Anal. Calcd. for $C_5H_8O_2Cl_2$: Chloroformate Cl, 21.0. Found:[37] 20.1.

14. **Preparation of Carbonate Ester of (I).**—Phosgene was passed into a stirred mixture of 121 g. (1.13 moles) of 1-chloro-3-buten-2-ol and 182 g. (2.3 moles) of pyridine in 425 ml. of benzene while cooling to keep the temperature at 0–10°. After standing for four hours at room temperature, the pasty product was shaken with water and the benzene layer separated, washed with 5% hydrochloric acid, then with water, and finally dried over anhydrous sodium sulfate. On distillation 103 g. (79% yield) of bis-(1-chloro-3-buten-2-yl)-carbonate (XII), b. p. 116–121° at 4 mm., $n^{20}D$ 1.4726, was obtained.

Anal. Calcd. for $C_9H_{12}O_3Cl_2$: saponification equiv., 79.7; Cl, 29.7. Found: saponification equiv., 79.7; Cl, 30.0.

Acknowledgment.—The helpful suggestions of Dr. A. Pechukas during the course of this study are gratefully acknowledged.

Summary

1. A number of reactions involving the functional groups of butadiene monochlorohydrin, 1-chloro-3-buten-2-ol, have been carried out and the compounds obtained are described.

2. The presence of chloride ion was found to retard the formation of polyethers in the chlorination of butadiene monochlorohydrin, and enabled the isolation of 1,3,4-trichlorobutan-2-ol in 77% yield. This was dehydrohalogenated to produce a nearly quantitative yield of a product probably consisting of a mixture of two dichloroepoxybutanes.

3. Chloromethyl vinyl ketone was prepared and observed to be a lachrymatory, easily polymerizable liquid.

4. The hydrolysis of butadiene monochlorohydrin with aqueous sodium bicarbonate was found to produce erythrol, 3,4-epoxy-1-butene and 2-butene-1,4,-diol. Mechanisms most probable for the formation of the latter compound are discussed.

5. Erythrol was found to undergo rearrangement in acid medium, forming 2-butene-1,4-diol and crotonaldehyde.

6. The cyclic sulfite and carbonate esters of erythrol were formed readily by the alcoholysis of dimethyl sulfite and diethyl carbonate, respectively, with erythrol.

7. Aqueous sodium cyanide converted butadiene monochlorohydrin to butadiene cyanohydrin, probably a mixture of isomers in which one compound, believed to be 1-cyano-3-buten-2-ol, was predominant. Dehydration of the cyanohydrin to cyanobutadiene was rather difficult. Catalytic reduction of the butadiene cyanohydrin to butylene cyanohydrin proceeded smoothly without any simultaneous hydrogenation of the hydroxyl or cyano groups. Hydrolysis and dehydration of the saturated cyanohydrin appeared to give γ-valerolactone, the formation of which indicates a cyano group on the terminal carbon atom of butadiene cyanohydrin.

8. The formal of butadiene monochlorohydrin was prepared; the chlorine atoms in this formal were found to be very unreactive toward magnesium metal, sodium cyanide and cuprous cyanide.

9. The phosgenation of butadiene monochlorohydrin to its chloroformate, in the absence of hydrogen chloride acceptors, was relatively slow. With pyridine, the carbonate ester formed readily.

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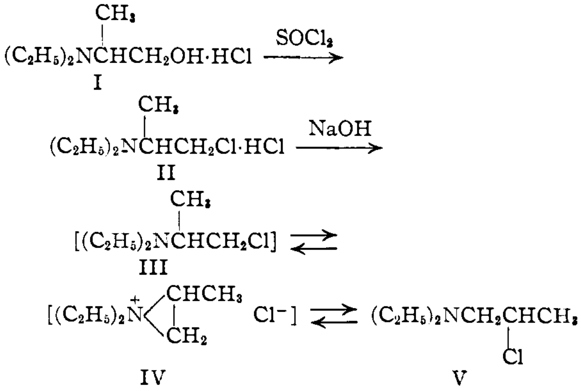
[37] This was determined by shaking a weighed sample with a 20% aqueous pyridine solution followed by Volhard determination of chloride ion.

