trate from the precipitated nickel salts and removal of the solvent under atmospheric pressure, was dissolved in absolute ethanol (10 cc. per 0.2 g. mixture) and treated with a cold 9% solution of ammonia in ethanol (1 cc.) at 0°. The precipitated ammonium salt of syringaldehyde was removed by filtration, washed with a 1% solution of ammonia in absolute ethanol (5 cc.) and converted to the *m*-nitrobenzoylhydrazone[9] of syringaldehyde. Vanillin was recovered from the acidified filtrate by extraction with benzene and also converted to its *m*-nitrobenzoylhydrazone. Yields obtained were vanillin hydrazone, 0.226 g.; syringaldehyde hydrazone, 0.190 g.; quinoxaline of vanilloyl methyl ketone, 0.225 g., and ammonium salt of syringoyl methyl ketone, 0.131 g.; equivalent to 70, 69, 70 and 76% of the free carbonyl derivatives, respectively.

Synthesis of Syringoyl Methyl Ketone.—α-Hydroxypropiosyringone[5] (5 g.) was added to a hot solution of copper sulfate (14.4 g.), pyridine (24 cc.) and water (12 cc.), the mixture heated for two hours on a steam-bath, and, after cooling, poured into a slight excess of dilute hydrochloric acid. The aqueous solution was extracted with ether, and the latter removed, leaving 3.5 g. of an oily residue distilling at 147° (0.04 mm.). This distillate (2.9 g.) was recrystallized, first from hot water, and then from petroleum ether (b. p. 100–110°); light orange-colored needle-shaped crystals; m. p. 80–81°. *Anal.* Calcd. for $C_{11}H_{12}O_5$: C, 58.9; H, 5.4; OCH_3, 27.7. Found: C, 58.7; H, 5.7; OCH_3, 27.7.

Monosemicarbazone.—Fine, white, needle-like crystals; m. p. 210–211° (with decomposition). *Anal.* Calcd. for $C_{12}H_{15}O_5N_3$: C, 51.2; H, 5.4; N, 14.9; OCH_3, 22.1. Found: C, 51.4; H, 5.7; N, 14.7; OCH_3, 22.0.

Quinoxaline.—The quinoxaline was prepared by dissolving the syringoyl methyl ketone (0.2 g.) in water (20 cc.) at 70° and adding to this a hot solution (70°) of *o*-phenylenediamine (0.12 g.) in water (10 cc.). After standing overnight, the precipitate (0.24 g.) was filtered and recrystallized first from water, then from dilute ethanol (1:6); light yellow-colored crystals, m. p. 161–161.5°. *Anal.* Calcd. for $C_{17}H_{16}O_3N_2$: C, 68.9; H, 5.5; N, 9.5; OCH_3, 20.9. Found: C, 69.0; H, 5.6; N, 9.4; OCH_3, 20.9.

Summary

1. The syringoyl and vanilloyl methyl ketones present in the bisulfite-soluble fraction obtained from the ethanolysis of maple wood have now been isolated in the pure crystalline state.

2. Their quantitative separation has been effected by conversion into the insoluble nickel glyoxime salts.

3. The total diketone fraction amounts to approximately 2 to 3% of the Klason lignin in the original maple wood.

MONTREAL, CANADA RECEIVED JUNE 30, 1941

---

[9] Tomlinson and Hibbert, THIS JOURNAL, **58**, 345 (1936).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE UNIVERSITY OF IDAHO]

The Action of Sodium on 2,2'-Dichlorodiethylamine[1]

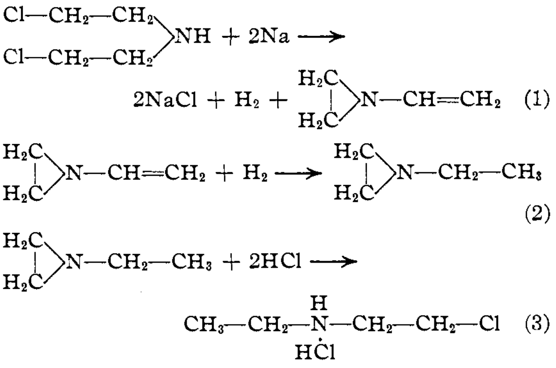
BY PERCY A. LASSELLE AND S. A. SUNDET

In an attempt to prepare pyrrolidine by the treatment of 2,2'-dichlorodiethylamine with metallic sodium no pyrrolidine was obtained. Ring closure or possibly chain formation was expected to take place.

