[CONTRIBUTION FROM THE METCALF LABORATORIES, BROWN UNIVERSITY]

Reactions of Ethylenimines. V. Hydrolysis[1]

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Hydrolysis of 2,2-dimethylethylenimine in hydrochloric acid gave 1-chloro-2-amino-2-methylpropane (II) and 1-amino-2-methyl-2-propanol (IV) in varying ratios depending on the temperature, concentration of acid and imine to acid ratio. In the special case of hydrolysis of 2,2-dimethylethylenimine picrate, water alone gave 95% of amino alcohol (IV) and 12 *N* hydrochloric acid gave 74% of chloroamine II and 12% of 2-chloro-1-amino-2-methylpropane (III). The results are interpreted as due to competing SN1 and SN2 processes and this is supported by the nature of the products and kinetic data.

Hydrolysis of 2,2-dimethylethylenimine in dilute sulfuric acid gave 1-amino-2-methyl-2-propanol in 65% yield as reported by Cairns.[3] Other workers have agreed that unsymmetrical ethylenimines open at the tertiary[4] (or secondary[5]) carbon rather than at the primary with hydrolytic conditions. Gabriel and Ohle,[6] on the other hand, reported that hydrochloric acid, with 2-methylethylenimine gave 1-chloro-2-aminopropane (in 35% yield according to later work[7]).

There is no conflict in these results. Strong acids such as sulfuric and picric are conjugated with weakly nucleophilic bases and are unable to compete with the solvent, water, in the ring opening. In the strong acid, hydrochloric, on the other hand, the conjugate base is strongly nucleophilic in comparison with water and a chloroamine is obtained as reported.[6]

Hydrochloric acid, therefore, appeared to be a felicitous choice of agents which could be used to study the competition between chloride ion and water in the ring opening of an ethylenimine. Such was the case. In 6 *N* hydrochloric acid an 85–90% yield of 1-chloro-2-amino-2-methylpropane (II) (as hydrochloride) was obtained at 25°, a much higher yield than Smith and Platon[7] reported for the homolog. In 1 *N* hydrochloric acid at 100°, the competition was more nearly on even terms, for II was obtained in 45% yield and 1-amino-2-methyl-2-propanol (IV) in 39% yield. Other results of these hydrolytic reactions are summarized in Table I.

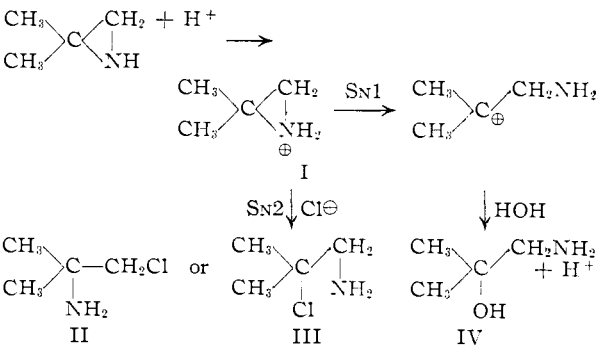
The formation of these products is probably the resultant of two independent nucleophilic substitutions, one an SN1 process and the other, SN2. None of the data found is in conflict with this interpretation. As Tarbell[8] has suggested in a similar case, formation of the amino alcohol IV would be favored by an SN1 mechanism since the intermediate tertiary carbonium ion (solvated or unsolvated) is energetically stable in comparison with the alternative primary carbonium ion. Conspicuous absence of the isomer, 2-amino-2-methyl-1-propanol, in the reaction mixtures under any of the conditions chosen for the hydrolysis supports the picture since this alcohol should be formed in a solvolytic reaction of the SN2 type.