[CONTRIBUTION FROM SMITH, KLINE AND FRENCH LABORATORIES AND THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Rearrangement of 1,2-Aminochloroalkanes

BY JAMES F. KERWIN, GLENN E. ULLYOT, REYNOLD C. FUSON AND CHARLES L. ZIRKLE[1]

In an earlier article[2] it was reported that when certain 2-hydroxyisopropyl sulfides were treated with hydrochloric acid the reaction involved rearrangement, yielding the corresponding normal chloropropyl sulfides. Although the expected 2-chloroisopropyl sulfides were not isolated, it seems certain that if formed they rearrange readily, the cyclic sulfonium chlorides being intermediates. We undertook to determine whether a similar rearrangement would occur in analogous nitrogen compounds. It was found that when the hydrochloride of 2-diethylamino-1-chloropropane (II), obtained from the corresponding amino alcohol hydrochloride (I) by treatment with thionyl chloride, was treated with alkali, the chloro amine isolated was the corresponding normal propylamine derivative (V).



$$(C_2H_5)_2N\overset{CH_3}{\overset{|}{C}}HCH_2OH\cdot HCl \xrightarrow{SOCl_2}$$

I

$$(C_2H_5)_2N\overset{CH_3}{\overset{|}{C}}HCH_2Cl\cdot HCl \xrightarrow{NaOH}$$

II

$$[(C_2H_5)_2N\overset{CH_3}{\overset{|}{C}}HCH_2Cl] \rightleftarrows$$

III

$$[(C_2H_5)_2\overset{+}{N}\langle\begin{matrix}CHCH_3\\ |\\ CH_2\end{matrix}\ Cl^-] \rightleftarrows (C_2H_5)_2NCH_2\underset{\underset{Cl}{|}}{C}HCH_3$$

IV V

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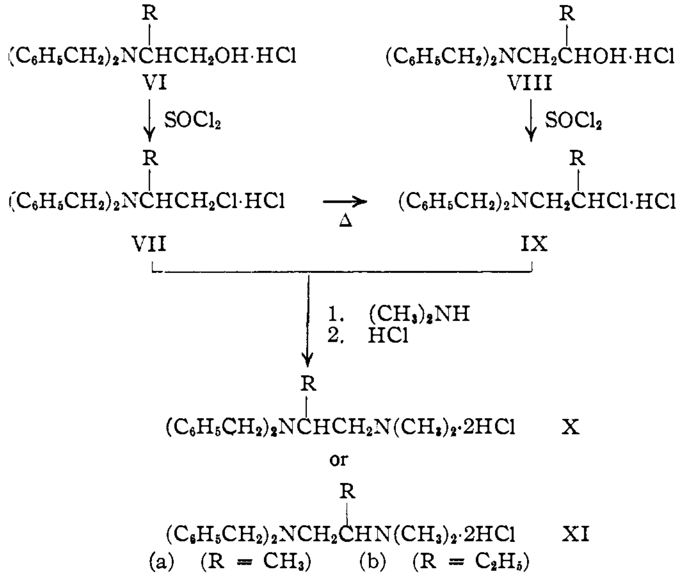
[1] Smith, Kline and French Laboratories Fellow, 1946–1947.

[2] Fuson, Price and Burness, *J. Org. Chem.*, **11**, 475 (1946).

Presumably the 2-diethylamino-1-chloropropane (III) undergoes rearrangement as rapidly as it is formed, the cyclic imonium salt (IV) being an intermediate. It had been shown earlier that ethylenimonium salts of this type are formed in other reactions of halogenated alkylamines.[3] The normal propyl amine derivative (V), prepared from 1-diethylamino-2-propanol hydrochloride, did not rearrange when liberated from its salt. In fact, the free base after being distilled formed a picrate identical with that from the original chloro amine hydrochloride.

While this work was in progress, however, our findings were anticipated to a large degree by others. Evidence, though of a somewhat different nature, was reported by Schultz, Robb and Sprague[4] for a similar rearrangement of 2-chloropropyldimethylamine. The striking feature of the rearrangement demonstrated by these authors is that it involves a change from the *n*-propylamine to the isopropylamine structure—a change which is the reverse of that observed by us. Even more recently Brode and Hill[5] have indicated that the free bases isolated from the hydrochlorides of the isomeric 1,2-dimethylaminochloropropanes are identical; but they were unable to state whether the products were a pure compound or a mixture of isomers.

