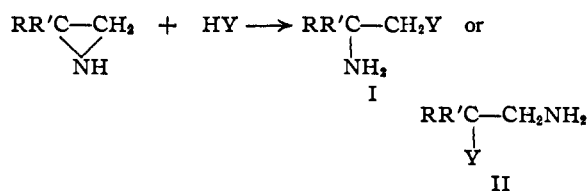[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY, BROWN UNIVERSITY]

Reactions of Ethylenimines: With Ammonia and Amines

BY LEALLYN B. CLAPP

Ammonia and amines[1] in aqueous solution react with imines to give α,β-diamines and polymeric substances. The reaction between ethylenimine and various amines to give N-substituted ethylenediamines has also been carried out under anhydrous conditions in the presence of aluminum chloride[2] as a catalyst. Coleman and Callen used aqueous reactions in working up the reaction mixtures, however, which introduces some obvious disadvantages. The present paper deals with the reactions of homologs of ethylenimine with amines and liquid ammonia in the presence of ammonium chloride as a catalyst at elevated temperature and pressure. The α,β-diamines, ethylenediamine, isobutylenediamine and 1,2-butylenediamine, which are very difficult to isolate completely free from water when prepared by wet methods, can be obtained in anhydrous condition by the present method. The yields are 55–68%.

When the three-membered ring in an unsymmetrically substituted ethylenimine breaks in the presence of a substance, HY, containing an active hydrogen, products of type I and II are possible.

$$\begin{array}{ccccc} RR'C\!\!-\!\!CH_2 & + & HY & \longrightarrow & RR'C\!\!-\!\!CH_2Y \quad \text{or} \\ \diagdown\!\!\diagup & & & & | \\ NH & & & & NH_2 \\ & & & & I \end{array}$$

$$\begin{array}{c} RR'C\!\!-\!\!CH_2NH_2 \\ | \\ Y \\ II \end{array}$$

A few such reactions are recorded in the literature. Hydrolysis of unsymmetrical C-substituted imines in acid solution gives products indicating a break in the ring at the tertiary carbon[3] rather than at the primary (or secondary[4]) carbon. In reactions other than hydrolysis (catalytic hydrogenation[5] and addition of hydrogen bromide[6]), the cyclic imine ring breaks at the primary carbon. It was found that when HY is a primary or secondary amine, the rupture is predominantly at the primary carbon, yielding product I, although some of type II was obtained in three cases (Table II).

Competition in the addition of HY to the imine is furnished by molecules of the imine itself, the result of which is a polymer. Polymerization becomes important when the reaction between an imine and liquid ammonia is allowed to proceed at room temperature (Table I). It was reduced to a

minimum by more rapid reactions at elevated temperature and pressure.

Polymerization may terminate at the dimeric stage to form a piperazine. The work of Jones[7] on the mechanism of polymerization suggests a symmetrical piperazine.

Proof that the principal product in the reactions of imines and amines is of type I where Y is –NHR or –NRR' was obtained in the following way. When morpholine was treated with 2-ethylethylenimine, the only product isolated was shown to be N-β-aminobutylmorpholine by synthesizing it by a series of known reactions. Formaldehyde and morpholine were condensed to methylolmorpholine, which then condensed with 1-nitropropane by the method of Cerf de Mauny[8] to give N-β-nitrobutylmorpholine. This substance was reduced to the corresponding diamine. The N-β-aminobutylmorpholine prepared by the two methods gave the same phenylthiourea.

When 2,2-dimethylethylenimine was treated with 2-amino-2-methyl-1-propanol, the product was N-2-(β-aminoisobutylamino)-2-methyl-1-propanol. This was synthesized by the method of Senkus[9] and the phenylthiourea derivative in each case was the same compound.

In the reaction between aniline and 2,2-dimethylethylenimine, two products resulted, b. p. 110–111° (3 mm.) and 145–146° (3 mm.), respectively. The lower boiling compound is 2-amino-2-methyl-1-phenylaminopropane and the second compound is assumed to be 1-amino-2-methyl-2-phenylaminopropane. Johnson[10] has reported the first compound, b. p. 110° (3 mm.), 99° (1 mm.). Two products were also obtained in the reaction with 2-ethylethylenimine and aniline (also cyclohexylamine) and are assumed to bear a like relation to each other.

