 15.72. Calcd for $C_{15}H_{27}N_3$: C, 72.24; H, 10.91; N, 16.85. Found: C, 69.25; H, 10.35; N, 16.30.

Attempts to obtain a single pure product (either the anhydrous material or the monohydrate) were not successful.

Mass spectrometric analysis gave a fragment of mass number 267 with a relative intensity of 0.4, based on a relative intensity of 100 for mass peak 55. This is consistent with what might be expected for the parent hydrated compound. A mass peak of 249 with an intensity of 1.4 was observed for the anhydrous material. The infrared pattern matched that reported for the same structure by Mecke.[10]

Reaction of Perchloryl Fluoride with 2,2,6,6-Tetramethylpiperidin-4-one.—The 2,2,6,6-tetramethylpiperidin-4-one was prepared by the method of Guareschi.[11]

A solution of 10.0 g (0.0644 mole) of 2,2,6,6-tetramethylpiperidin-4-one in 200 ml of ether was treated with excess perchloryl fluoride gas at a flow rate of about 5 cc/min. The solution became cloudy at once and a small temperature rise was noted. After 5–10 min a fine, white precipitate separated. The perchloryl fluoride flow was continued for 0.5 hr and the solid product was filtered off and dried under vacuum for 24 hr at 56° (40 mm) to yield 7.1 g (92.2% yield), mp 174° dec. The product was identified as 2,2,6,6-tetramethylpiperidin-4-one hydrochlorate.

Anal. Calcd for $C_9H_{18}ClNO_4$: C, 45.10; H, 7.57; Cl, 14.79; N, 5.84. Found: C, 45.87; H, 7.86; Cl, 14.76; N, 6.31.

The pale yellow filtrate was stripped of the ether solvent to yield 4.5 g (80.4% crude yield) of oily residue. Distillation under reduced pressure in a spinning-band column gave a pure, colorless oil [bp 70° (2 mm), $n^{29}\mathrm{D}$ 1.4518] and was identified as N-fluoro-2,2,6,6-tetramethylpiperidin-4-one by the following data.

Anal. Calcd for $C_9H_{16}FNO$: C, 62.40; H, 9.31; F, 10.97; N, 8.09. Found: C, 62.41; H, 9.62; F, 10.83; N, 7.94.

Mass spectral analysis afforded a remarkably clear spectrum with a parent peak at m/e 173.

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(6) A. Ladenburg and W. Herz, *Ber.*, **30**, 3043 (1897).

(7) R. Huisgen and W. Kolbeck, *Tetrahedron Letters*, 783 (1965).

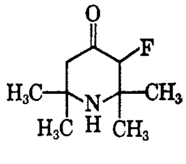
(8) C. A. Grob, *Gazz. Chim. Ital.*, **92**, 902 (1962). See also preceding papers: C. A. Grob, R. M. Hoegerle, and M. Ohta, *Helv. Chim. Acta*, **45**, 1823 (1962); C. A. Grob, *Bull. Soc. Chim. France*, 1360 (1960); C. A. Grob in "Theoretical Organic Chemistry" (Papers presented at the Kekulé Symposium, London, Sept 1958), Butterworth and Co. (Publishers) Ltd., London, 1959, p 14; P. Brennersen, C. A. Grob, R. A. Jackson, and M. Ohta, *Helv. Chim. Acta*, **48**, 146 (1965).

(9) D. H. Rosenblatt, *et al.*, unpublished observations.

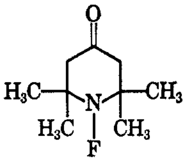
(10) "Documentation of Molecular Structure," Butterworth and Co. (Publishers) Ltd., London, 1963, Card No. 10057, source, R. Mecke, Collection of the Institute of Physical Chemistry, University of Freiburg, Breisgau.

(11) J. Guareschi, *Ber.*, **28**, R 160 (1895).

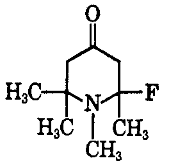
There are three possible structures containing fluorine. Of these, A and B are likely candidates, whereas structure C implies a molecular rearrangement. The proton nmr spectrum



A



B



C

of the original piperidone consists of two sharp lines: one at a shift of −1.25 ppm relative to that of tetramethylsilane (CH_3 groups) and a second at a shift of −2.27 ppm (CH_2 groups). In addition, there is a smaller, broad peak at a shift of −1.81 ppm (>NH).

