[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

POLYMERIZATION OF β,β'-DICHLORODIETHYLAMINE

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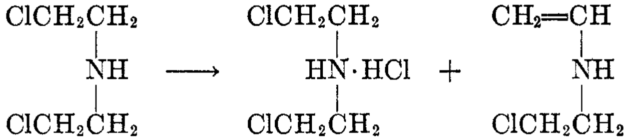
Although Ward (1) mentioned the conversion of β,β'-dichlorodiethylammonium chloride (II) to its free base (I) in terms which implied a reasonable stability for the latter compound, we have found that β,β'-dichlorodiethylamine (I) is extremely susceptible to decomposition. Only small amounts (15 g.) can be distilled without violent conversion to a charred solid. When a small distillate was obtained it began to solidify after two hours at room temperature; the reaction was complete in twelve days. This conversion could be accelerated to completion within two days with respect to the formation of β,β'-dichlorodiethylammonium chloride (II) if the amine was diluted with methanol. All the products were very soluble in water.

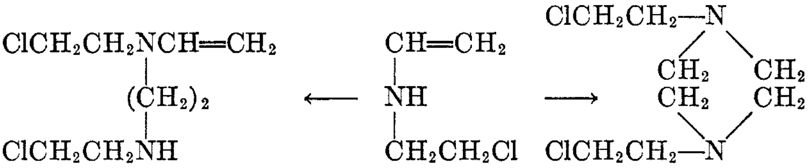
This reaction might be expected to follow the simple course:



I II III

but examination of the products failed to reveal the presence of β-chloroethylvinylamine (III), although β,β'-dichlorodiethylammonium chloride (II) was found in abundance. After ether extraction to remove an oil, which will be discussed later, the salt (II) was removed by elution with acetone. There remained a water-soluble solid which gave a positive test for chloride ion. According to its elemental analysis this latter salt must be the monohydrochloride of a dimer derived from N-β-chloroethyl-N-vinylamine (III).

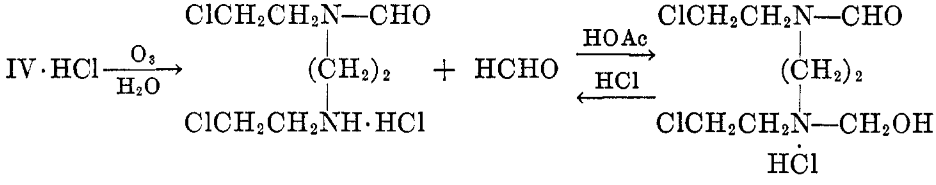
Several structures can be written for such a dimer:



IV III V

but the structure IV (as N,N'-*dis*-β-chloroethyl-N-vinyl-1,2-diaminoethane hydrochloride) is favored over that of di-β-chloroethylpiperazine (V). The latter compound ought to be strongly basic and thus form a dihydrochloride, but only the monohydrochloride was obtained. Furthermore the piperazine (V) should not give formaldehyde after ozonization although N,N'-*bis*-β-chloroethyl-N-vinyl-1,2-diaminoethane (IV) hydrochloride should yield this aldehyde. The fact that formaldehyde was obtained, even in the small yield of 5% of that theoretically possible confirms that IV is the structure of the dimer.

Certain difficulties in the ozonization procedure would seem to confirm that the dimer has structure IV. The ozonization of the salt has been carried out in formic acid. When this solvent is removed *in vacuo* and replaced by water, a qualitative test for formaldehyde (2) is obtained, but this disappears after a short time and indeed, cannot be obtained at all when the ozonide is decomposed slowly under reductive conditions (3). The reappearance of this formaldehyde was effected by boiling the aqueous solutions with hydrochloric acid. Since this is a treatment which might be expected to decompose a methylolamine, it is thought that the following sequence of reactions occurs during and after ozonization.