TABLE I

HYDROLYSIS OF 2,2-DIMETHYLETHYLENIMINE IN HYDROCHLORIC ACID

Concn. of acid, *N*[a]	Temp., °C.	Yields, % II + III[b]	II[c]	IV[d]	Rates II × 10³, min.⁻¹	Rates IV × 10³, min.⁻¹	(Half-reaction, hr.)
1	0	70[e]		16[e]	0.0139	0.0059	570
1	25	63.4	66	28	0.44	0.25	16
1	35	61.2		..	1.85	1.17	3.5
1	62	58.5		31	31	22	0.25
1	100		45	39			
6	25	90.4	85	1.3	3.4	0.36	3

[a] Acid:imine = 3:1. [b] Yield of 1-chloro-2-amino-2-methylpropane (II) and 2-chloro-1-amino-2-methylpropane (III) by titration. The yield of compound III is negligible. [c] Yield of pure 1-chloro-2-amino-2-methylpropane (II) by isolation. [d] Yield of 1-amino-2-methyl-2-propanol determined as *p*-bromobenzenesulfonamide. Approximately 75% of correct value (see Experimental). [e] Yield calculated from the half-reaction.



Formation of the chloroamine II is well accounted for by an SN2 mechanism. Here one would expect competition for chloride ion by the primary and tertiary carbons in the ethylenimine ring and the yield of products obtained, II and/or III, should be governed by the relative electron densities at the two carbons. Since the tertiary carbon has the greater electron density (inductive or hyperconjugative effect) compound II should predominate. Actually none of the 2-chloro-1-amino compound, III, was isolated when imine was added directly to the hydrochloric acid solution and could not have been present in any instance given in Table I to a greater extent than 4%.

Conditions for hydrolysis were found, however, which allowed the isolation of 2-chloro-1-amino-2-methylpropane (III). Treatment of the relatively stable picrate of 2,2-dimethylethylenimine with 12 *N* hydrochloric acid at 25° gave 74% of 1-chloro-2-amino-2-methylpropane (II) and 12% of 2-

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(2) Edwin P. Anthony Fellow, 1952–1954.

(3) T. L. Cairns, THIS JOURNAL, **63**, 871 (1941); R. Adams and T. L. Cairns, *ibid.*, **61**, 2464 (1939).

(4) K. N. Campbell, B. K. Campbell, J. F. McKenna and E. P. Chaput, *J. Org. Chem.*, **8**, 103 (1943).

(5) F. Wolfheim, *Ber.*, **47**, 1440 (1914).

(6) S. Gabriel and H. Ohle, *ibid.*, **50**, 804 (1917).

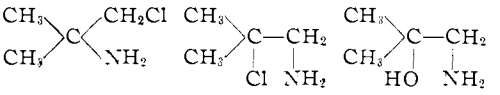
(7) L. Smith and B. Platon, *ibid.*, **55**, 3143 (1922).

(8) D. S. Tarbell and P. Noble, Jr., THIS JOURNAL, **72**, 2657 (1950).

chloro-1-amino-2-methylpropane (III) (both as hydrochlorides). Other data on the hydrolysis of the imine picrate are given in Table II. These results are not essentially different from those presented in Table I but use of the picrate undoubtedly minimized the dimerization[9] of the imine which may have made the isolation of the more soluble chloramine III difficult in the reactions involving direct addition of imine to acid (Table I).

TABLE II

HYDROLYSIS OF 2,2-DIMETHYLETHYLENIMMONIUM PICRATE IN HYDROCHLORIC ACID



Concn. of acid,[a] N	Temp., °C.	II, %[b]	III, %[b]	IV, %[b]
1	25	63	7	
1	62	61	4	26
1	100	50		
12	30	74	12	

[a] Acid:imine = 3:1. [b] Yield by isolation of the hydrochloride (see Experimental).

Kinetic data on the hydrolysis of 2,2-dimethylethylenimine in hydrochloric acid (Table I) also allow the interpretation given here for the paths of the competing reactions. Direct calculation of a second-order rate constant for the SN2 process was not possible in the face of the SN1 reaction. However, a pseudo first-order rate constant was obtained for each reaction on the assumption that chloride ion concentration was constant (it was present in a 3:1 excess), at least for the first half of the reactions. In this way both reactions could be treated as first order. Evidence that the formation of chloroamine II was, indeed, an SN2 process came from the fact that the pseudo first-order rate constant increased eightfold when the acid concentration but not the acid to imine ratio was changed from 1 to 6 N. In a simpler case, Salomon and Freundlich[10] found that ring opening of 2-phenylethylenimine with hydrochloric acid followed second-order kinetics. At the same time, the rate constant for the SN1 process remained essentially constant when the acid concentration was changed from 1 to 6 N (2.5×10^{-4} and 3.6×10^{-4} per minute, respectively).

