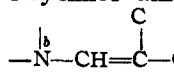
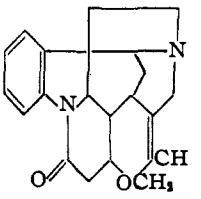
quantity of volatile acid consistent with that obtained from a blank determination.

The small volume of acid in the first fraction, and the constancy of the amount in successive fractions of distillate, led to the conclusion that hydrolysis of the amide linkage was occurring at the same time as the acid produced was being distilled.

When acidic hydrolysis was employed the sample was refluxed for two hours with 2 *N* sulfuric acid before distillation was started. Here again the collection of fractions of distillate was continued until they contained constant amounts of volatile acid of the same size as was found in a blank determination.

Summary

It has been shown that the *neo* bases derived from the strychnos alkaloids contain the part structure  . This demonstration resolves previous difficulties in the way of the acceptance of the structure (I) for strychnine. The general situation has now advanced to the point at which it is conclusive in favor of the expression (I), and the structure of the major strychnos alkaloids is regarded as established.



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Chemical Reactions of Caprolactam

BY RICHARD E. BENSON AND THEODORE L. CAIRNS

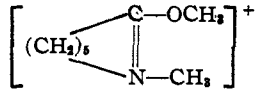
This paper reports the results of a general investigation of the chemistry of caprolactam with emphasis on the O-alkyl imino ethers and their reactions, and on nitrogen-substituted derivatives obtainable by alkylation and acylation. The general reactivity of caprolactam parallels that of related open-chain amides but several unusual transformations were observed and some discrepancies in the literature were clarified.

The preparation of O-methylcaprolactim (I) was accomplished by the direct action of dimethyl sulfate on caprolactam in benzene solution.[1a] Dur-

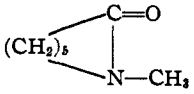
I, R = CH_3
II, R = C_2H_5

ing this preparative work, it was noticed that the proportion of N-methylcaprolactam formed along with the O-methylcaprolactim increased as the scale of the preparation was increased and that, in particular, the amount of N-methyl derivative formed was very much greater when all the dimethyl sulfate was added at once compared with the amount formed when a gradual addition over a long period of time was used. These observations lead to the hypothesis that dimethyl sulfate reacts with I to convert it to N-methylcaprolactam as shown in the equation

I + $(CH_3)_2SO_4$ ⟶



$OSO_3CH_3^-$ ⟶



+ $(CH_3)_2SO_4$

That this may actually be the case is demonstrated by the fact that treatment of O-methylcaprolactim in benzene solution with 0.1 mole equivalent of dimethyl sulfate brought about its conversion to N-methylcaprolactam in 80% yield. In addition, the action of excess dimethyl sulfate on the lactam gave the N-methyl derivative in 70% yield. The report[2] that the interaction of dimethyl sulfate and caprolactam leads only to the N-methyl derivative may well be accounted for by the assumption that a slight excess of the alkylating agent was used. O-Ethylcaprolactim (II)[1b] was prepared in an analogous fashion. It was found that heating caused rearrangement of both I and II to the corresponding N-alkyl compounds in a manner similar to that reported for open-chain imino ethers.[3]

O-Methylcaprolactim was found to be a water-insoluble basic material that could be converted by the action of boiling water into a mixture of caprolactam and ϵ-aminocaproic acid. Treatment of the imino ether with amines led to the corresponding amidines; these are listed in Table I. In the case of the unsubstituted amidine it was found that the action of ammonia on the imino ether was not a satisfactory preparative method, while the use of ammonium chloride readily yielded the desired amidine as the hydrochloride, in accord with the experience of Knorr[4]

(1) (a) Schlack, U. S. Patent 2,356,622. Other methods for the preparation of this and related imino ethers may be found in (b) French Patent 673,628; Schmidt and Zutavern, German Patents 532,969 and 531,403.

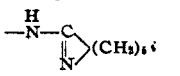
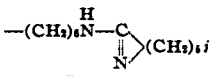
(2) Prochazka, *Chem. Listy*, **37**, 208 (1943); *C. A.*, **40**, 2113 (1946).

(3) Chapman, *J. Chem. Soc.*, 1992 (1925).

(4) Knorr, *Ber.*, **50**, 229 (1917).