In the proton nmr spectrum of the fluorinated product, the >NH peak has disappeared and the lines owing to CH_3 and CH_2 occur slightly downfield from their original positions and are doubled. The CH_3 doublet with J = 1.7 cps is at −1.31 ppm and the CH_2 doublet with J = 2.4 cps is at −2.44 ppm.

The fluorine nmr spectrum consists of a single, broad line about 30 cps in width located at a shift of 7.76 ppm above that of the trifluoroacetic acid reference line (+85.6 ppm upfield from $CFCl_3$).

Both the proton and fluorine nmr spectra are compatible with structure B above and not with the structures A and C. The fluorine spectrum line width is consistent with that to be expected for a single fluorine atom split with a small J value (about 2 cps) by 16 approximately equivalent protons.

The proposed structure is supported by the infrared spectrum which shows a disappearance of a band at 2.8 μ attributed to NH absorption and the appearance of strong bands at 11 and 12 μ attributed to NF absorptions.

The semicarbazone (mp 166–168°) and the 2,4-dinitrophenylhydrazone (mp 143–145°) were both prepared, and the elemental analysis for the latter is given.

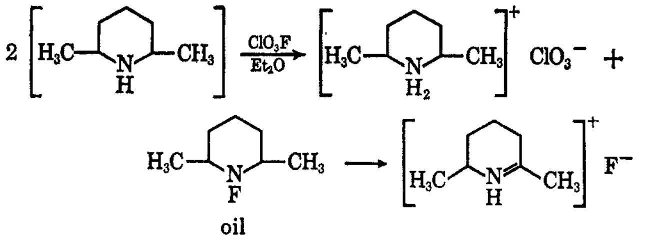
Anal. Calcd for $C_{15}H_{20}FN_5O_4$: C, 50.99; H, 5.71; F, 5.38; N, 19.82. Found: C, 51.21; H, 6.01; F, 6.08; N, 18.92.

Reaction of Perchloryl Fluoride with 2,2,6,6-Tetramethylpiperidine.—The 2,2,6,6-tetramethylpiperidine was obtained by reducing the carbonyl group of 2,2,6,6-tetramethylpiperidin-4-one according to the method used by Leonard and Nommensen.[12]

To a 2% sodium hydroxide solution was added 2.5 g (0.0177 mole) of 2,2,6,6-tetramethylpiperidine, and the two-phase liquid mixture was stirred while a stream of perchloryl fluoride gas was passed through it at about 5 cc/min. After several minutes an orange-brown oil began to accumulate on the surface. After 1.5 hr the perchloryl fluoride flow was stopped and the mixture was extracted with ether. After drying the ether extract and stripping off the solvent, a dark brown oil was obtained which had a strong, camphor-like odor; the yield was 0.7 g (50.0%). The crude product was distilled *in vacuo* at 28° (0.5 mm). Mass spectral analysis showed a strong parent peak at m/e 159 and infrared analysis indicated that the basic structure of the 2,2,6,6-tetramethylpiperidine was unchanged except that an absorption band at 2.9 μ attributed to NH stretching had disappeared and strong bands at 11 and 11.5 μ attributed to the NF bond had appeared.

Reaction of Perchloryl Fluoride with 2,6-Dimethylpiperidine.—A solution of 5.06 g (0.050 mole) of 2,6-dimethylpiperidine in 200 ml of anhydrous ether was treated with perchloryl fluoride gas at about 10 cc/min. Within 3–5 min the temperature began to rise steadily and a white solid separated from the mixture. After 30 min the reaction appeared to be complete, the perchloryl fluoride flow was stopped, and the mixture was filtered under a nitrogen atmosphere to give 4.3 g (93.5% yield) of 2,6-dimethylpiperidinium chlorate, mp 83–85°.

Evaporation of the ether solvent of the filtrate yielded a pale yellow oil having a sweet, camphor-like odor. On standing for 1 or 2 hr, the oil gradually darkened and turned into a water-soluble, brown sludge. From the infrared spectrum, a tentative identification of the quaternary grouping $>NH^+$ was made and the ring structure was found to be intact. The following sequence of reactions is suggested to explain the observed phenomena.

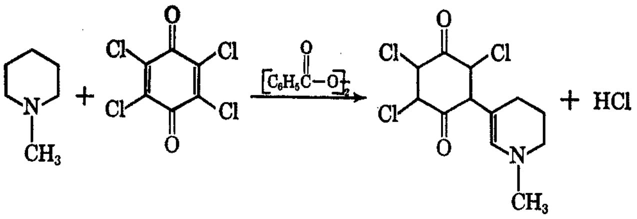


Other preparations of the oily reaction product were made; however, attempts to purify it by distillation failed when the product decomposed.