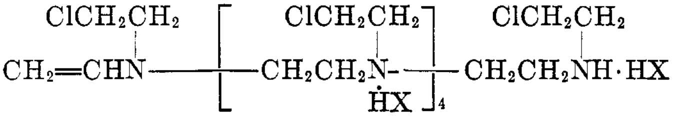
$$\mathrm{IV\cdot HCl} \xrightarrow[\mathrm{H_2O}]{\mathrm{O_3}} \begin{array}{c} \mathrm{ClCH_2CH_2N{-}CHO} \\ | \\ \mathrm{(CH_2)_2} \\ | \\ \mathrm{ClCH_2CH_2NH\cdot HCl} \end{array} + \mathrm{HCHO} \underset{\mathrm{HCl}}{\overset{\mathrm{HOAc}}{\rightleftarrows}} \begin{array}{c} \mathrm{ClCH_2CH_2N{-}CHO} \\ | \\ \mathrm{(CH_2)_2} \\ | \\ \mathrm{ClCH_2CH_2N{-}CH_2OH} \\ \cdot \\ \mathrm{HCl} \end{array}$$

VII

Since the methylolation reaction requires either a primary or a secondary amine, the tertiary amine (V) could not have partaken in this reaction sequence.

When the salt (IV as the monohydrochloride) was dissolved in water and treated with 40% sodium hydroxide and oil separated. When this oil was dissolved in acetone and treated immediately with hydrogen chloride, about a fourth of the salt of IV was regenerated, but when treatment with hydrogen chloride was delayed it was evident that the free base represented as IV had undergone a change.

Further evidence for this change was obtained from a solution of the oil in ether (in which it was not very soluble). When this ether solution was treated immediately with picric acid a picrate melting at 215–216° was formed. This picrate gave an analysis conforming closely to $C_{64}H_{63}Cl_6N_{21}O_{35}$. This would be the formula expected if the free base represented as IV would trimerize linearly, since the terminal β-chloroethylvinylamino linkage should be too weakly basic to form a salt. In consequence only a pentapicrate (VI), and not a hexapicrate, might be expected (In the formulation the picrate radical is denoted by X).



$$\begin{array}{c}\mathrm{ClCH_2CH_2}\\ |\\ \mathrm{CH_2{=}CHN{-}}\end{array}\left[\begin{array}{c}\mathrm{ClCH_2CH_2}\\ |\\ \mathrm{{-}CH_2CH_2N{-}}\\ \cdot\\ \mathrm{HX}\end{array}\right]_4\begin{array}{c}\mathrm{ClCH_2CH_2}\\ |\\ \mathrm{{-}CH_2CH_2NH\cdot HX}\end{array}$$

VI

Although the analyses are in closest agreement with the pentapicrate of the hexamer of β-chloroethylvinylamine (III), it is realized that some multiple other than 4 may be the correct one for structure VI.

Compound IV (N,N′-*bis*-β-chloroethyl-N-vinyl 1,2 diaminoethane) as hydrochloride was isolated as the residue after ether and then acetone extraction of the original reaction product. Evaporation of the ether left an oil. It was not very stable and it gradually became more viscous; the oily product was no longer soluble in ether and evidently had suffered advanced polymerization. However if the ether extract was treated immediately with picric acid an impure picrate was precipitated which, when purified, was identical with VI, the pentapicrate of the hexamer of β-chloroethylvinylamine. Identical treatment of the ether solution with styphnic acid also resulted in a precipitate which gave analysis expected for the pentastyphnate of the hexamer of β-chloroethylvinylamine.

The acetone extract from the reaction mixture was a mixture from which bis-β-chloroethylammonium chloride and the oil yielding the hexamer pentapicrate could be separated by evaporation of the acetone followed by extraction with cold ethyl acetate. The separation of these two components was effected by elution with ether in which the salt (II) was insoluble. That part of the mixture which was insoluble in ethyl acetate was a highly intractable oil of the same type obtained when the ether solution of the hexamer [corresponding to the salt (VI)] was allowed to stand.

It seems, therefore, that when bis-β-chloroethylamine is treated with alkali the original product is β-chloroethylvinylamine, but this compound is not isolable owing to its tendency towards polymerization. This polymerization stops at the dimer stage insofar as hydrogen chloride is available to stabilize the dimer as the salt of IV. However since part of the liberated hydrogen chloride will be consumed in re-formation of *bis*-β-chloroethylammonium chloride (II) the system is deficient with respect to salt formation. The free bases must then polymerize further, since a picrate or styphnate of the hexamer (VI) can be isolated. Likewise the heavy oils remaining after the identifiable products are isolated are evidently more highly polymerized.

