being used during distillation of the selenide. The yields are approximately 80% with simple benzene derivatives.

(2) **By the Action of an Arylselenium Monobromide on a Mercury Diaryl.**—A solution containing 0.01 mole of arylselenium monobromide is prepared from 0.005 mole of bromine and 0.005 mole of the diaryldiselenide in 25–50-ml. of carbon tetrachloride. This solution is added slowly to 0.01 mole of the mercury diaryl contained in approximately 100 ml. of carbon tetrachloride, shaking the mixture frequently during the addition. Although the mercury diaryl does not dissolve completely in the quantity of solvent specified, this is immaterial since solution takes place as the reaction proceeds. The reaction is usually rapid but may be hastened by warming if desired. If the solution has a dark color after standing a few minutes, an excess of the bromide is indicated and a small amount of the mercury diaryl should be added until no more than a slight red or brown color remains. A nearly quantitative precipitation of arylmercuric bromide accompanies the reaction. After standing for about an hour, the solution is filtered and the filtrate distilled, using reduced pressure during distillation of the selenide. If the selenide is a solid, distillation is unnecessary, in which case the carbon tetrachloride is driven off and the solid is recrystallized from methanol. The yields are nearly quantitative and fall short of 100% only through losses in handling and purification.

Purification of Unsymmetrical Selenides.—Solid selenides are conveniently purified by recrystallization from methanol. Liquid selenides may be distilled at reduced pressure but purification is more conveniently accomplished by conversion to the dibromide, or, where this compound is unstable, to the dichloride, followed by recrystallization from carbon tetrachloride. Dibromides are reduced back to selenides by dissolving in acetone[12] followed by the addition of water after the solution has become colorless, causing the separation of the selenide as a colorless oil. Dichlorides are reduced by means of powdered zinc in carbon tetrachloride or by refluxing with aqueous sodium sulfite–sodium carbonate solution.

The dihalides of unsymmetrical selenides tend to be less stable, lower melting and more soluble than those of symmetrical selenides and show a greater tendency to form supersaturated solutions. A more difficult problem of isolation and purification is therefore presented.

The validity of the new methods was established through the synthesis of seven known and four new selenides. The known selenides included di-*p*-tolyl, 4-bromodiphenyl, 4-methyldiphenyl, 4-methoxydiphenyl, phenylbutyl, phenylbenzyl and di-α-naphthyl. These were identified by means of their melting points as well as by the melting points and equivalent weights[1] of their dihalides. The melting points agree with literature values within 1° in all cases except for 4-methyl-diphenylselenium dibromide where decomposition makes an accurate determination difficult. The equivalent weights show a maximum deviation of 1.1% in the case of the unstable phenylbutylselenium dibromide and a mean deviation of 0.4% from theoretical values. The new selenides include **4-chloro-4′-methyldiphenyl**, m. p. 72–3°, m. p. dibromide 120°; **3-chlorodiphenyl**, b. p. 200–205° (28 mm.), m. p. dichloride 102–104°; **2-phenyl-4′-methyldiphenyl**, m. p. 80°, dichloride decomposes with evolution of HCl at ∼160° and **phenyl-α-naphthyl** selenide, b. p. 180° (1 mm.). The equivalent weights of the dihalides showed a maximum of 1.1% deviation in the case of the unstable phenyl-α-naphthylselenium dichloride and a mean deviation of 0.5%.

In a number of cases selenides were synthesized by use of both of the new methods and identity of products established by mixed melting points.

Summary

Two new methods for the synthesis of unsymmetrical selenides are described. One method involves the action of a diselenide on a Grignard reagent, the other interaction of an arylselenium monobromide with a mercury diaryl. The yields in both cases are for the most part quite good and the products easily isolated. The methods were validated by synthesis of eleven selenides including four new compounds for which physical constants are given.

LOS ANGELES 24, CALIF. RECEIVED JULY 17, 1945

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(12) H. M. Leicester, THIS JOURNAL, **57**, 1901 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WEST VIRGINIA UNIVERSITY]

Pyrolysis of Some Polyethylene Amines

BY WILLIAM M. HUTCHINSON,(1) A. R. COLLETT AND C. L. LAZZELL

In the commercial preparation of ethylene diamine by such reactions as 1,2-dichloroethane and ammonia there are also formed many other compounds, including diethylenetriamine, triethylenetetramine, tetraethylenepentamine and other similar compounds of higher molecular weights. The lower members of this series are separated by distillation, leaving as a residue a mixture of high boiling amines, known as "amine residue." The work described in this article was undertaken for the purposes of determining whether it were possible to convert these higher amines into ethylenediamine by pyrolysis.