By employing the corresponding amino alcohol hydrochlorides as precursors, we have been able to prepare 2-dialkylamino-1-chloroalkane hydrochlorides without rearrangement. At higher temperatures, however, the hydrochlorides do undergo rearrangement to the isomeric 1-dialkylamino-2-chloroalkane hydrochlorides. The hydrochlorides of the diethylaminochloropropanes (III and V) and a mixture of the two salts have the same melting point[6] although the picrates prepared from the hydrochlorides differ in melting point. A more striking demonstration of this rearrangement by heat is shown by the 2-dibenzylamino-1-chloropropane and -butane hydrochlorides (VII). These compounds melt at a lower temperature than their isomers (IX) but rearrange to the latter at or slightly above the melting point. Thus when 2-dibenzylamino-1-chloropropane hydrochloride (VIIa) is heated at its melting point (137–139°) for a few minutes and allowed to cool, the salt is found to melt at a higher temperature (157–161°; recrystallized, m. p. 161–163°) and does not lower the melting point of 1-dibenzylamino-2-chloropropane hydrochloride (IXa). The aminobutane hydrochloride (VIIb) behaves similarly, melting initially at 136.5–138.5°, then at 143–146°. After recrystallization a mixture with IXb showed no depression in melting point.



VI VIII VII IX X XI

(a) (R = CH_3) (b) (R = C_2H_5)

Mixtures of the isomers (VIIa and IXa; VIIb and IXb) soften at a temperature lower than the melting point of either and finally melt at the higher temperature.

The direction of rearrangement so far noted by us has been

$$R_2NCH(R)CH_2Cl \longrightarrow R_2NCH_2CH(R)Cl$$

The ease with which one isomer rearranges into the other undoubtedly depends upon steric factors and the base strength of the tertiary amino group.

Reaction of the isomeric pairs with dimethylamine in aqueous alcohol solution yields identical diamine dihydrochlorides (X or XI). Although the structures of the diamines have not been elucidated, it is obvious that a rearrangement has occurred in one member of each pair during the amination reaction. We have concluded that XI is the more probable structure. This conclusion is supported by hydrolysis experiments.

Hydrolysis of 2-dibenzylamino-1-chlorobutane hydrochloride (VIIb) in the presence of sodium bicarbonate resulted in the isolation of 1-dibenzylamino-2-butanol hydrochloride (VIIIb), a transformation which may have occurred *via* an intermediate ethylenimonium ion (XII). However, because of the low yield (10%) of product isolated, the possibility that some hydrolysis also took place without rearrangement cannot be excluded.

Experiments designed to study the behavior of the isomeric pair, 2-dibenzylamino-1-chloro-2-methylpropane and 1-dibenzylamino-2-chloro-2-methylpropane, have not been completed because of the failure to obtain a satisfactory product in

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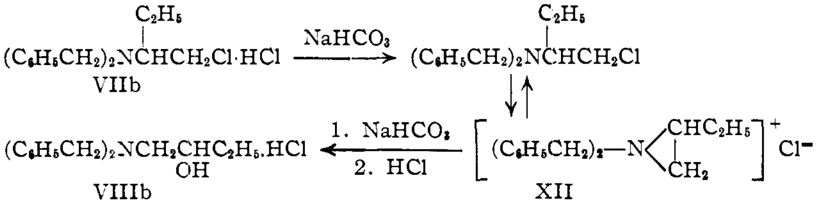
[3] (a) Gilman and Phillips, *Science*, **103**, 409 (1946); (b) Golumbic, Fruton and Bergmann, *J. Org. Chem.*, **11**, 518 (1946); (c) Golumbic and Bergmann, *ibid.*, **11**, 536 (1946); (d) Fruton and Bergmann, *ibid.*, **11**, 543 (1946); (e) Golumbic, Stahmann and Bergmann, *ibid.*, **11**, 550 (1946).

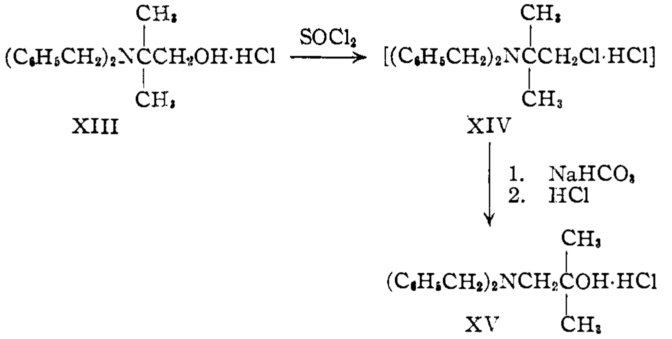
[4] Schultz, Robb and Sprague, This Journal, **69**, 188 (1947).

