prepared by the method of Bleyberg and Ulrich.[8] Octadecyl cyanide was prepared according to Levene and Taylor,[9] who have found two melting points for some of the higher cyanides, but say nothing regarding this property for the octadecyl cyanide. In some preliminary work the authors have noticed a lower melting modification of octadecyl cyanide, m. p. 34–34.5°. Further work will be done on the various cyanides from this standpoint. The cyanide was hydrolyzed by boiling with alcoholic sodium hydroxide. It was found that by blowing air through the boiling solution, the hydrolysis was greatly speeded up. The acid obtained was crystallized from alcohol and benzene, m. p. 68–68.5°. Bleyberg and Ulrich[8] have reported m. p. 68–69°, Levene and Taylor,[9] m. p. 69–70°, and very recently, Shiina,[10] m. p. 68.2–68.4°. The neutral equivalent was 300.0; calculated for $C_{19}H_{38}O_2$, 298.3.

Trinondecylin was made from nondecylic acid and glycerol. It was crystallized once from ether, once from alcohol and four times from toluene. The phenomenon of "triple melting" was observed, *viz.*, α, 66.5–67°; β, 70.5°; glass, 60°. The phenomenon of alternation was evident in the case of the β-form. Loskit[2] has reported for β-tristearin, m. p. 71.8°; Clarkson and Malkin,[2] m. p. 71.5°; with the Abbé refractometer, n^{72}D 1.4430.

Anal. Calcd. for $C_{00}H_{116}O_6$: C, 77.16; H, 12.54. Found: C, 77.11 and 77.50; H, 12.46 and 12.59.[11] The saponification equivalent was 310.8; calcd., 311.0. Alkaline hydrolysis of trinondecylin gave nondecylic acid with the same melting point as the original acid. Trinondecylin was hydrolyzed by lipase.

Summary

The preparation of trinondecylin is described. Trinondecylin occurs as the α, β and glassy modifications melting, respectively, at 66.5–67, 70.5 and 60°. The phenomenon of alternation is evident in the case of the β modification.

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[8] Bleyberg and Ulrich, *Ber.*, **64**, 2504 (1931).

[9] Levene and Taylor, *J. Biol. Chem.*, **59**, 905 (1924).

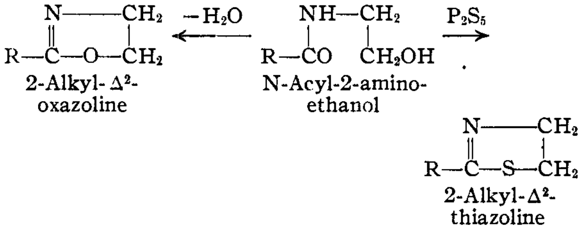
[10] Shiina, *J. Soc. Chem. Ind.*, Japan, **36**, Suppl. binding, 569 (1933).

[11] The authors are indebted to Mr. W. A. Lang for the combustion analysis.

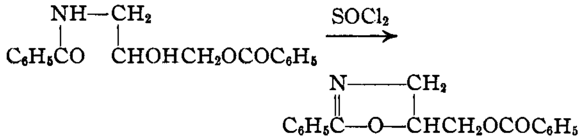
The Synthesis of Δ²-Oxazolines and Δ²-Thiazolines from N-Acyl-2-aminoethanols

BY HENRY WENKER

A study of the chemistry of N-acyl-2-aminoethanols of the formula $RCONHCH_2CH_2OH$ was considered of interest with regard to possible heterocyclic syntheses according to the scheme



Bergmann and Brand[1] have described the preparation of a Δ²-oxazoline from a N-acyl-2-aminoalcohol



The method has not been used for the preparation of other Δ²-oxazolines, nor does the literature contain any reference concerning the synthesis of a Δ²-thiazoline from a N-acyl-2-aminoalcohol.

Since data on N-acyl-2-aminoethanols, the starting material used for the present investigation, are few and partly not in agreement,[2,3,4] a general method for their preparation seemed desirable. It was found that compounds of this class can be prepared conveniently by heating equimolar proportions of acid and 2-aminoethanol to 200°, followed by vacuum distillation. The acids used were formic, acetic, propionic and benzoic.

Attempts at cyclization showed that the corresponding Δ²-oxazolines can be prepared from N-acetyl- and -propionyl-2-aminoethanol by thermal decomposition, while phosphorus pentoxide is required as condensing agent in the case of the benzoyl compound. N-Formyl-2-aminoethanol, under various experimental conditions, decomposed with evolution of carbon monoxide and regeneration of 2-aminoethanol.

Under the influence of phosphorus pentasulfide, all of the N-acyl-2-aminoethanols under consideration yielded the corresponding Δ²-thiazolines.

Experimental

Materials Used.—2-Aminoethanol was commercial monoethanolamine,[5] boiling within 2°. Formic, acetic

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[1] Bergmann and Brand, *Ber.*, **56**, 1280 (1923).

[2] French Patent 638,023 (1928).

[3] Fränkel and Cornelius, *Ber.*, **51**, 1657 (1918).

[4] Knorr, *ibid.*, **36**, 1278 (1903).