This "amine residue," obtained from the Carbide and Carbon Chemicals Corporation, and dried for twenty-four hours over fused potassium hydroxide, was used as the basic material for this investigation. By use of vacuum distillation, molecular distillation and fractional crystallization of the picrates, it was found that this mixture contained about 10% triethylenetetramine; about 25% tetraethylenepentamine and over 30% pentaethylenehexamine. The remaining constituents were unidentified.

Experimental

The results reported in this paper are those obtained by pyrolysis studies carried out with the "amine residue" in the apparatus shown in Fig. 1. The "amine residue" was heated in a 500-cc. flask (h) and the vapors flowed through a tube (i), 1.0 × 55 cm., wound with 24-gage resistance wire and with suitable asbestos insulation. The temperature of the vapors was measured with a 360° thermometer (c) placed in a 2.0 × 15 cm. tube (k) insulated with one inch asbestos pipe covering. The gases were cooled in passing through tube (j), 1.0 × 41.0 cm., on which the degree of insulation was varied to avoid flooding the fractionating column (d). This column, 2.0 × 72.0

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cm., was packed with $^1/_8$-inch glass helices and jacketed with one-inch pipe covering over asbestos paper. The still head was a total condensation, partial take-off type with trough, dephlegmator (b), capillary take-off with stopcock (m) and thermometer (c'). The distillate was caught in adapter (o). Reflux from the column was returned to flask (h) through trap (f) in the 2.0 × 45 cm. tube insulated with two layers of asbestos paper. Noncondensable gases passed through an 0.8-cm. diameter tube (p) into two 500-cc. wash-bottles, the first of which served as a trap while the second was two-thirds full of dilute hydrochloric acid. Non-basic gases were caught by displacing water from one aspirator bottle into another.

Standard taper joints were used at (g) and (e) for flexibility and rubber stoppers were used at (a), (l) and (n). Other than the soft glass thermometers everything in contact with the hot amines was made of Pyrex glass.

A number of pyrolyses have been carried out in the apparatus described. A typical pyrolysis that yielded a high percentage of ethylenediamine is given below: One hundred and ninety-two grams of dried "amine residue" was placed in the pyrolysis flask and heated with a bare, luminous flame from a Meker burner. It began to boil at about 230° and during the pyrolysis the temperature increased to about 400°.

When the cracking chamber (k) was filled with vapor its temperature was adjusted to 400° by passing a regulated current through the heating coil.

The time consumed in the pyrolysis depended upon the reflux ratio of the column. In this case it was about 1 to 50. After two hours the first drop of distillate was collected and, after three and one-half hours, 25 g. of water had been collected. Up to this time the distillation temperature was 99°. From this point it varied from 135 to 160°, depending on slight changes in the reflux ratio. The temperature of the vapors issuing from the heating tube ranged from 310 to 330°. After seventeen and one-half hours a total of 149.5 g. of condensed distillate had collected, and only a little residue remained in the pyrolysis flask. Upon cooling, piperazine solidified throughout the column and tubing below it.

Of the total condensed distillate 25 g. was water. Fifty-seven and one-half grams of the remaining 124.5 g. of pyrolysis product was distilled through an electrically lagged, Vigreux[2] column (1.5 × 100 cm.) with a Whitmore-Lux[3] total condensation, partial take-off still head. The composition of the pyrolysis product was determined by the weight of the fractions. These fractions were further purified by fractionating through a 0.6 × 30 cm. unpacked column insulated with an evacuated glass jacket which was silvered on the inside surface.

TABLE I

Fraction, °C.	Substance	Fraction in condensed distillate, g.	% of anhyd. amine residue	% of dried[a] amine residue
Non-basic gas	Hydrogen	..	0.17	0.15
	Nitrogen	..	.17	.15
Basic gas	Ammonia	..	1.2	1.0
	Ethylamine	..	9.9	8.6
	Water	25	...	13
110–115	Impure, ethylenediamine	3.0	1.8	1.6
115–118	Ethylenediamine	46.0	27.6	24.0
118–145	Mixture	2.0	1.2	1.0
145–166	Piperazine	10.4	6.2	5.4
166–203	Mixture	3.0	1.8	1.6
203–248	Mixture	6.3	3.8	3.3
Residue from fractionation		54.2	32.4	28.2
Residue from pyrolysis (calcd.)		..	13.8	12.0

[a] Dried "amine residue" released 13% of its weight as water at the beginning of pyrolysis.