[5] Brode and Hill, *ibid.*, **69**, 724 (1947).

[6] An observation reported by Brode and Hill (ref. 5) for the analogous dimethylamino hydrochlorides.



attempting to convert 1-dibenzylamino-2-methyl-2-propanol hydrochloride into the corresponding chloro amine hydrochloride. On the other hand, 2-dibenzylamino-2-methyl-1-propanol hydrochloride XIII was transformed readily into a chloro amine hydrochloride to which we tentatively ascribe the structure XIV.



$$(C_6H_5CH_2)_2NC(CH_3)_2CH_2OH\cdot HCl \xrightarrow{SOCl_2} [(C_6H_5CH_2)_2NC(CH_3)_2CH_2Cl\cdot HCl] \xrightarrow{1.\ NaHCO_3;\ 2.\ HCl} (C_6H_5CH_2)_2NCH_2C(CH_3)_2OH\cdot HCl$$

Hydrolysis of XIV in the presence of sodium bicarbonate led to a 32% recovery of 1-dibenzylamino-2-methyl-2-propanol hydrochloride (XV). Although the structure of XIV needs confirmation, and although we cannot exclude the possibility that some XIII was formed in the hydrolysis of XIV, there is no doubt that in the two-step transformation of XIII into XV rearrangement occurred, probably through an intermediate ethylenimonium ion.

Experimental

Preparation of Amino Alcohols.—With the exception of 2-diethylamino-1-propanol, the amino alcohols were prepared from the appropriate alkene oxides and amines or by benzylation of a primary amino alcohol according to the general procedure of Eisleb.[7] The free bases were converted into hydrochlorides in ether solution and the salts were recrystallized to constant melting point.

2-Diethylamino-1-propanol.—Hydrogenation[8] of ethyl α-diethylaminopropionate[9] in absolute ethanol at 175° and 3500 lb. pressure with a copper chromite catalyst gave a 63% yield of amino acohol; b. p. 65–66° (18 mm.)[10]; $n^{20}D$ 1.4332. The *p*-nitrobenzoate hydrochloride melted at 154°. The hydrochloride, recrystallized from acetone, melted at 94–95°.

Anal. Calcd. for $C_7H_{18}ONCl$: Cl, 21.15. Found: Cl, 21.15.

1-Diethylamino-2-propanol.—Diethylamine and propylene oxide[11] gave an 81% yield of amino alcohol; b. p. 59–60° (21 mm.); $n^{20}D$ 1.4265 (Goldfarb reported a boiling point of 62.5–63.5° (22 mm.)). The hydrochloride crystallized from acetone in fine, colorless needles; m. p. 138.5–139.5°.

Anal. Calcd. for $C_7H_{18}ONCl$: C, 50.14; H, 10.82. Found: C, 50.62; H, 10.92.

1-Dibenzylamino-2-propanol Hydrochloride (VIIIa).—Benzylation of 1-amino-2-propanol by the method of Eisleb[7] resulted in a 67% yield of viscous oil; b. p. 132–137° (1 mm.). It formed a hydrochloride which, after recrystallization from acetone, melted at 181–183°.

Anal. Calcd. for $C_{17}H_{22}ONCl$: Cl, 12.15. Found: Cl, 12.11.

2-Dibenzylamino-1-propanol Hydrochloride (VIa).—From benzyl chloride and 2-aminopropanol (b. p. 82° (18 mm.)), prepared according to the procedure of Blicke, Faust, Warzynski and Gearien,[12] there was obtained a 67% yield of amino alcohol; b. p. 155–159° (1–2 mm). The hydrochloride, recrystallized from alcohol, melted at 180.5–182.5°.

Anal. Calcd. for $C_{17}H_{22}ONCl$: Cl, 12.15. Found: Cl, 12.17.

A mixture with 1-dibenzylamino-2-propanol hydrochloride melted at 164–169°.

1-Dibenzylamino-2-butanol Hydrochloride (VIIIb).—One-half mole each of 3,4-epoxy-1-butene and dibenzylamine, heated at 90–95° for four hours and then at 140° over a two-hour period, yielded 123 g. (92%) of 1-dibenzylamino-3-buten-2-ol; b. p. 188–196° (5–6 mm.). It formed a hydrochloride which melted at 157–158° after recrystallization from alcohol–ether.