The data in Table I suggest that the rate of disappearance of immonium ion I for the proposed mechanism is given by the expression

$$\frac{-d[I]}{dt} = (k_{alc} + k_{Cl}[Cl^-])[I]$$

where k_{alc} is the rate of formation of IV and k_{Cl} is the rate of formation of II (+III). It is assumed that the concentration of free imine is negligible in comparison with the concentration of the conjugate acid I and need not be included in this approximation from the following consideration. If the ionization constant, $K_b = [Imine\ H^+][OH^-]/[Imine] \geqq 3.8 \times 10^{-10}$ (K_b for aniline), then [Imine] in molar (and in 6 M) hydrochloric acid is very small. That K_b for the imine is very much greater than 3.8×10^{-10} has been suggested by Brown[11a] (probably 10^{-4}). A fairly stable benzoate salt[11b] of 2,2-dimethylethylenimine has been isolated, also implying that the imine is a stronger base than aniline.

The activation energies calculated for the two processes over a temperature range of 62° (0 to 62°) also fit the picture. An increasing yield of amino alcohol, IV, with elevated temperature would be expected with a higher activation energy for the SN1 process. The values found were 22.7 kcal. per mole for the chloramine II and 24.1 kcal. per mole for the amino alcohol IV.

The argument that the tertiary halide III was a precursor of the amino alcohol IV in the direct hydrolysis of 2,2-dimethylethylenimine is untenable. When the halide, 2-chloro-1-amino-2-methylpropane was subjected to severe conditions, namely, hydrolysis with 1 N hydrochloric acid at 62° for 27 hours, less than 3% was converted to the amino alcohol. The reverse argument that the amino alcohol IV was first formed in the hydrolysis of the imine picrate and subsequently converted to the tertiary halide III is likewise untenable. 1-Amino-2-methyl-2-propanol was only converted to 2-chloro-1-amino-2-methylpropane by treatment with fuming hydrochloric acid at elevated temperature in a closed tube in accordance with Dersin's[12a] report.

When the ethylenimine ring opens with hydrochloric acid, one mole of acid is removed in addition to one forming the salt. Back titration of the excess acid and the salt to the methyl orange endpoint, therefore, gave a measure of the amount of 1-chloro-2-amino-2-methylpropane formed. Any 2-chloro-1-amino-2-methylpropane formed would be included in the determination but this must have been less than 4% in any kinetic run because the yields of pure II by actual isolation were essentially the same as those determined by titration.

In the hydrolysis of the imine picrate the two hydrochlorides II and III were separated by fractional crystallization. The two hydrochlorides were easily sublimed without decomposition and have sharp melting points. They were converted to different picrates and to known benzamides.[12a,b] 1-Chloro-2-benzamido-2-methylpropane slowly changed into 4,4-dimethyl-2-phenyl-2-oxazoline hydrochloride. The free oxazoline and its picrate had been identified previously.[13]

The amino alcohol IV was estimated by conversion to the *p*-bromobenzenesulfonamide by a standardized procedure. Although the yield was only 75%, no better method was found which could be duplicated. On pure samples of the amino alcohol IV and synthetic mixtures of IV with II and III the procedure was consistent within 2%. Realis-

(9) Dimerization of the imine became important in the hydrolysis when the molar ratio of acid to imine was reduced to 1. In one experiment at 25°, 12% of the chloroamine II and 32% of the amino alcohol IV were obtained along with 30% of a diaminoalcohol, an isomer of 5-amino-2,2,5-trimethyl-3-aza-1-hexanol.

(10) H. Freundlich and G. Salomon, *Z. physik. Chem.*, **A166**, 161 (1933).