[5] From Carbide and Carbon Chemicals Corporation.

and propionic acids were C. P. Benzoic acid was U. S. P. grade. Nitrogen was determined by the Kjeldahl method. Substances not described hitherto are marked with an asterisk(*).

Preparation of N-Acyl-2-aminoethanols.—The method employed was the same for all four compounds. A mixture of equimolar quantities of acid and 2-aminoethanol was heated in an open flask until the loss of weight corresponded with 1 mole of water. Boiling began at 160° and almost ceased at 200°, indicating the end of the reaction. The three aliphatic compounds distilled under reduced pressure at constant temperatures, leaving no residue; the benzoyl compound contained a considerable amount of higher boiling material. Results are shown in Table I. The aliphatic compounds are colorless, almost odorless, slightly viscous liquids, miscible with water and with ethanol, sparingly soluble in ether. The benzoyl compound is a thick oil, fairly soluble in water. Contrary to the data given in the literature,[3,4] it could not be obtained in crystalline form.

TABLE I

Substance -2-amino-ethanol	B. p. (10 mm.), °C.	Spec. gr. $^{25}/_{25}$	Yield, %	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
Formyl	191–193	1.180	75	$C_3H_7NO_2$	15.73	15.59
Acetyl	195–196	1.115	78	$C_4H_9NO_2$	13.50	13.70
Propionyl*	201–203	1.071	74	$C_5H_{11}NO_2$	11.97	11.74
Benzoyl	230–231	1.179	62	$C_9H_{11}NO_2$	8.48	8.15

Preparation of Δ²-Oxazolines.—2-Methyl- and -ethyl-Δ²-oxazoline were prepared by heating 20–30 g. of the respective acyl compound in a 250-ml. flask to 260–280°. The rate of distillation was regulated so that the temperature of the vapor did not exceed 160°. The distillate amounted to about 75% of the material used; it was purified first by distillation, in order to eliminate higher boiling material, then dried several times with fresh portions of potassium hydroxide, and finally fractionated.

The benzoyl compound, under the conditions described, decomposed without formation of 2-phenyl-Δ²-oxazoline. Cyclization in this case was effected as follows: 33 g. of N-benzoyl-2-aminoethanol and 33 g. of phosphorus pentoxide were mixed in a nickel crucible. After short standing, a violent reaction set in, and the crucible was cooled by immersion in water. When the reaction was finished, the solid, transparent mass was dissolved in 250 ml. of 10% sodium hydroxide solution, the oily base taken up in ether, dried with potassium hydroxide and fractionated.

Experiments in order to obtain the hitherto unknown Δ²-oxazoline from N-formyl-2-aminoethanol included thermal decomposition and the use of phosphorus pentoxide, metallic sodium, sodamide and calcium carbide. In all cases 2-aminoethanol was recovered and evolution of carbon monoxide was observed. The Δ²-oxazolines prepared are shown in Table II.

TABLE II

Substance -Δ²-oxazoline	B. p., °C. Found	B. p., °C. Lit.	Picrate, m. p., °C. Found	Picrate, m. p., °C. Lit.	Yield, %
2-Methyl	110–111	109.5–110.5	163	159–160	30
2-Ethyl*[a]	124–125	....	154	.....	35
2-Phenyl	246–248	242–243	177	177	22

[a] 2-Ethyl-Δ²-oxazoline. The base is a colorless liquid, miscible with water, ethanol and ether. *Anal.* Calcd. for C_5H_9ON: N, 14.14. Found: N, 13.85.

Preparation of Δ²-Thiazolines.—The procedure given below for 2-methyl-Δ²-thiazoline was used also for the preparation of the two other aliphatic thiazolines: 45 g. of N-acetyl-2-aminoethanol was mixed with 20 g. (5:1 mole) of phosphorus pentasulfide in a 1000-ml. retort connected with a large water-cooled condenser. Soon a violent reaction started, during which the major part of the 2-methyl-Δ²-thiazoline distilled over. Subsequent heating yielded a little more base. The distillate was dried with potassium hydroxide; it distilled almost without residue. For the preparation of 2-phenyl-Δ²-thiazoline, the method was modified as follows: 50 g. of N-benzoyl-2-aminoethanol and 27 g. of phosphorus pentasulfide (5:2 mole) were heated in a beaker until reaction started, and the base was isolated from the mass, after cooling, in the manner described for 2-phenyl-Δ²-oxazoline. The thiazolines prepared are shown in Table III.

TABLE III

Substance -Δ²-thiazoline	B. p., °C. Found	B. p., °C. Lit.	Picrate, m. p., °C. Found	Picrate, m. p., °C. Lit.	Yield, %
Δ²-Thiazoline	139–140	138–139	150–151	150–151	38
2-Methyl-	144	144	171	171	38
2-Ethyl-	162	162	138	135	34
2-Phenyl-	276–277	275–277	172	171–172	68

Summary

A preparative method for N-acyl-2-aminoethanols is described and the following members of the series have been prepared: N-formyl, acetyl, propionyl and benzoyl-2-aminoethanol.

With the exception of the formyl compound, these N-acyl-2-aminoethanols yield Δ²-oxazolines under conditions favoring dehydration.

All of the described N-acyl-2-aminoethanols yield Δ²-thiazolines when heated with phosphorus pentasulfide.

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