Anal. Calcd. for $C_{18}H_{22}ONCl$: Cl, 11.64. Found: Cl, 11.60.

The unsaturated amino alcohol in ethanol solution rapidly absorbed the calculated amount of hydrogen in the presence of Raney nickel at an initial hydrogen pressure of 3.5 atmospheres to give a 90% yield of 1-dibenzylamino-2-butanol; b. p. 188–192° (5 mm.). The amino alcohol hydrochloride was recrystallized from alcohol; m. p. 177–179°.

Anal. Calcd. for $C_{18}H_{24}ONCl$: Cl, 11.57. Found: Cl, 11.52.

2-Dibenzylamino-1-butanol Hydrochloride (VIb).—Prepared from benzyl chloride and 2-amino-1-butanol in 68% yield, the amino alcohol (b. p. 157–158° (1 mm.)) formed a hydrochloride which melted at 170–171° after recrystallization from alcohol–ether.

Anal. Calcd. for $C_{18}H_{24}ONCl$: Cl, 11.57. Found: Cl, 11.45.

2-Dibenzylamino-2-methyl-1-propanol (XIII).—Reaction of benzyl chloride with 2-amino-2-methyl-1-propanol gave a 48% yield of product which melted at 76–78° after recrystallization from alcohol.

Anal. Calcd. for $C_{18}H_{23}ON$: C, 80.25; H, 8.61. Found: C, 80.22; H, 8.62.

The hydrochloride, recrystallized from alcohol–acetone mixture, melted at 137–138°.

Anal. Calcd. for $C_{18}H_{24}NOCl$: Cl, 11.57. Found: Cl, 11.57.

1-Dibenzylamino-2-methyl-2-propanol Hydrochloride (XV).—A mixture of 0.5 mole each of benzylamine and isobutylene oxide, heated from 79 to 130° over a period of eight hours, gave 58 g. of product; b. p. 113–117° (3 mm.). The distillate solidified on chilling and melted at 48.5–49.5° after recrystallization from hexane. 1-Benzylamino-2-methyl-2-propanol hydrochloride, recrystallized from alcohol, melted at 163.5–165°.

Anal. Calcd. for $C_{11}H_{18}ONCl$: Cl, 16.44. Found: Cl, 16.39.

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[7] Eisleb, U. S. Patent 1,949,247.

[8] The hydrogenation was performed by Mr. David J. Wallace.

[9] Fuson, THIS JOURNAL, **50**, 1448 (1928).

[10] Burnett, Jenkins, Peet, Dreger and Adams, THIS JOURNAL, **59**, 2248 (1937), reported 56–58° (13 mm.); $n^{20}D$ 1.4305; *p*-nitrobenzoate hydrochloride, m. p. 155.6° (cor.).

[11] Goldfarb, *ibid.*, **63**, 2280 (1941).

[12] Blicke, Faust, Warzynski and Gearien, *ibid.*, **67**, 206 (1945).

A mixture of 55 g. (0.31 mole) of 1-benzylamino-2-methyl-2-propanol, 39 g. (0.31 mole) of benzyl chloride and 21 g. (0.15 mole) of anhydrous potassium carbonate was heated with stirring at 90–100° for two hours. The dibenzylated product (yield 39 g., b. p. 173–175° (3 mm.)) formed a hydrochloride which separated from alcohol in small prisms; m. p. 170–172.5°.

Anal. Calcd. for $C_{18}H_{24}ONCl$: Cl, 11.57. Found: Cl, 11.57.

Preparation of β-Chloroethylamine Hydrochlorides.—The chloro amine hydrochlorides were prepared according to a general procedure by treatment of the β-hydroxyethylamine hydrochlorides (the hydrochlorides were used in place of the free amines to minimize the possibility of rearrangement occurring during the reaction) with thionyl chloride in dry benzene or chloroform. The reactants and solvent were mixed, with cooling when necessary, and gradually warmed until reaction occurred (usually 35–40°). During this time the amino alcohol hydrochloride dissolved with evolution of sulfur dioxide and hydrogen chloride. In most experiments the solution was refluxed for a short period to complete the reaction. The solvent and excess thionyl chloride were then removed *in vacuo* and the residue was purified by recrystallization from a suitable solvent.