(11) (a) H. C. Brown and M. Gerstein, THIS JOURNAL, **72**, 2926 (1950); (b) D. H. Powers, Jr., Ph.D. Thesis, Brown University, 1955.

(12) (a) H. Dersin, *Ber.*, **54B**, 3158 (1921); (b) G. H. Coleman, G. M. Multins and E. Pickering, THIS JOURNAL, **50**, 2739 (1928).

(13) R. N. Boyd and R. H. Hansen, *ibid.*, **75**, 5896 (1953).

tically, the yields of IV in Table I should be multiplied by 100/75. This is a necessary assumption for the kinetic studies.

Acknowledgment.—The authors are indebted to Dr. John O. Edwards for valuable talks in connection with the kinetic studies reported in this paper.

Experimental[14]

Hydrolysis of 2,2-Dimethylethylenimine with Hydrochloric Acid.—The hydrolyses of 2,2-dimethylethylenimine tabulated were worked up in the same way, of which the following example with 1 *N* hydrochloric acid at 25° is typical.

Three hundred milliliters of 1.051 *N* hydrochloric acid was measured (and weighed) into a tared flask protected from atmospheric carbon dioxide and kept at 25° for several hours. Then 7.048 g. of 2,2-dimethylethylenimine[3] was added from a weight buret. At intervals over a four-week period, portions of about 25 ml. (weighed) were removed from the reaction mixture and titrated with sodium hydroxide to the methyl orange end-point. The rate of disappearance of hydrogen chloride gave the rate of formation of 1-chloro-2-amino-2-methylpropane hydrochloride. The reaction was half complete in 15 hours and complete after six days; total yield 63.4%. By actual isolation from a portion of the solution the yield was 66%. The chloroamine hydrochloride crystallized when the water was evaporated to a small volume at room temperature.

The titrations were continued for four weeks to determine whether any hydrolysis of the chloroamine compound II occurred. The yield of 63.4% did not vary more than 0.1% during this period. At higher temperatures some hydrolysis of the chloramine was observed but the rate by which it hydrolyzed was very slow in comparison with the rate at which it was formed from the imine.

The amount of 1-amino-2-methyl-2-propanol formed during the reaction was determined by isolation of its *p*-bromobenzenesulfonamide derivative. A 25-ml. portion of the reaction mixture was made strongly basic with 20 ml. of 25% sodium hydroxide and shaken at 50–65° for 15 minutes with 4.2 g. of *p*-bromobenzenesulfonyl chloride. The 1-chloro-2-amino-2-methylpropane was converted under these conditions to the *p*-bromobenzenesulfonamide of 2,2-dimethylethylenimine[3] in 80% yield. This insoluble material was removed from the water solution by two extractions with 20 ml. of benzene. Acidification of the water layer and cooling gave the *p*-bromobenzenesulfonamide of 1-amino-2-methyl-2-propanol, m.p. 93–95°; yield, half reaction, 12%; complete reaction, 28%. A mixed m.p. of the recrystallized product with an authentic sample[3] was not depressed; m.p. 96.5–98.0°.

That 2-chloro-1-amino-2-methylpropane was not a precursor of the corresponding amino alcohol in this hydrolysis was shown in the following experiment. The 2-chloro-1-amino-2-methylpropane hydrochloride (0.44 g., 0.003 mole) was dissolved in 25 ml. of 1 *N* hydrochloric acid and kept at 62° for 27 hours. The solution was cooled and treated with base and *p*-bromobenzenesulfonyl chloride as described above. Only a trace of a base-soluble *p*-bromobenzenesulfonamide (<3%) was obtained.

2,2-Dimethylethylenimmonium Picrate.—Three grams of 2,2-dimethylethylenimine in 15 ml. of dry toluene was added dropwise to a stirred solution of 9.0 g. of picric acid in 100 ml. of dry toluene at 0–5° over 15 minutes. The imine picrate was collected, washed with toluene and then carbon tetrachloride and dried in a vacuum desiccator; m.p. 124–126°, but the melt only becomes clear at 160°; yield 11.9 g. (99%).