These last three cases indicate that the product of type (I) is only the predominant one and not the exclusive product in the reaction of an amine and an imine.

Only traces of products were found in the reactions between 2,2-dimethylethylenimine and diethylamine, di-n-butylamine and n-dodecylamine. Probably there is not enough room for the secondary amino nitrogen of diethylamine and di-n-butylamine to approach the primary carbon of the imine (where the bond is to be ruptured) and hence no reaction takes place at all. Added import is given to this view from the fact that the expected products are readily synthesized from a condensation of the secondary amine, formaldehyde, and

(1) Wilson, U. S. Patent 2,318,729 (1943), U. S. Patent 2,318,730 (1943).

(2) Coleman and Callen, THIS JOURNAL, 68, 2006 (1946).

(3) Cairns, ibid., 63, 871 (1941).

(4) Campbell, Campbell, McKenna and Chaput, J. Org. Chem., 8, 103 (1943).

(5) Karabinos and Serijan, THIS JOURNAL, 67, 1856 (1945); Campbell, Sommers and Campbell, ibid., 68, 140 (1946).

(6) Gabriel and Ohle, Ber., 50, 804 (1917).

(7) Jones, J. Org. Chem., 9, 484 (1944).

(8) Cerf de Mauny, Bull. soc. chim., [5] 4, 1460 (1937).

(9) Senkus, THIS JOURNAL, 68, 10 (1946).

(10) Johnson, ibid., 68, 14 (1946).

2-nitropropane to a nitroamine, followed by a catalytic reduction.[11] Johnson[10] suggests that the nitroamine is formed, first, by a condensation of the amine and formaldehyde to a methylolamine succeeded by a second condensation to form the nitroamine. These reactions are not subject to the steric effects pictured for the rupture of the imine ring.

When the imines were heated with amines without ammonium chloride present, essentially all the original imine was recovered. The imines alone in the presence of ammonium chloride at 100° for one week gave polymers having properties described by Jones.[7]

Experimental

1,2-Butylenediamine.—Thirty-five grams of 2-ethylethylenimine[12] with 5.3 g. of ammonium chloride and 500 cc. of liquid ammonia were heated in an iron bomb (capacity, 3 liters) by an air-bath to 100 ± 2° for fifty-one hours (maximum gage pressure, 800 lb., in about five hours). After the excess ammonia was allowed to boil away (carrying about 5 g. unreacted imine along), the reaction mixture was distilled rapidly from the dissolved ammonium chloride. The distillate was then fractionally distilled through an insulated bubble-cap column (4 bubble caps). One gram of unreacted imine, 19 g. of pure 1,2-butylenediamine, b. p. 140° (55% yield), 1 g. of an oil, b. p. 160–240°, and 2 g. of residue, were obtained.

It is concluded from results of other reactions carried out in similar manner (Table I) that the best yields of α,β-diamines obtain under the following conditions: temperature 100°, a forty-fold excess of liquid ammonia, about 0.2 mole of catalyst per mole of imine, and more than twelve hours heating time.

The head of the iron reactor was sealed with a lead washer and was also equipped with a thin iron blow-out patch obtained from the American Instrument Company. The system was similar in construction to the type which may be purchased from that company.

TABLE I
REACTIONS OF RR'C—CH₂ WITH LIQUID AMMONIA[a]
$$\mathrm{RR'C\!\!-\!\!CH_2 \atop \diagdown N\!H\diagup}$$

R	R'	Wt. of imine. g.	NH₄Cl. g.	Time. hrs.	Temp., °C.	Max. pressure. lb.	Recovered imine. %	Diamine. %	Polym.[b] %
H	H	35	8	40	100	740		55	24[c]
H	H	40	2	100	25	150		15	38[d]
Et	H	37	0.2	54	70	380	65	11	9
Et	H	28	5.3	50	70	430	40	14	45
Et	H	35	1	46	100	760	74	11	12
Et	H	35	5.3	51	100	800	4	55	10
Et	H	35	5.3	12	100	780	3	48	10
Et	H	36	8	72	25	150	8		87
Me	Me	35	1	100	25	135	3	7	74
Me	Me	35	8	46	100	800		68	16
Me	Me	40	8	46	100	640		58	27