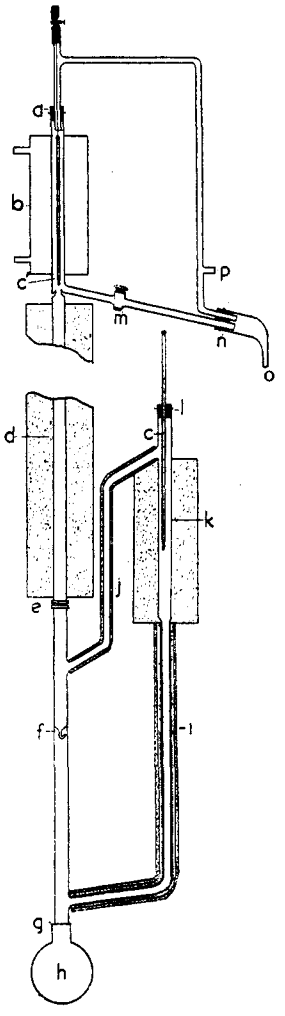

Fig. 1.

The uncondensed, basic gases were recovered as hydrochlorides and the amine hydrochlorides separated from ammonium chloride with absolute alcohol. The nonbasic gases were analyzed by the Orsat adsorption method.

The results of the above pyrolysis are given in Table I.

Discussion of Results

Since all the products separated from the above pyrolysis are well known, the identification procedure will not be discussed. However, in other pyrolyses with the fractionating column operating at a lower reflux ratio some of these higher boiling fractions could be separated and identified. Their formation was at the expense of ethylenediamine.

In a pyrolysis carried on for eight hours with a reflux ratio of 1 to 20, about 8% of the dried amine residue was converted into diethylene triamine, 15% into a fraction boiling at 208.5°, and about 5% into a fraction boiling at 248°. The following fractions could not be identified by physical properties nor by derivatives.

The fraction boiling at 208.5° had d^{25}_4 0.9691, n^{25}_D 1.4878, and a picrate decomposing at 196°. Its composition corresponded with that calculated for 1,2-di-(N-piperazyl)-ethane:

Anal. Calcd.: C, 60.6; H, 11.1; N, 28.3; 1° amino N, none. Found: C, 60.1; H, 11.3; N, 28.1; 1° amino N, none. Eq. wt. of picrate by reduction with $TiCl_3$: calcd. 15.4; found 15.4. *MR* calcd. 59.7; found 59.0.

The fraction boiling at 248° had d^{25}_4 0.9675, n^{25}_D 1.4966 and a picrate decomposing at 223°.

Anal. Calcd. for 1,4-di-(2-aminoethyl)-piperazine: N, 32.5; 1° amino N, 16.3. Found: N, 32.3; 1° amino N, 16.6. *MR* calcd. 52.3; found 52.1. This compound is reported[4,5] as melting at 40–41°, its hydrate at 63°, the dibenzoate as melting at 207–208° and the picrate at 220°. A solid benzoate could not be prepared from our sample neither did the amine exhibit a solid form or solid hydrate at room temperature. Perhaps this was due to impurities.

Pyrolysis of tetraethylenepentamine in the above apparatus resulted, with comparable runs, in some decrease in ethylenediamine, an absence of the 208.5 and 248° fractions and the formation of new fractions boiling at 210.5 and 233.5°. About 10% of tetraethylenepentamine was converted into the 210.5° fraction, about the same percentage into diethylenetriamine, and about 5% into the 233.5° fraction.

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[2] H. Vigreux, *Bull. soc. chim.*, **15**, 682 (1914).

[3] F. C. Whitmore and A. R. Lux, THIS JOURNAL, **54**, 3448 (1932).

[4] Kramer, *Chem. Zentr.*, **42**, I. 1532 (1910).

[5] A. P. N. Franchimont and Kramer, *Rec. trav. chim.*, **31**, 40–75 (1912).

The following fractions could not be identified by their physical properties nor by their derivatives: The fraction boiling at 210.5° had d^{25}_4 0.9525, n^{25}_{D} 1.4878, a picrate and a phenyl urea melting at 202 and 221°, respectively.

Anal. Calcd. for ethyl-di-(2-aminoethyl)-amine: N, 32.1; 1° amine N, 21.4; N of phenyl urea 18.9. Found: N, 32.1; 1° amine N, 21.4; N of phenyl urea, 18.3. Specific dispersion did not indicate unsaturation. *MR* calcd., 41.1; found, 39.8.

The fraction boiling at 233.5° had d^{25}_4 0.997, n^{25}_{D} 1.5098 and a picrate decomposing at 208°.

Anal. Calcd. for 1-[N-(2-aminoethyl)-2-aminoethyl]-pyrroline: N, 27.0; 1° amino N, 9.00. Found: N, 26.9; 1° amino N, 9.00. The double bond was indicated by its specific dispersion of 155 instead of the usual 120. *MR* calcd. 47.9; found: 46.5.

The products isolated are the type that would be expected from the splitting of the C–N linkage in the primary reaction. Piperazine derivatives might be expected as products in this kind of pyrolysis due to their stability and volatility. They are relatively more volatile than the corresponding linear polyethylene amines.