Reaction of Perchloryl Fluoride with N-Methylpiperidine.—If N-methylpiperidine is dissolved in a nonaqueous solvent (ether, carbon tetrachloride, etc.) and treated with perchloryl fluoride, N-methylpiperidinium fluoride and chlorate precipitate from solution with a simultaneous darkening of the solution and the separation of brownish oils and tars.

The same reaction proceeds in aqueous solution with perchloryl fluoride gas with the exception that the salts do not precipitate and the organic products remain dissolved to give an amber solution.

According to Buckley, *et al.*,[5] N-methylpiperidine is oxidized by benzoyl peroxide to form 1-methyl-Δ^2-piperidine which condenses *in situ* with chloranil to give an intensely blue derivative. This work was repeated; the blue product was isolated as reported and the melting point was confirmed.



mp 105–107°

In order to determine whether perchloryl fluoride oxidizes N-methylpiperidine in a similar fashion, the following work was carried out.

A solution of 0.3 g (0.0012 mole) of chloranil was dissolved in 50 ml of benzene to which was added 0.1 g (0.0022 mole) of N-methylpiperidine. Another 40 ml of benzene was saturated with perchloryl fluoride gas and was added dropwise to the quinone–amine solution prepared above. The solution turned dark blue and was washed, in turn, with 1 N sulfuric acid and 5% sodium hydroxide then dried over magnesium sulfate and evaporated to dryness to yield a small amount of dark solid, mp 105–107°. The infrared spectrum of this solid was identical with that of a known sample of the blue condensation product which was synthesized independently from N-methylpiperidine, benzoyl peroxide, and chloranil according to the method of Buckley and co-workers.[5c]

Reaction of Perchloryl Fluoride with Triethylamine.—A solution of 5.0 g of triethylamine in 100 ml of 1,1,2-trifluoro-2,2,1-trichloroethane was treated with a slow flow of perchloryl fluoride gas (about 1–2 cc/min). An immediate, vigorous oxidation occurred and the temperature increased at an alarming rate. The temperature was controlled to below 35° by a constant monitoring of the oxidant flow rate. After 2 hr of reaction, the mixture had separated into two liquid phases; the lower organic layer was dried and evaporated to give a dark tar; the upper aqueous layer (the water resulted from uncontrolled oxidation of the amine) yielded an oily, viscous product that seemed too complex to resolve into its many components. The aqueous layer did contain fluoride and chlorate ions formed in the reaction by reduction of the perchloryl fluoride.

Volatile products from the above reaction were trapped at liquid nitrogen temperature and analyzed using infrared and gas chromatographic techniques. The products were identified as water, carbon dioxide, and acetaldehyde (small amount).

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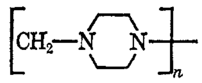
[12] N. J. Leonard and E. W. Nommensen, *J. Am. Chem. Soc.*, **71**, 2810 (1949).

The same reaction was attempted in aqueous solution at the same concentration. Again an exothermic reaction occurred, but the temperature was much easier to control. The initially colorless solution gradually turned yellow concomitant with the pH approaching 7 and the aqueous solution contained both chlorate and fluoride ions.

Since the above reactions again appeared to involve the formation of an enamine, an attempt was made to trap the enamine by condensation with 2,3-dichloronaphthoquinone. A mixture of 0.125 g of triethylamine (0.00128 mole) and 0.145 g of 2,3-dichloronaphthoquinone (0.00063 mole) was dissolved in 100 ml of ethyl acetate and to this solution was added dropwise 25 ml of ethyl acetate saturated with perchloryl fluoride gas. A deep blue-purple color developed immediately and, on evaporation of the solvent, a dark purple solid was obtained which was taken up in ether, and extracted with 5% sodium hydroxide to remove traces of amine hydrochloride salt. The extract was dried over anhydrous magnesium sulfate, the ether was evaporated off, and the solid product was recrystallized from acetone–water. A study of the infrared spectrum proved this product to be identical with the condensation product of 2,3-dichloronaphthoquinone and the enamine formed by the reaction of triethylamine with benzoyl peroxide as reported by Buckley, *et al.*,[5] and repeated during this work. It is to be noted however that the condensation product formed using benzoyl peroxide and perchloryl fluoride gave a melting point of 178–181° in contrast to the values of 92–95° reported in the literature.