Anal. Calcd. for $C_{10}H_{12}N_4O_7$: C, 40.01; H, 4.03; N, 18.65. Found: C, 40.65; H, 4.21; N, 18.91.

Hydrolysis of 2,2-Dimethylethylenimmonium Picrate. A. With Water.—Six grams of 2,2-dimethylethylenimmonium picrate in 15 ml. of water was heated to boiling for five minutes. The solvent was evaporated at room temperature to half the original volume. The first crop of crystals was collected and the process repeated three times; total yield 6.05 g. (95%), m.p. 127–131°. Recrystallization from ethyl acetate raised the m.p. to 134–135° but last traces of water were not removed until the picrate was recrystallized twice from acetonitrile; m.p. 139.4–140.8°. The picrate made from an authentic sample of 1-amino-2-methyl-2-propanol had the same m.p. and showed no depression in a mixed m.p.

Anal. Calcd. for $C_{10}H_{14}N_4O_8$: C, 37.74; H, 4.44; N, 17.60. Found: C, 38.03; H, 4.57; N, 17.41.

B. With Hydrochloric Acid.—The hydrolyses of 2,2-dimethylethylenimmonium picrate were all worked up in the same manner regardless of the concentration of acid used or the reaction temperature. The following experiment is typical.

The picrate (6.35 g., 0.021 mole) was covered with 30 ml. of concentrated hydrochloric acid at 30° and allowed to stand overnight. The picric acid was removed and washed with 5 ml. of ice-water. The water solution was extracted with 20-ml. portions of toluene (generally three) until the toluene was colorless, an indication that picric acid was extracted. The water was evaporated from the hydrochloride solution at room temperature until a volume of about 2 ml. was attained. Upon cooling in ice, some 1-chloro-2-amino-2-methylpropane hydrochloride was obtained. Careful removal of a small amount of water from the mother liquor in two successive evaporations in a vacuum desiccator gave a total yield of 1.81 g., m.p. 190–192°. The mother liquor was taken to dryness in a vacuum desiccator. The residue, 1.15 g., was dissolved in 10 ml. of chloroform and 10 ml. of carbon tetrachloride was added, precipitating an additional 0.41 g. of the 1-chloro-2-amino-2-methylpropane hydrochloride II of the same m.p.; total yield, 74%.

Adding 10 ml. more of carbon tetrachloride gave 0.36 g. of material of m.p. 170–190° (mostly compound II) and evaporation of the chloroform–carbon tetrachloride solution left 0.36 g., 12%, of 2-chloro-1-amino-2-methylpropane hydrochloride, m.p. 155–160° (see below). The compound was identified as the picrate, m.p. 156–159°, and the benzamide,[12a] m.p. 93–95°.

The analytical sample of 1-chloro-2-amino-2-methylpropane hydrochloride was obtained after two recrystallizations from chloroform, m.p. 192.0–194.0°.

Anal. Calcd. for $C_4H_{11}NCl_2$: C, 33.35; H, 7.70; N, 9.72. Found: C, 33.29; H, 7.77; N, 9.70.

Jones[15] reported this compound, m.p. 205–207°, but in the same paragraph 2-amino-2-methyl-1-propanol hydrochloride was reported with m.p. 195–196° and the two may have been interchanged since the latter has been reported[16] with m.p. 203–206°. We have verified the report of J. H. Jones.

The 1-chloro-2-amino-2-methylpropane hydrochloride was identified by conversion to the benzamide using pyridine as the base in a Schotten–Baumann reaction; m.p. 83–84°. This established the structure of the chloroamine compound since Coleman[12b] had synthesized it by an independent path. When 1-chloro-2-benzamido-2-methylpropane was warmed slowly above its melting point (to 95°) it resolidified and melted at 147–150°. This 4,4-dimethyl-2-phenyl-2-oxazoline hydrochloride gave a picrate, m.p. 130.0–130.5°,[13] which was not depressed in a mixed m.p. with an authentic sample made from the oxazoline. The oxazoline was obtained by thermal dehydration of 2-benzamido-2-methyl-1-propanol.[17]