1-Diethylamino-2-chloropropane Hydrochloride.—Reactants, 6.1 g. (0.036 mole) of 1-diethylamino-2-propanol hydrochloride and 5.7 g. (0.048 mole) of thionyl chloride; solvent, dry benzene; temperature, reflux; crystallizing solvent, ethyl acetate. The colorless, hygroscopic needles melted at 105–106°; yield 5.2 g. (78%). Recrystallization of the salt raised its melting point to 106–107°.

Anal. Calcd. for $C_7H_{17}NCl_2$: C, 45.17; H, 9.21. Found: C, 45.28; H, 9.32.

A picrate prepared by adding a concentrated solution of the chloro amine hydrochloride to a saturated aqueous solution of picric acid was recrystallized from ethanol as felted, yellow needles; m. p. 125.5–126°.[13]

Anal. Calcd. for $C_{13}H_{19}O_7N_4Cl$: C, 41.22; H, 5.06. Found: C, 41.22; H, 4.86.

2-Diethylamino-1-chloropropane Hydrochloride (II).—Reactants, 4.3 g. (0.026 mole) of 2-diethylamino-1-propanol hydrochloride and 4.2 g. (0.035 mole) of thionyl chloride; solvent, benzene; crystallizing solvent, ethyl acetate containing a small amount of absolute ethanol. The very hygroscopic, colorless needles melted at 102–103°; yield, 3.5 g. (73%). Recrystallization of the compound raised its melting point to 106–107°. A mixture with 1-diethylamino-2-chloropropane hydrochloride showed no depression or widening of the melting range, indicating that on heating the two isomeric salts rearrange to the same compound.

Anal. Calcd. for $C_7H_{17}NCl_2$: C, 45.17; H, 9.21. Found: C, 45.05; H, 9.16.

The picrate was prepared as described above. After two recrystallizations from ethanol, the small, yellow needles melted at 113–113.5°.

Anal. Calcd. for $C_{13}H_{19}O_7N_4Cl$: C, 41.22; H, 5.06. Found: C, 41.23; H, 4.96.

1-Dibenzylamino-2-chloropropane Hydrochloride (IXa).—Reactants, 58.6 g. (0.2 mole) of 1-dibenzylamino-2-propanol hydrochloride and 35 g. (0.3 mole) of thionyl chloride; solvent, chloroform; crystallizing solvents, alcohol–ether and chloroform–ether; yield was 49 g. (79%); m. p. 161.5–163°.

Anal. Calcd. for $C_{17}H_{21}NCl_2$: C, 65.81; H, 6.82; Cl, 22.87; Cl (ionic), 11.43. Found: C, 65.94; H, 6.93; Cl, 23.03; Cl (ionic), 11.37.

2-Dibenzylamino-1-chloropropane Hydrochloride (VIIa).—Reactants, 40 g. (0.14 mole) of 2-dibenzylamino-1-propanol hydrochloride and 25 g. (0.21 mole) of thionyl chloride; solvent, chloroform; crystallizing solvent, alcohol–ether; yield was 36 g. (83%); m. p. 137–139°.

Anal. Calcd. for $C_{17}H_{21}NCl_2$: C, 65.81; H, 6.82; Cl, 22.87; Cl (ionic) 11.43. Found: C, 65.98; H, 6.86; Cl, 22.81; Cl (ionic), 11.47.

A mixture with 1-dibenzylamino-2-chloropropane hydrochloride softened at 128° and melted at 161.5–163°.

1-Dibenzylamino-2-chlorobutane Hydrochloride (IXb).—Reactants, 42 g. (0.13 mole) of 1-dibenzylamino-2-butanol hydrochloride and 31 g. (0.26 mole) of thionyl chloride; solvent, chloroform; crystallizing solvents, chloroform–ether and alcohol–ether; yield 28 g. (67%); m. p. 149–151°.

Anal. Calcd. for $C_{18}H_{23}NCl_2$: C, 66.66; H, 7.14; Cl, 21.87; Cl (ionic), 10.93. Found: C, 66.82; H, 7.06; Cl, 21.76; Cl (ionic), 10.98.

2-Dibenzylamino-1-chlorobutane Hydrochloride (VIIb).—Reactants, 25 g. (0.081 mole) of 2-dibenzylamino-1-butanol hydrochloride and 23 g. (0.2 mole) of thionyl chloride; solvent, chloroform; crystallizing solvents, alcohol–ether and acetone; yield was 18 g. (68%) of long, slender needles from acetone; m. p. 136.5–138.5°.