Reaction of Perchloryl Fluoride with Triethylenediamine.—Gaseous perchloryl fluoride was passed through a dilute solution of triethylenediamine in 1,1,2-trifluoro-2,2,1-trichloroethane (1 g/200 ml) at about 10 cc/min resulting in an immediate precipitation of a mixture of triethylenediammonium chlorate and fluoride. It was apparent that an oxidation of the amine had occurred owing to the reduction of the perchloryl fluoride gas to the chlorate and fluoride ions; however, no isolable products were obtained from the filtered and evaporated solution.

A solution of 5.6 g (0.05 mole) of triethylenediamine in 75 ml of water was treated for 1 hr with gaseous perchloryl fluoride. There was no visual change but the temperature initially rose from 25 to 39°, then dropped off slowly, the pH decreasing to about 7. The aqueous solution was passed through an anion-exchange resin (Amberlite IRA-400) to substitute hydroxyl ions for chlorate and fluoride and the eluent was evaporated under reduced pressure on the steam bath. This resulted in 2.7 g of a fine, white, polymeric solid (no melting point, charred) which was identified as polymeric methylenepiperazine.



Anal. Calcd for $C_5H_{10}N_2$: C, 61.1; H, 10.27; N, 28.5; neut equiv, 49.1. Found: C, 61.0; H, 10.75; N, 28.18; neut equiv, 52.5.

An infrared spectrum of an authentic sample of methylene piperazine prepared from formaldehyde and piperazine[6] was identical with that obtained using the above material.

When the white solid product was isolated by evaporation of the aqueous solution under reduced pressure at room temperature, the analysis indicated a product equivalent in empirical composition to the hemihydrate of methylene piperazine.

Anal. Calcd for $C_{10}H_{22}N_4O$: C, 56.04; H, 10.35; N, 26.14; neut equiv, 53.5. Found: C, 56.07; H, 10.69; N, 25.77; neut equiv, 53.

No further work was done on this material.

The presence of a substantial amount of free formaldehyde in the original aqueous product solution was indicated by the preparation of the 2,4-dinitrophenylhydrazone, mp 160–163° (lit. 166°), by addition of acidified 2,4-dinitrophenylhydrazine.

The presence of piperazine was indicated by the benzene sulfonyl chloride derivative, mp 275–278° (lit.[13] 282°), and by the *p*-toluenesulfonyl chloride derivative, mp 292–294° (lit.[14] 295–296°). A mixture melting point determination of the latter derivative with an authentic sample confirmed its identity.

It is interesting to note that the presence of chloride ion was found in substantial amounts in the aqueous product solution after standing several hours. This was not the case when the solution was tested immediately after the perchloryl fluoride gas flow was terminated. It was found that neutral, aqueous chlorate solutions will be reduced slowly in the cold to chloride by dilute, aqueous formaldehyde. It is important to note that the chloride test using silver nitrate solution was carried out in the absence of the usual nitric acid since its addition would liberate chloric acid and produce chloride ions through immediate reduction by formaldehyde (see Table I).

TABLE I

Reactant	Product	Amt used, mmoles	Amt found, mmoles
Triethylenediamine		50	
Perchloryl fluoride		26	
	Fluoride ion		26.7 mg-atoms
	Chlorate ion		19.2
	Chloride ion		6.1 mg-atoms
	Formaldehyde		47.6

From the above data it was deduced that 2 moles of triethylenediamine react with 1 mole of perchloryl fluoride to give 2 moles of formaldehyde, 1 equiv of fluoride ion, and 1 equiv of chlorine (as chlorate and chloride ion). These results are summarized by the equation $2N(C_2H_4)_3N + ClO_3F + 2H_2O \rightarrow N(C_2H_4)_3NH^+ + NH(C_2H_4)_2NH_2^+ + ClO_3^- + F^- + 2CH_2O$.

Registry No.—Perchloryl fluoride, 7616-94-6; N-perchlorylpiperidine, 768-34-3; 2,2,6,6-tetramethylpiperidin-4-one hydrochlorate, 7650-76-2; N-fluoro-2,2,6,6-tetramethylpiperidin-4-one, 7649-31-2; semicarbazone of **4**, 7616-95-7; 2,4-dinitrophenylhydrazone of **4**, 7616-96-8; 2,2,6,6-tetramethylpiperidione, 768-66-1; 2,6-dimethylpiperidine, 504-03-0; N-methylpiperidine, 626-67-5; triethylamine, 121-44-8; triethylenediamine, 280-57-9; polymeric methylenepiperazine, 109-01-3.

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