It was in an attempt to prepare N-vinylethyleneimine that the action of other alkaline reagents on 2,2'-dichlorodiethylamine was studied. The instability of the free dichloroalkylamine, resulting in decomposition and polymerization, apparently made these attempts fruitless.

The fractionation of the toluene solution resulting from the reaction with sodium yielded an amine mixture. The hydrogenation of this mixture resulted in N-ethylethyleneimine which upon evaporation with an excess of hydrochloric acid gives the hydrochloride of 2-chlorethylethylamine. This hydrochloride was prepared by another method for purposes of comparison.

The rapid, although partial, hydrogenation and the properties of the amine mixture indicate the presence of N-ethylethyleneimine and some less saturated compound. The following reaction of 2,2'-dichlorodiethylamine with sodium was suggested as taking place



The N-vinylethyleneimine (1, as yet unknown) would be hydrogenated in part by the hydrogen

---

[1] This paper was presented at the Northwest Scientific Association meeting at Spokane, Washington, December 28, 1940.

formed in the reaction and a resulting mixture of N-vinylethyleneimine (1) and N-ethylethyleneimine (2) might be expected to exhibit the properties observed for the amine mixture.

Experimental

Organic reagents used were of practical quality as supplied by the Eastman Kodak Company. All melting points were determined with a set of total immersion thermometers made by Arthur H. Thomas of Philadelphia and calibrated by the Bureau of Standards. The two columns used in fractionations were jacketed columns of the total condensation, partial take-off type.

2,2'-Dichlorodiethylamine.—The hydrochloride of this amine was prepared from diethanolamine by the method used by Ward.[2] It was purified by crystallization from *n*-butanol. The free amine reacts readily with aryl isocyanates and isothiocyanates to form viscous liquids. Attempts were made to prepare some of the substituted amides as derivatives. In the case of the β-naphthalene sulfonamide, the only one that crystallized, the amide was found to be slowly converted to the substituted ammonium salt by recrystallization from dilute ethanol. This was mentioned by Mann[3] with reference to the benzamide.

Ethanolethylamine.—This amine was prepared from ethylene oxide and ethylamine by the method used by Knorr and Schmidt.[4] It was obtained in 55% yield using an excess of ethylamine.

2-Chloroethylethylamine Hydrochloride (3).—Seventy-eight grams (0.88 mole) of ethanolethylamine was converted to the hydrochloride by treating with a slight excess of concentrated hydrochloric acid and removing the excess water and acid by boiling, finally heating to 200°. At this point strong fuming began and on cooling the hydrochloride crystallized in the form of white flakes. The hydrochloride was then mixed with 250 cc. of chloroform by warming gently and 100 cc. (1.38 moles) of thionyl chloride was added slowly to the well-stirred mixture. The solvent and volatile reaction products were finally removed on the steam plate and the resulting product was crystallized from *n*-butanol, washed with petroleum ether and dried; yield, 115 g. or 91%.

This hydrochloride is soluble in water, ethanol, *n*-butanol and chloroform, difficultly soluble in acetone, and insoluble in ether. When crystallized twice from *n*-butanol, the resulting white flakes melt at 223°.

Analysis for ionizable chlorine. Calcd. for $C_4H_{11}NCl_2$: Cl, 24.62. Found: Cl, 24.62.

The free base reacts readily with aryl isocyanates and isothiocyanates to form very thick and sticky colored liquids. The benzenesulfonamide and β-naphthalenesulfonamide were yellow liquids which did not crystallize.

Chloroaurate.—Golden-brown needles, recrystallized from water, m. p. 131.5°.