Anal. Calcd. for $C_{18}H_{23}NCl_2$: Cl, 21.87; Cl (ionic), 10.93. Found: Cl, 21.90; Cl (ionic), 11.01.

A mixture with the isomer, 1-dibenzylamino-2-chlorobutane hydrochloride, softened at 128°, melted at 146–148.5°.

2-Dibenzylamino-1-chloro-2-methylpropane Hydrochloride (XIV).—Reactants, 14 g. (0.045 mole) of 2-dibenzylamino-2-methyl-1-propanol hydrochloride and 21 g. (0.18 mole) of thionyl chloride; solvent, chloroform; crystallizing solvent, alcohol–ether; yield was 12 g. (70%) of colorless crystals; m. p. 152–154°.

Anal. Calcd. for $C_{18}H_{23}NCl_2$: C, 66.66; H, 7.14; Cl (ionic), 10.93. Found: C, 66.90; H, 7.62; Cl (ionic), 11.01.

The Free Amine from 1-Diethylamino-2-chloropropane Hydrochloride.—A solution of 0.5 g. of sodium hydroxide in 2 ml. of water was added to 2.0 g. of the chloro amine hydrochloride in 3 ml. of water. The layer of amine which separated was taken up in chloroform and removed. The aqueous layer was extracted three times with 5-ml. portions of chloroform and the combined extracts dried over anhydrous calcium sulfate. After removal of the chloroform at reduced pressure, the chloro amine (1.4 g.) distilled at 69° (35 mm.); $n^{20}D$ 1.4332. Kharasch and Fuchs[13] report a boiling point of 57–58° (22–23 mm.); $n^{20}D$ 1.4335. The amine was reconverted to the hydrochloride which yielded a picrate appearing as felted, yellow needles from ethanol; m. p. 125.5–126°. A mixture with the picrate obtained from the chloro amine hydrochloride before treatment with alkali showed no depression.

The Free Amine from 2-Diethylamino-1-chloropropane Hydrochloride.—The chloro amine hydrochloride (2.0 g.) was treated with sodium hydroxide according to the procedure described above. The isolated chloro amine distilled at 69–70° (35 mm.); $n^{20}D$ 1.4336.[14] These constants agree with those of the chloro amine obtained from the *n*-propylamine salt. The amine was reconverted to the hydrochloride which yielded a picrate in the form of felted, yellow needles from ethanol; m. p. 125.5–126°. A mixture with the picrate prepared from 1-diethylamino-2-chloropropane hydrochloride showed no depression of melting point, indicating that the amines liberated from the two isomeric chloro amine salts are identical. Furthermore, the crude, undistilled chloro amine formed a picrate identical with that from the distilled material—a fact which shows that rearrangement occurred before distillation. A mixture with the picrate from 2-diethylamino-1-chloropropane hydrochloride (m. p. 113–113.5°) melted at 110–114°.

Rearrangement of 2-Dibenzylamino-1-chloropropane Hydrochloride.—One-half gram of the chloro amine hydrochloride (m. p. 137–139°) was heated in an oil-bath at 145–

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[13] Kharasch and Fuchs, *J. Org. Chem.*, **10**, 163 (1945), reported a melting point of 126–127°.

[14] Elderfield, *et al.*, This Journal, **68**, 1584 (1946), report a boiling point of 79–80° (50 mm.), $n^{25}D$ 1.4310 for 2-diethylamino-1-chloropropane.

150° for five minutes. The material began to melt and then solidified without becoming completely liquid. The rearranged hydrochloride melted at 157–161°; recrystallization from chloroform–ether gave 0.4 g. of needles; m. p. 161–163°. A mixture with 1-dibenzylamino-2-chloropropane hydrochloride (m. p. 161–163°) showed no depression.

Rearrangement of 2-Dibenzylamino-1-chlorobutane Hydrochloride.—One-half gram of the chloro amine hydrochloride (m. p. 136.5–138.5°) was heated in an oil-bath at 145° for a few minutes. The hydrochloride solidified on cooling; it then melted at 143–146°. Recrystallization from alcohol–ether raised the melting point to 147–149°; yield, 0.35 g. A mixture with a sample of 1-dibenzylamino-2-chlorobutane hydrochloride melted at 148–149.5° without preliminary softening.