Summary

Pyrolyses of "amine residue" in the apparatus described has been found to yield as high as 24% ethylenediamine. Higher boiling fractions consisting mainly of cyclized amines can be formed in yields of 5 to 15% at the expense of ethylene diamine yield.

Analyses and physical properties indicate that some of the other fractions are diethylene triamine, 1,2-di-(N-piperazyl)-ethane, and 1,4-di-(2-aminoethyl)-piperazine.

Pyrolysis of tetraethylenepentamine yielded somewhat similar results but two of the above products did not appear while two new fractions were formed. Analyses and physical properties indicate that these were ethyl-di-(2-aminoethyl)-amine and 1-[N-(2-aminoethyl)-2-aminoethyl]-pyrroline.

MORGANTOWN, WEST VIRGINIA
RECEIVED SEPTEMBER 10, 1945

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

The Condensation of Diethylamine and Formaldehyde with Phenol, *o*-, *m*- and *p*-Cresols[1]

BY GERALD F. GRILLOT AND WILLIAM T. GORMLEY, JR.[2]

Studies of the Mannich reaction in which a variety of phenols were condensed with formaldehyde and secondary amines such as dimethylamine[3] or piperidine[4] have been reported, but we have been unable to find in the literature[5] any reference to the interaction of a phenol with formaldehyde and diethylamine. The latter amine appears to be less reactive than certain other secondary amines.[5]

The authors have been successful in the condensation of phenol and *o*-, *m*- and *p*-cresol with formaldehyde and diethylamine. When about equimolar quantities of the reacting materials were employed, 2-diethylaminomethylphenol, 6-diethylaminomethyl-2-methylphenol, 2- or 6-diethylaminomethyl-3-methylphenol and 2-diethylaminomethyl-4-methylphenol, respectively, were formed. When an excess of diethylamine and formaldehyde was condensed with phenol, 2,6-di-(diethylaminomethyl)-phenol was isolated. Although the position of the entering diethylaminomethyl group was not determined, it has been assumed, in view of the experiments of Décombe[3b] with dimethylamine, that the substituent entered the benzene ring in a position ortho to that of the phenolic hydroxyl group.

Experimental

2-Diethylaminomethylphenol.—General Procedure. Diethylamine (13.4 g., 0.18 mole) was added dropwise with stirring to 15.7 g. (0.17 mole) of pure phenol. The temperature was kept below 20° during this addition and was maintained in the same range while 15.8 g. of formalin (35–40% formaldehyde solution, 0.18 mole of formaldehyde) was added drop by drop. When about half of the formalin had been added, the reaction mixture separated into an oily and an aqueous layer. The mixture was allowed to stand for one hour at about 20° and was then warmed for two hours on a water-bath at about 80°.

The oily layer was extracted with ether and the ether was evaporated. Low-boiling impurities were removed by warming the residue to 80° at a pressure of about 17 mm. The pale amber oil boiled at 63–67° (1–2 mm.); yield 21 g. (68.6%); d^{25}_4 0.9780; n^{25}_{D} 1.5108; *MR* calcd. 55.01; found 54.81.

Anal. Calcd. for $C_{11}H_{17}NO$: N, 7.82. Found: N, 7.85; 7.82.

2,6-Di-(diethylaminomethyl)-phenol.—Using the procedure described above, 51.1 g. (0.7 mole) of diethylamine and 60 g. (0.7 mole) of formalin were condensed with 18.8 g. (0.2 mole) of phenol. A fraction, b. p. 63–80° (1–2 mm.), yielded on redistillation 13 g. of 2-diethylaminomethylphenol, b. p. 63–67° (1–2 mm.).

In addition, there was obtained 12 g. (22.4%) of the disubstituted phenol boiling at 120–125° (1–2 mm.); d^{25}_4 0.9561; n^{25}_{D} 1.5120; *MR* calcd. 86.85; found, 84.05.

Anal. Calcd. for $C_{16}H_{32}N_2O$: N, 14.44. Found: N, 14.44.

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(1) Abstracted from the M. S. thesis of William T. Gormley, Jr., submitted in 1945.

(2) Present address: The William S. Merrell Co., Cincinnati, Ohio.

(3) (a) German Patent 92,309; (b) Décombe, *Compt. rend.*, **196**, 866 (1933); (c) Décombe, *ibid.*, **197**, 258 (1933); (d) Bruson and MacMullen, THIS JOURNAL, **63**, 270 (1941); (e) Caldwell and Thompson, *ibid.*, **61**, 765 (1939).

(4) (a) Hildebrandt, *Arch. für exp. Path. Pharmakol.*, **44**, 278 (1900); *Ber.*, **37**, 4456 (1904); (b) Auwers and Dombrowski, *Ann.*, **344**, 280 (1906).

(5) F. F. Blicke, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, chapter 10.