2-Chloro-1-amino-2-methylpropane Hydrochloride.—Dersin's[11] method of preparing 2-chloro-1-amino-2-methylpropane hydrochloride was improved in the following way. 1-Amino-2-methyl-2-propanol (1.33 g., 0.015 mole) was dissolved in 13 ml. of concentrated hydrochloric acid and was then saturated with hydrogen chloride at 0°. This fuming hydrochloric acid solution was sealed in glass and heated to 100° for 70 minutes. (Longer heating caused deammoniation.) Evaporation of the solution on a steam-bath gave purple crystals which were carefully dried *in vacuo*. The hydrochloride was dissolved in 100 ml. of chloroform to separate a small amount of ammonium chloride and precipitated with 125 ml. of anhydrous ether; yield 1.49 g. (69%), m.p. 175°. Sublimation at 130° (0.4 mm.) gave an analytical sample, m.p. 184.0° dec. Dersin reported 183° but gave no analysis.

(14) Melting points given to tenths of a degree are corrected. Analyses by S. M. Nagy, Microchemical Laboratory, Massachusetts Institute of Technology, Cambridge, Mass.

(15) G. D. Jones, *J. Org. Chem.*, **9**, 484 (1944).

(16) J. H. Jones, *J. Assoc. Official Agr. Chem.*, **27**, 467 (1944); *C. A.*, **38**, 6275 (1944).

(17) P. F. Tryon, U. S. Patent 2,368,073 (1945).

Anal. Calcd. for $C_4H_{11}NCl_2$: C, 33.35; H, 7.70; N, 9.72. Found: C, 33.57; H, 7.74; N, 9.92.

By treatment of 1-amino-2-methyl-2-propanol with 12 *N* hydrochloric acid at the boiling point for one hour no 2-chloro-1-amino-2-methylpropane was formed.

2-Chloro-1-amino-2-methylpropane Picrate.—The picrate of 2-chloro-1-amino-2-methylpropane was prepared in 79% yield by neutralizing a solution of the corresponding hydrochloride with sodium picrate solution; m.p. 166–167°. One recrystallization from water gave an analytical sample, m.p. 169.0–170.0°. Dersin[12c] reported the m.p. 159° and gave no analysis.

Anal. Calcd. for $C_{10}H_{13}N_4O_7Cl$: C, 35.67; H, 3.89; N, 16.64. Found: C, 35.82; H, 4.01; N, 16.35.

1-Chloro-2-amino-2-methylpropane Picrate.—The picrate of 1-chloro-2-amino-2-methylpropane was prepared in 78% yield in like manner. Two recrystallizations from water gave an analytical sample, m.p. 177.0–178.0°. A lower melting point was obtained by recrystallization from ethanol.

Anal. Calcd. for $C_{10}H_{13}N_4O_7Cl$: C, 35.67; H, 3.89; N, 16.64. Found: C, 35.81; H, 4.00; N, 16.77.

Determination of Rate Constants.—The rates of formation of 1-chloro-2-amino-2-methylpropane (II) and 1-amino-2-methyl-2-propanol given in Table I were determined on the assumption that the formation of these two compounds was the only reaction consuming 2,2-dimethylethylenimine in its hydrolysis with 1 *N* hydrochloric acid. The percentage of chloroamine II was determined accurately by titration with sodium hydroxide to a methyl orange end-point (within 1%) and the remainder was presumed to be amino alcohol IV. The validity of the analytical method was tested on the two pure chloroamines II and III. When either of these hydrochlorides was dissolved in hydrochloric acid the excess acid was accurately measured by the end-point of methyl orange with sodium hydroxide solution.

From the product ratio and the per cent. chloroamine formed at each point, the total rate of disappearance of 2,2-dimethylethylenimine was determined for each reaction. The validity of the method was demonstrated by plotting, as for a single first-order reaction, the logarithm of the per cent. imine remaining in solution against time. These data gave straight lines for the reactions run at 35° or lower and only a slight curvature for the reaction at 62°.