If this mechanism is valid a decrease in the activity of hydrogen chloride should favor polymerization of the free bases. The decrease ought to be effected by the use of a hydroxylic solvent. This expectation was realized by solution of the *bis*-β-chloroethylamine in methanol. In this solvent the yields of *bis*-β-chloroethylammonium chloride (II), N,N′-bis-β-chloroethyl-N-vinyl-1,2-diaminoethane (IV hydrochloride), and the hexamer (VI) as its free base were each about 20 weight per cent of the whole, while the more highly polymerized material constituted 30 weight per cent of the whole leaving 10% unaccounted for. By contrast the decomposition without solvent yielded about 40 weight per cent each of II and IV while only a trace (0.3%) of the hexamer (VI) and only 10 weight per cent of the high polymer were obtained.

EXPERIMENTAL[1]

Bis-β-chloroethylammonium chloride. This salt was prepared essentially by Ward's method (1) in 70% yield and was crystallized from 98:2 ethanol–acetone. It melted at 214–217°.

Bis-β-chloroethylamine. Equimolecular quantities of *bis*-β-chloroethylammonium chloride (89.5 g., 0.5 mole) and aqueous sodium carbonate were mixed at 5° and the oil which separated was taken up in ether, washed with water, and dried with calcium sulfate. After vacuum distillation of the ether, the yellow oil (crude yield 86%) was distilled rapidly

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[1] All melting points are corrected against known standards.

at 75–80° (6 mm.). Some decomposition accompanied every distillation at this pressure, and it was usually violent and complete if more than 15 cc. was distilled at one time. The polymeric decomposition product is soluble in water. The distillate (50 g.; 70% of theoretical; n_D^{25} 1.472) could be preserved for at least a week at −80°, but at 25° decomposition with salt precipitation commenced after several hours.

Decomposition of bis-β-chloroethylamine. The polymerization of 8 g. (0.056 mole) of *bis*-β-chloroethylamine was complete in two days in methanol solution (21 grams per cc.) but twelve days at 25° were required when no solvent was used. In the polymerization without solvent the semi-solid was boiled with 100 cc. of ether. Evaporation of the ether left a non-volatile, non-distillable oil. With age this oil was no longer soluble in ether. If, however, the ether solution was treated immediately with picric acid in ether solution a crystalline precipitate separated, and could be removed by centrifugation. It weighed 0.067 g. (0.3% yield) and melted at 214–215° or 215–216° after wasteful crystallization from toluene. A comparable decomposition in methanol gave 2 g. (9.1% yield) of *pentapicrate*.

Anal. Calc'd for $C_{54}H_{63}Cl_6N_{21}O_{53}$: C, 36.4; H, 3.57; Cl, 11.9; N, 16.5.
Found: C, 36.4; H, 3.53; Cl, 11.8; N, 16.5.

The *styphnate* was prepared and purified in the same manner.

Anal. Calc'd for $C_{54}H_{63}Cl_6N_{21}O_{40}$: C, 34.8; H, 3.39; N, 15.8.
Found: C, 34.9; H, 3.37; N, 16.0.

These analyses indicate that there must have been present in the ether-soluble oil a hexamer of β-chloroethylvinylamine $[C_4H_8ClN]_6$ which formed a pentapicrate or a pentastyphnate.

The residue remaining after ether extraction was further extracted with 100 cc. of hot acetone to leave a solid. The extract was vacuum-evaporated and the residue extracted with unheated ethyl acetate to yield an oil. Repetition of this ether–acetone–ethyl acetate extraction finally left an oil which seemed to be a polymer similar to that which precipitated from the aged ether extract. This oil is believed to be a high polymer, $[C_4H_8ClN]_n$.

The substances soluble in ethyl acetate could be separated by ether extraction into the soluble fraction which yielded (VI), the pentapicrate or styphnate of hexameric β-chloroethylvinylamine, and an ether insoluble portion which was identified as *bis*-β-chloroethylammonium chloride (II) (m.p. 215–217°).