TABLE I

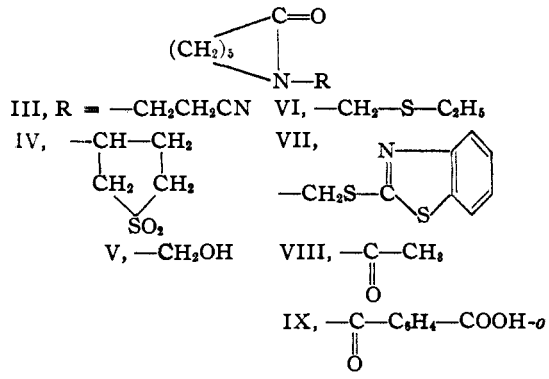
AMIDINES PREPARED BY THE CONDENSATION OF O-METHYLCAPROLACTIM WITH AMINES $(CH_2)_5\langle C(=N-R)-NH \rangle$

Product, R =	Yield, %	M. p., °C.[a]	Conditions	Formula	Analyses, % Calculated C	H	N	Found C[b]	H[b]	N[b]
—$C_6H_4OCH_3$-o	83	86–88[c]	175°, 3 hours	$C_{12}H_{16}N_2O$	71.52	8.31	12.83	71.70	8.66	12.98
—C_6H_4Cl-o	45	126–128[d]	190°, 3.5 hours, 1 ml. 10% KOH	$C_{12}H_{15}N_2Cl$	64.71 (Cl, 15.92)	6.79	12.58	64.13 (Cl, 16.4)	6.88	12.26
	36	129–130[d]	100–110°, 65 hours	$C_{13}H_{22}N_2$	74.17	11.41	14.42	74.21	11.54	14.62
—$C_{12}H_{27}$[e]	85	73–74[f]	165°, 4 hours	$C_{24}H_{48}N_2$	79.05	13.27	7.68	79.05	12.67	6.72
—NH_2[g]	88	103.5–104.5[h]	Steam-bath 0.5 hour							
	50	125.5–126.5[d]	Steam-bath 0.5 hour							
	78	160–160.5[h]	Methyl alcohol, steam-bath, 17 hr.	$C_{18}H_{34}N_4$	70.54	11.18	18.28	70.37	11.22	18.31
—H·HCl	85	159.5–160.5[k]	NH_4Cl, abs. EtOH, room temp., 3 days	$C_6H_{12}N_2Cl$	48.48 (Cl, 23.85)	8.82	18.85	48.35 (Cl, 23.6)	8.70	18.80

[a] The m. p. values are uncorrected. [b] Average of two determinations. [c] From hexane–ether. [d] From acetone. [e] Oxalate salt, m. p. 105.5–107°, from ethanol. *Anal.* Calcd. for $C_{24}H_{48}N_2 \cdot C_2H_2O_4$: C, 68.68; H, 11.08; N, 6.16. Found: C, 68.56; H, 10.83; N, 6.82. [f] From ether. [g] Lit.[5] m. p. 112°. [h] From benzene. [i] Lit.[11] m. p. 126°. [j] Preparation described,[1a] but not isolated or characterized. [k] From absolute ethanol–ether.

with acetamidine. The hydrogenation of O-methylcaprolactim over Raney nickel, ruthenium oxide, or barium–copper chromite catalyst yielded hexamethylenimine, while the use of platinum gave the amidine derived from interaction of the O-ether and hexamethylenimine.

In addition to N-methyl- and N-ethylcaprolactam, it was found that other nitrogen-substituted derivatives could be prepared from caprolactam by the following types of reactions: (1) addition to active unsaturated compounds, (2) reaction with formaldehyde, and (3) reaction with acid anhydrides. Treatment of caprolactam with acrylonitrile gave the corresponding N-β-cyanoethyl derivative (III),[6] and 2,5-dihydrothiophene-1-dioxide gave an analogous product IV.