Reaction of the Dibenzylaminochloropropanes with Dimethylamine.—Three grams of each chloro amine hydrochloride in 50 ml. of alcohol was added in portions to a mixture of 15 ml. of 20% aqueous dimethylamine and 15 ml. of alcohol. After standing overnight at room temperature, the solution was concentrated *in vacuo* and the oil which separated was extracted into ether. The ether solution was dried with anhydrous potassium carbonate, filtered and saturated with dry hydrogen chloride. The diamine dihydrochloride from 1-dibenzylamino-2-chloropropane weighed 2.5 g. after two recrystallizations from alcohol–ether; m. p. 190–191.5°.

Anal. Calcd. for $C_{19}H_{28}N_2Cl_2$: Cl, 19.96. Found: Cl, 19.80.

From 2-dibenzylamino-1-chloropropane there was obtained 2.3 g. of product which melted at 191–193° and showed no depression when mixed with the above hydrochloride.

Reaction of Dibenzylaminochlorobutanes with Dimethylamine.—The isomeric chloro amine hydrochlorides (3.2 g.) were added to dimethylamine in aqueous alcohol as described above. The products were isolated as gummy dihydrochlorides which were triturated with acetone and recrystallized from alcohol–ether. 1-Dibenzylamino-2-chlorobutane yielded 1.7 g. of diamine dihydrochloride; m. p. 161–163°.

Anal. Calcd. for $C_{20}H_{30}N_2Cl_2$: Cl, 19.20. Found: Cl, 19.03.

The monopicrate, prepared from the hydrochloride in aqueous solution, crystallized from alcohol in long, yellow prisms, m. p. 127–128°.

Anal. Calcd. for $C_{26}H_{31}N_5O_7$: C, 59.41; H, 5.95. Found: C, 59.26; H, 6.04.

The diamine dihydrochloride from 2-dibenzylamino-1-chlorobutane weighed 1.7 g.; m. p. 161–163°. The monopicrate melted 127–128° and mixed melting points of these salts with those above showed no depression.

Hydrolysis of 2-Dibenzylamino-1-chlorobutane Hydrochloride.—A solution of 0.52 g. of sodium bicarbonate in 100 ml. of water was added to one gram of chloro amine hydrochloride dissolved in 300 ml. of alcohol. The solution was allowed to stand overnight at room temperature, acidified with dilute hydrochloric acid and evaporated to dryness at reduced pressure. Warm alcohol was added to the residue, the solution was filtered from sodium chloride and evaporated to dryness. The oily residue was dissolved in a few milliliters of alcohol and by addition of ether there was obtained a crystalline hydrochloride, which, after recrystallization from alcohol–ether, weighed 0.1 g.; m. p. 175–176.5°. A mixture with a sample of 1-dibenzylamino-2-butanol hydrochloride melted at 176–178° while 2-dibenzylamino-1-butanol hydrochloride depressed the melting point to 148–153°.

Hydrolysis of 2-Dibenzylamino-1-chloro-2-methylpropane Hydrochloride.—One gram of chloro amine hydrochloride and 0.52 g. of sodium bicarbonate were dissolved in 400 ml. of 75% aqueous alcohol. After twenty-four hours, the solution was treated as previously described. Addition of ether to an alcohol solution of the residue, after separation from sodium chloride, caused separation of 0.3 g. of crystalline hydrochloride. The filtrate was evaporated to dryness and from the remaining oil a further 0.1 g. of solid was obtained by treatment with alcohol followed by ether. The two crops were combined and recrystallized again from alcohol–ether; yield, 0.3 g.; m. p. 170–171°. There was no depression of melting point when this material was mixed with an authentic sample of 1-dibenzylamino-2 methyl-2-propanol hydrochloride.

Summary

2-Diethylamino-1-chloropropane, when liberated from its hydrochloride salt, rearranges to the isomeric 1-diethylamino-2-chloropropane. The hydrochlorides of 2-dibenzylamino-1-chloropropane and -butane rearrange under the influence of heat to the 1-dibenzylamino-2-chloro hydrochlorides. The pairs of isomers, 2-dibenzylamino-1-chloropropane and 1-dibenzylamino-2-chloropropane; 2-dibenzylamino-1-chlorobutane and 1-dibenzylamino-2-chlorobutane, on interaction with dimethylamine, give, in the case of each pair of isomers, the same 1,2-diaminoalkane. 1-(Disubstituted amino)-2-chloroalkanes undergo transformations which probably involve ethyleniminonium ion formation.

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