Reaction of 2,2'-Dichlorodiethylamine with Sodium.—Three hundred fifty-seven grams (two moles) of the hydrochloride of 2,2'-dichlorodiethylamine was dissolved in 500 cc. of water, decolorized with Norite and cooled in an ice water mixture to 0°. To it was added a thoroughly cooled solution of 80 g. of sodium hydroxide in 100 cc. of water. The unstable amine separated in the form of a water-white liquid (sp. gr. greater than one) and was extracted with five 100-cc. portions of toluene. The toluene solution was dried with calcium chloride in the refrigerator for twelve to eighteen hours. There was no indication of any reaction of the amine with the calcium chloride. Ninety-two grams (four moles) of sodium in 300 cc. of boiling toluene—very finely divided by violent mechanical stirring—was treated with the filtered solution of the free base. The reaction was carried out in a two-liter flask fitted with a dropping funnel, mercury-seal stirrer and reflux condenser. As the reaction was exothermic, the base was added just fast enough to maintain a small reflux. An attempt was made to carry out the reaction at a lower temperature, but the addition of the amine to slight excess under those conditions resulted only in an uncontrollable reaction. Some volatile amine(s) was carried over to a hydrochloric acid trap by a gas which gave all evidences of being hydrogen. The cooled and filtered toluene solution was then fractionated in the larger column. The fractions boiling up to 107° were refractionated twice in the smaller column and a 43-g. fraction was obtained boiling 46.7–8.7° and 690 mm. with a refractive index, constant over this boiling range, of n^{20}_D 1.3960. This amine mixture was formed in a yield of approximately 35%. Fractions above 107° were obtained in the form of clear, colorless liquids, darkening rapidly, and possessing very unpleasant odors. These have not yet been investigated.

Amine Mixture.—The mixture was strongly alkaline, possessing an unpleasant ammoniacal odor, and soluble in the common solvents. It was readily oxidized with 2% neutral permanganate, stable to nitrous acid in the cold, but reacted violently with aryl isocyanates and isothiocyanates to form resins. A molecular weight determination by the depression of the freezing point of purified benzene gave the values 73.7 and 74.7.

Hydrochloride.—The hydrochloride, prepared by the evaporation of the amine mixture with an excess of hydrochloric acid, was oxidized readily by 2% neutral permanganate. The results of chlorine analyses, both ionizable and total, revealed the addition of hydrogen chloride as well as the expected salt formation.

Hydrogenation of Amine Mixture.—Fifty grams (approx. 0.7 mole) of the amine mixture in 170 cc. of cyclohexane was hydrogenated at room temperature and 50 lb. pressure making use of Raney nickel as catalyst. Absorption of 0.23 mole of hydrogen took place rapidly, then absorption ceased and further shaking brought about no change in pressure. The resulting solution after filtration and two fractionations yielded 12 g. of N-ethylethyleneimine boiling at 48.5–49° and 690 mm. This cut constituted a 25% yield.

N-Ethylethyleneimine (2).—This amine, a colorless volatile liquid of unpleasant ammoniacal odor, is soluble in all the common solvents: b. p. 48.5–49° and 690 mm., n^{20}_D 1.3938, sp. gr. $^{20}_{20}$ 0.7583. The amine does not react with nitrous acid in the cold, but reacts very slowly with 2% neutral permanganate. It reacts explosively with methyl iodide. It reacts violently with aryl isocyanates and isothiocyanates to form resins of various colors. This peculiar

---

[2] Ward, THIS JOURNAL, **57**, 914 (1935).

[3] Mann, *J. Chem. Soc.*, 464 (1934).

[4] Knorr and Schmidt, *Ber.*, **31**, 1072 (1898).

reaction is in agreement with previous observations on ethyleneimines.[5]

The molecular refractivity as calculated with the Lorentz–Lorenz equation is 22.41. The value obtained from the structural formula is 22.412.

Anal. Calcd. for C_4H_9N: C, 67.5; H, 12.8. Found: C, 67.3; H, 13.0.

This amine was also obtained in 7% yield by the treatment of the hydrochloride of 2-chloroethylethylamine with 40% aqueous sodium hydroxide.

Picrate.—Fine yellow needles, melting when dry at 111°.

Chloroaurate.—The amine forms with chloroauric acid a light yellow precipitate which decomposes sharply at 104°.