[a] Five hundred cc of liquid ammonia was used in all reactions except the last where 250 cc. was used. [b] Percentage based on formula $\left(\mathrm{RR'C\!-\!CH_2 \atop \diagdown N\!H\diagup}\right)_n$. [c] Includes 19% diethylenetriamine. [d] Includes 20% piperazine.

The higher polymeric products obtained as designated in Table I from the reaction of ammonia with 2-ethylethylenimine were subjected to fractional distillation. Sixty-two grams of material, b. p. 150–255°, from the rapid distillation of the reaction mixture of ammonia and 2-ethylethylenimine was redistilled and various fractions collected. By a Kjeldahl nitrogen analysis, an estimate of the amount of nitrogen liberated with nitrous acid treatment, and/or the appearance of an insoluble nitroso compound, the probable content of these polymeric products was deduced: fraction b. p. 150–195°, mostly 1,2-butylenediamine; b. p. 195–235°, polymer and 2,5-diethylpiperazine; above 235°, polymer and a diethylenetriamine derivative.

A Diethylpiperazine.—From the fraction b. p. 195–235° just mentioned, 2 g. of a solid separated on standing at zero for several days. Three recrystallizations from acetone gave 0.5 g. of white crystalline plates, m. p. 87–89°, resembling piperazine in odor and crystalline character. It formed a white hydrochloride and an insoluble oily nitroso compound. This compound is probably 2,5-diethylpiperazine.

Anal. Calcd. for C₈H₁₈N₂: N, 19.70. Found: N, 19.56, 19.59.

Two-tenths gram of the piperazine was converted to the dibenzamide derivative, m. p. 167–168°.

Anal. Calcd. for C₂₂H₂₈N₂O₂: N, 7.99. Found: N, 8.13.

β-Nitrobutylmorpholine.—Using the method of Cerf de Mauny,[8] a condensation of methylolmorpholine and 1-nitropropane gave a 75% yield of β-nitrobutylmorpholine, b. p. 130–135° (10 mm.).

β-Aminobutylmorpholine. Method A.—The β-nitrobutylmorpholine was reduced to the corresponding diamine (following Cerf de Mauny[8] again) in alcohol using zinc amalgam[12a] and hydrogen chloride gas with a yield of 58%; b. p. 218–223°.

Method B.—Eight grams (0.11 mole) of 2-ethylethylenimine was sealed with 11 g. (0.15 mole) of morpholine and 0.1 g. of ammonium chloride in a glass tube and heated to 80° for twenty-four hours. The reaction mixture was distilled once rapidly from the solid ammonium chloride and then fractionally distilled through an insulated bubble-cap column (4 bubble-caps). The β-aminobutylmorpholine was collected, b. p. 220–222°; yield 8 g., 50%. With the same quantity of imine, a three-fold and a ten-fold excess of morpholine gave yields of 85 and 95%, respectively.

Phenylthiourea derivatives were made from portions of the products obtained by Methods A and B, which gave m. p.'s 138–139 and 140–141°, respectively. The mixed melting point gave no depression.

N-2-(β-Aminoisobutylamino)-2-methyl-1-propanol. Method A.—In the manner just described (Method B above) 9 g. of pure N-2-(β-aminoisobutylamino)-2-methyl-1-propanol was obtained, b. p. 233° (yield 20%)[13] from 25 g. (0.28 mole) of 2,2-dimethylethylenimine and 79 g. (0.9 mole) of 2-amino-2-methyl-1-propanol. After standing, the oil changed to a solid, m. p. 51–53°.