The first-order rate constant for the total reaction is given by

$$k_T = \frac{2.303}{t} \log \frac{C_0}{C} = \frac{2.303}{t} \log \frac{100}{P}$$

where C_0 is initial concentration of imine and C is concentration at the time t, for which P, per cent. imine remaining at time t, may be substituted. The rate constant, k_T, then is the slope of the line obtained by plotting log P against t. If now the per cent. yield of each product is a measure of its rate contribution, then $k_T = k_{Cl} + k_{alc}$.

Activation energies for the two reactions were calculated by the method of least squares from the rate constants at four temperatures in 1 *N* acid.

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Reactions of Ethylenimines. VI. Picrates

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The picrate of 2,2-dimethylethylenimine (I) rearranges upon heating in inert solvents into the picramide (IV) of 1-amino-2-methyl-2-propanol. Alcohols and phenol acting on the ethylenimine picrates open the imine ring at the more substituted carbon to give β-amino ethers, of the type $R_1R_2(R_3O)CCH_2NH_2$. The aliphatic β-aminoethers may be recovered from the corresponding picrates in 54–83% yields.

The ethylenimine ring has been found to open in the presence of weak acids such as thiophenol,[2] phenols[3] and benzoic acids[4] but forms a stable picrate[5] in non-protonic solvents.

In attempting to purify the picrate of 2,2-dimethylethylenimine by recrystallization from various solvents it was found that the product melted at a constant point (124–126°) but the melt was always opaque until a temperature of 160° was reached. Further investigation revealed that the picrate I rearranged on heating to the picramide of 1-amino-2-methyl-2-propanol (IV) (m.p. 160°). In polar solvents such as acetonitrile and nitromethane, the 2,2-dimethylethylenimmonium picrate (I) rearranged to the extent of 40% and only slightly less in ethyl acetate or methyl ethyl ketone. The picramide IV was identified by direct synthesis from 1-amino-2-methyl-2-propanol and picryl chloride.

No new theory seems necessary to account for this rearrangement. Isolation of ether picrates of type V suggests the ether II as a logical intermediate in the present case. Migrations from O to N by acyl groups through a heterocyclic five-membered ring are well established in the literature.[6] By analogy, the picryl group which resembles an acyl group in many ways could participate in the five-membered heterocyclic intermediate III in the path to the picramide IV.

Alternatively, the rearrangement may be considered as one of the Smiles[7] type as exemplified in the work of Roberts.[8] However, only amino diaryl ethers have been reported to take part in Smiles rearrangements.

When the picrate of 2,2-dimethylethylenimine was refluxed in a reacting solvent such as methanol or ethanol, ring opening by the alcohol[9] predominated over the rearrangement and amino ether picrates of type V were formed (Table I). No appreciable ring opening took place with *n*-propyl or isopropyl alcohols as solvents and the imine picrate was recovered unchanged in short heating periods. Upon prolonged heating in these solvents some re-

(1) (a) Taken in part from Senior theses for the Sc.B. degree, Brown University; (b) Edwin P. Anthony Fellow, 1952–1954.

(2) G. Meguerian and L. B. Clapp, THIS JOURNAL, **73**, 2121 (1951).

(3) L. B. Clapp, *ibid.*, **73**, 2584 (1951).

(4) D. H. Powers and V. B. Schatz, unpublished data, Brown University.

(5) V. B. Schatz and L. B. Clapp, THIS JOURNAL, **77**, 5113 (1955).

(6) See for example: E. E. van Tamelen, THIS JOURNAL, **73**, 5773 (1951); G. Fodor and J. Kiss, *ibid.*, **72**, 3495 (1950); *Acta Chim. Hung.*, **1**, 130 (1951); *J. Chem. Soc.*, 1589 (1952).

(7) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 362 (1951).

(8) K. C. Roberts and C. G. De Worms, *J. Chem. Soc.*, 727 (1931); K. C. Roberts, C. G. De Worms and H. B. Clark, *ibid.*, 196 (1935).

(9) D. S. Tarbell and D. K. Fukushima, THIS JOURNAL, **68**, 2499 (1946).