Hydrochloride.—The evaporation of N-ethylethyleneimine with an excess of hydrochloric acid results in the formation of the hydrochloride of 2-chlorethylethylamine. Three crystallizations from *n*-butanol yielded a pure white product which melted at 223°. An intimate mixture of this with the known hydrochloride of 2-chlorethylethylamine melted at 223°.

Anal. Calcd. for $C_4H_{11}NCl_2$: ionizable chlorine, 24.62; total chlorine, 49.24. Found: ionizable chlorine, 24.73; total chlorine content, 49.69.

Summary

1. N-Ethylethyleneimine has been obtained from the reaction of 2,2′-dichlorodiethylamine with metallic sodium. Its properties have been studied briefly and a few derivatives prepared. The presence of N-vinylethyleneimine also was indicated.

2. The hydrochloride of 2-chlorethylethylamine obtained by the evaporation of N-ethylethyleneimine with hydrochloric acid has been compared with the same compound prepared by another method.

3. N-Ethylethyleneimine and 2-chloroethylethylamine hydrochloride are apparently new to literature.

MOSCOW, IDAHO RECEIVED MAY 3, 1941

---

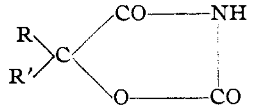
[5] British Patent 501,595; *Chem. Abs.*, **33**, 6479 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY, VANDERBILT UNIVERSITY SCHOOL OF MEDICINE]

5,5-Dialkyl-2,4-oxazolidinediones[1,2]

BY ROGER W. STOUGHTON

In a recent study of diacylureas,[3] we made the observation that the properties of the diureides derived from simple aliphatic acids differed from those of a group of compounds reported by Clemmensen and Heitman[4] as diureides of α-hydroxy acids. The latter had been prepared by the condensation of the ethyl ester of an α-hydroxy acid with urea in the presence of sodium ethylate, a procedure by which it is impossible to prepare simple diureides. Consequently, this condensation was repeated, and while the products which were obtained were similar in general properties to those described by Clemmensen and Heitman, the analytical data indicated that they were not diureides but might be substituted oxazolidinediones. A comparison of the product obtained from the condensation of ethyl lactate and urea with a sample of 5-methyl-2,4-oxazolidinedione prepared by the method of Traube and Ascher[5] showed these two substances were identical. After this part of the work had been completed, the same conclusion was reported independently by Aspelund[6] while working with the hydrolysis products of certain dialuric acids. Therefore, the hydroxy diureides of Clemmensen and Heitman are actually 5-substituted-2,4-oxazolidinediones.



Only a few of these 2,4-oxazolidinediones are recorded in the literature. They have been prepared by the action of bromine water or lead acetate on 2-thio-4-oxazolidone[7]; by the condensation of an α-hydroxy ester with guanidine and the subsequent hydrolysis of the 2-imino-4-oxazolidone[5,8]; by the reaction of ethyl chlorocarbonate and the amide of an α-hydroxy acid[9]; and by the action of alkali on an α-substituted-α-bromoacetylurea.[10]

---

[1] Presented before the Division of Medicinal Chemistry at the St. Louis meeting of the American Chemical Society, April 10, 1941.

[2] This investigation was supported by a grant from the Mallinckrodt Chemical Works, St. Louis, Missouri.

[3] Stoughton, *J. Org. Chem.*, **2**, 514 (1938).

[4] Clemmensen and Heitman, *Am. Chem. J.*, **40**, 280 (1908); **42**, 319 (1909).

[5] Traube and Ascher, *Ber.*, **46**, 2077 (1913).

[6] Aspelund, *Acta Acad. Aboensis. Math. et Phys.*, **11**, no. 7 (1938); **11**, no. 14 (1939).

[7] (a) Urech, *Ber.*, **11**, 467 (1878); **13**, 485 (1880); (b) Ahlquist, *J. prakt. Chem.*, **99**, 45 (1919); (c) Erlenmeyer, Kleiber and Loebenstein, *Helv. Chim. Acta*, **21**, 1010 (1938).

[8] Erlenmeyer and Kleiber, *ibid.*, **21**, 111 (1938).

[9] Altwegg and Ebin, U. S. Patent 1,375,949 (1921); British Patent 159,153 (1920).

[10] Newberry, *J. Chem. Soc.*, **127**, 295 (1925).