The white amorphous solid insoluble in acetone was a salt not identical with II. It was soluble in water and this solution gave a positive test with silver nitrate for chloride ion. It melted at 322–325°. Since no proper crystallizing medium could be found it was analyzed in this form. Polymerization without solvent gave a yield of 3.1 g. (38%) while polymerization in methanol yielded 2.3 g. (30%).

Anal. Calc'd for $C_8H_{17}Cl_3N_2$: C, 38.8; H, 6.93; Cl, 43.2; N, 11.3.
Found: C, 39.2; H, 7.0; Cl, 43.2; N, 11.5.

This salt was not very soluble in methanol. When 0.2 g. of salt was dissolved in aqueous picric acid, 0.4 g. of a *picrate* was formed. This picrate decomposed without melting at a high temperature. When the water solution of this N,N'-*bis*-β-chloroethyl-N-vinyl-1,2-diaminoethane hydrochloride (IV) was treated with 40% aqueous sodium hydroxide an oil appeared. When the oil was separated immediately, dissolved in acetone and this solution treated with hydrogen chloride, about 25% of the original salt (m.p. 311–312°) was regenerated.

The oil was not very soluble in ether. When 300 mg. of the dimer (IV hydrochloride) was treated with saturated aqueous sodium carbonate, the resulting oil could be dissolved by a 6-fold extraction with 20-cc. portions of ether. The ether solution when treated with picric acid precipitated a *picrate,* m.p. 215–216°, which was identical, according to its mixed melting point, with the picrate obtained from the original ether extraction of the reaction mixture.

Ozonization studies. A solution of 1.23 g. (0.005 mole) of N,N'-*bis*-β-chloroethyl-N-vinyl 1,2-diaminoethane (IV hydrochloride) in 22 cc. of 98–100% formic acid was treated for one hour with an oxygen stream containing 13% ozone. The solvent was then evaporated under 15 mm. pressure. The residue was treated with 10 cc. of water. At first this gave a positive test for formaldehyde by the Schryver method (2) but this test was negative after the solution had aged for thirty minutes.

The solution was treated with 25 cc. of concentrated hydrochloric acid and boiled under reflux for thirty minutes. Three-fourths of the solution was then distilled (until the distillate gave a negative Schryver test). This distillate was saturated with sodium chloride, filtered, and neutralized with strong sodium hydroxide and acetic acid to *p*H 3.4. A 2% solution of dimedon in dilute alkali was added (4 cc. per 100 cc. of neutralized filtrate), the mixture aged at 5° for twelve hours, and then filtered cold through a fritted-glass filter. The *formaldehyde dimedon* derivative (m.p. 189–190°) weighed 0.7 g. This represents a 5% yield of the formaldehyde expected by ozonization of IV·HCl. The yield was lower when ozonization was continued over a longer time. The residual acid solution after distillation of the formaldehyde deposited 0.32 g. of a precipitate which was filtered off and dissolved in 10 cc. of hot water. Addition of this solution to a hot solution of 0.28 g. of picric acid in 20 cc. of water gave 0.32 g. of *picrate,* m.p. 238–9° which was not analyzed. When the salt of IV was boiled with hydrochloric acid the aqueous distillate gave no Schryver test and no dimedon derivative.

A similar ozonization of ethyl acrylate also gave a 5% yield of the expected formaldehyde.

SUMMARY

1. The distillation of *bis*-β-chloroethylamine can be effected, but the distillate decomposes to form a series of salts, all of which are water soluble.

2. This decomposition evidently involves polymerization. The dimer hydrochloride has been isolated and shown by formaldehyde formation, following ozonization, to be N,N′-*bis*-β-chloroethyl-N-vinyl-ammonium chloride.

3. After hydrolysis of the ozonide the formaldehyde is consumed, probably by methylolation of the amine fragment, since the latter can be regenerated when the solution is boiled with hydrochloric acid.

4. A picrate and a styphnate of a polymer can be isolated from the polymerized mixture. According to their analyses these are the salts of hexameric β-chloroethylvinylamine.

TORONTO, CANADA

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