Method B.—N-2-(β-nitroisobutylamino)-2-methyl-1-propanol was prepared by the method described by Senkus.[8] Reduction of this compound at three atmospheres pressure of hydrogen with platinum oxide (Adams catalyst) gave 61% yield of N-2-(β-aminoisobutylamino)-2-methyl-1-propanol, b. p. 231–233°.

Phenylthiourea derivatives of the products from methods A and B gave m. p. 133–134° and 132–134°, respectively, and a mixed melting point gave no depression.

The results of other reactions between 25 g. of each of the two imines and a three-fold excess of various amines are shown in Table II, along with a number of derivatives and the analyses. The derivatives were all prepared by standard methods; the nitrogen analyses were run by the semi-

(11) Johnson, *ibid.*, **68**, 12 (1946).

(12) Imines were prepared by the method of Wenker, *ibid.*, **57**, 2328 (1935); see also refs. 3 and 7.

(12a) Adams, "Organic Reactions," Vol. I, p. 163.

(13) Mr. C. E. Schilling in this Laboratory increased the yield to 40% by carrying out the reaction at 108° for fifty hours.

TABLE II

α,β-DIAMINES (RR'CNH₂—CH₂NR''R''') AND THEIR DERIVATIVES

R''	R'''	Temp., °C	Time, hrs.	Yield, %	B. p., °C	n²⁰D	Formula	Nitrogen, % Calcd. Found	Phenylthiourea M. p., °C	Nitrogen, % Calcd. Found	Benzamide M. p., °C	Nitrogen, % Calcd. Found
							R = CH₃ R' = CH₃					
H	C₂H₅	80	41	42	140–141	1.4300	C₆N₁₆N₂	24.12 23.85			106–108ᶜ	8.35 8.15
H	n-C₄H₉	100	49	84	183–185	1.4345	C₈H₂₀N₂	19.43 19.19	104–105	15.04 15.01	105–106ᵇ	7.95 8.03
H	C₅H₁₁	100	50	82	230–230.5	1.4672	C₁₀H₂₄N₂	16.46 16.32	116–117	13.76 13.74	176–177ᵇ	7.40 7.42
C₄H₈O	(morpholine)	80	25	85	208–210	1.4677	C₈H₁₈N₂O	17.71 17.60	153–153.5	14.32 14.24	119–121	10.68 10.53
H	C(CH₃)₂CH₂OH	80	25	20	233.5ᵈ		C₈H₂₀N₂O	17.49 17.34	133–134ᵉ	14.23 14.21		
Hᶠ	C₄H₈	100	50	40	110–111ᵍ	1.5450	C₁₀H₁₄N₂	17.06 16.85	132.5–133	14.03 13.81	145.5–147ᵇ	7.52 7.30
ʰ	ⁱ			23	145–146ᵍ	1.5270	C₁₀H₁₄N₂	17.06 17.16			193–194	10.44 10.35
							R = H R' = C₂H₅					
H	H	100	51	55	140	1.4490	C₄H₁₂N₂	31.80 31.72	174ᵃ	15.63 15.50	186–187ᵇ	9.45 9.38
H	C₂H₅	80	25	20	156–157	1.4431	C₆H₁₆N₂	24.12 23.92	110–111	16.72 16.65	115–116ᵇ	8.64 8.71
H	n-C₄H₉	100	48	68	199–200	1.4422	C₈H₂₀N₂	19.43 19.17	105–106.5	15.04 14.80		
n-C₄H₉	n-C₄H₉	100	48	20	238–239	1.4463	C₁₂H₂₈N₂	13.99 13.82	54–55	12.53 12.42		
C₂H₅	C₂H₅	100	100	34	173	1.4347	C₈H₂₀N₂	19.43 19.20	73–74	15.04 15.02		
H	C₅H₁₁	100	50	55	242–244	1.4711	C₁₀H₂₄N₂	16.46 16.45	108–109.5	13.76 13.74	82–83ᵉ	7.20 7.41
ʲ				12	265–270	1.4832	C₁₀H₂₄N₂	16.46 16.45	148–148.5ᵃ	12.72 12.80		
C₄H₈O	(morpholine)	80	25	85	222	1.4660	C₈H₁₈N₂O	17.71 17.48	140–141	14.32 14.24		
H	CH(C₂H₅)CH₂OH	100	50	51	258–260	1.4706	C₈H₂₀N₂O	17.49 17.42	159.5–160ᵏ	11.19 11.01	185–186	7.60 7.50
H	C₁₃H₂₇	100	48	60	162–163ᵈ	1.4550	C₁₆H₃₆N₂	10.93 10.93			102–102.5	6.03 5.95
H	C₆H₅	100	100	19	125–126ᵍ	1.5491	C₁₀H₁₆N₂	17.06 16.92	118–119ᵃ	12.88 12.73	117–118ᵇ	7.52 7.47
ˡ				9	164–165ᵍ	1.5275	C₁₀H₁₆N₂	17.06 17.13	156–157	14.03 13.78		
CH₃	C₆H₅	120	100	14	124–125ˡ	1.5354	C₁₁H₁₈N₂	15.72 15.97	112–113	13.41 13.23	115–115.5	9.92 9.93

ᵃ Diphenylthiourea. ᵇ Dibenzamide. ᶜ p-Bromobenzenesulfonamide. ᵈ M. p., 51–53°. ᵉ The phenylthiourea derivative of a sample of this compound obtained from Commercial Solvents Corporation through the courtesy of Dr. Murray Senkus gave a m. p. 133°. ᶠ Forms an oxalate, m. p. 190.5–191°. *Anal.* Calcd. for C₁₂H₁₈N₂O₄: N, 11.02. Found: N, 11.07. ᵍ Boiling point at 3 mm. ʰ Forms an oxalate, m. p. 225–226°. *Anal.* Calcd. for C₁₂H₁₈N₂O₄: N, 11.02. Found: N, 10.89. ⁱ Assumed to have the structure RR'C(NHC₆H₅)CH₂NH₂. ʲ Assumed to have the structure CH₃CH₂CH(NHC₅H₁₁)CH₂NH₂. ᵏ Oxalate. ˡ Boiling point at 5 mm.

micro Kjeldahl method; and all melting points were taken in a copper block with an ASTM thermometer calibrated for 40-mm. immersion.

Summary

1. An improved method of preparing anhydrous α,β-diamines (both amine groups primary) has been found.

2. A number of α,β-diamines (one amine group primary and the other secondary or tertiary) and their derivatives have been prepared.

3. It has been shown that cyclic ethylenimine rings rupture preferentially but not exclusively at the primary carbon atom in the presence of amines and ammonium chloride, an acid catalyst.

PROVIDENCE, R. I.

Allyl Esters of Phosphonic Acids. I. Preparation and Polymerization of Allyl and Methallyl Esters of Some Arylphosphonic Acids

By A. D. F. TOY

The use of organic esters of phosphoric acid as plasticizers for various resins is well known. These phosphorus containing esters have been of special importance because they not only are good plasticizers, but also impart a certain degree of flame resistance to the resins with which they are used. All these esters are incorporated with the resin as physical mixtures, but their usefulness is probably due to the fact that they serve as excellent hydrogen bonding agents.[1] It was thought to be of interest to study some phosphorus compounds which are not only plasticizers, but which (a) by themselves are capable of undergoing the process of polymerization into a resin or (b) upon mixing with other polymerizable monomers are capable of

actually copolymerizing with and modifying the latter. Certain allyl esters of phosphoric acid, and substituted phosphoric acids, have been found to be modifiers for compounds such as styrene through copolymerization.[2] These compounds have been suggested for use in the preparation of polymeric materials.[3]

In our study of the chemistry of the esters of the organic phosphonic acids it has been noted that these substances are significantly different in many respects from the corresponding trisubstituted alkyl and aryl phosphates. For example, dioctyl benzenephosphonate possesses a somewhat higher thermostability than trioctyl phosphate. Likewise

(1) Audrieth and Toy, THIS JOURNAL, 64, 1553 (1942).

(2) Britton and Marshall, U. S. Patent 2,186,360 (1940).

(3) Whitehill and Barker, U. S. Patent 2,394,829 (1946).