The N-methylol derivative V was obtained by the action of formaldehyde on caprolactam. Compound V with mercaptans, such as ethyl mercaptan and 2-mercaptobenzothiazole, yielded the corresponding alkylthiomethyl derivatives VI and VII. Refluxing caprolactam with acetic anhydride formed N-acetylcaprolactam (VIII) as reported by Prochazka.[2] The structure of the product obtained by Prochazka[2] from caprolactam and phthalic anhydride is not clear, but it was apparently regarded as the bisamide from two moles of caprolactam and one mole of the anhydride. Such a formulation is at variance with a German report[7] which states that the compound is the monoamide, N-(*o*-carboxybenzoyl)-caprolactam (IX), and that the bisamide could not be formed. In our work only the monoamide IX was obtained.

Hydrolysis of N-methylcaprolactam with concentrated hydrochloric acid has been reported by Ruzicka[8] to give the expected N-methyl-ϵ-aminocaproic acid, m. p. 130–131°, while the use of 10% sulfuric acid has been reported by Lukes and Smolek[9] to form N-methyl-α-aminocaproic acid, m. p. 66°.* We have repeated the work of Lukes and Smolek and obtained a compound melting at 66–67° which has been shown conclusively to be the dihydrate of N-methyl-ϵ-aminocaproic acid and not the α-amino derivative. In view of the fact that the analytical data reported by Lukes and Smolek are correct for the free amino acid and not the dihydrate, it is believed that the water of hydration was lost during drying of their sample for analysis and that they failed to observe the change in melting point which accompanies this dehydration.

Experimental

O-Methylcaprolactim (I).—A modification of the procedure given in the literature[1a] gave increased yields on large runs. To a refluxing, stirred solution of 678 g. (6 moles) of caprolactam[10] in 2 l. of benzene was added 569 ml.

(5) Stolle, *Ber.*, **62B**, 1032 (1930).

(6) This compound is mentioned in Office of Publication Board Report 693 but no experimental details are given.

(7) Office of Publication Board Report 621.

(8) Ruzicka, *Helv. Chim. Acta*, **4**, 472 (1921).

(9) Lukes and Smolek, *Coll. Czech Chem. Commun.*, **11**, 506 (1939); *C. A.*, **34**, 7868 (1940).

(10) Obtained from Explosives Department, E. I. du Pont de Nemours & Company, Wilmington, Delaware.

(6 moles) of dimethyl sulfate over a period of two and one-half hours. The mixture was refluxed for sixteen hours longer. The cold mixture was made alkaline with excess 50% potassium carbonate, the organic layer was separated, and the product was distilled. There was obtained 517 g. (68% yield) of I, b. p. 65–67° (24 mm.), $n^{25}D$ 1.4610, d^{25}_4 0.9598; lit.[1a,b] b. p. 50–52° (4 mm.), 160°.

Anal. Calcd. for $C_7H_{13}NO$: C, 66.10; H, 10.30; N, 11.01. Found: C, 66.10, 65.86; H, 10.44, 10.31; N, 10.87, 11.04.

There was also obtained 10 g. (1.3% yield) of N-methylcaprolactam, b. p. 133–135° (26 mm.).

O-Ethylcaprolactim (II).—In a manner similar to the preparation of I, O-ethylcaprolactim was prepared in 52% yield, b. p. 81–82° (26 mm.), $n^{25}D$ 1.4564, d^{25}_4 0.9440; lit.,[1b] b. p. 180°.

Anal. Calcd. for $C_8H_{15}NO$: C, 68.04; H, 10.71; N, 9.92. Found: C, 67.71, 67.67; H, 10.63, 10.62; N, 9.40, 9.56.

Hydrolysis of O-Methylcaprolactim.—A mixture of 15 g. of I and 50 ml. of water was refluxed for ten minutes, and the resulting homogeneous solution was then cooled and extracted with ether. Concentration of the ether extract by distillation gave 2 g. (15% yield) of caprolactam m. p. 69–70°, mixed m. p., 69–70°.

Concentration of the water solution gave, after crystallization from ethanol–water, 7 g. (45% yield) of ϵ-aminocaproic acid, m. p. 192–194°, mixed m. p. with authentic ϵ-aminocaproic acid, m. p. 196°. The authentic sample melts at 196.5°.

N-Methylcaprolactam (Method A).—The preparation was similar to that of I except that 0.32 molar excess of the dialkyl sulfate was used per mole of the lactam. There was obtained a 70% yield, b. p. 120° (19 mm.), $n^{25}D$ 1.4818, d^{25}_4 1.0154.

Anal. Calcd. for $C_7H_{13}NO$: N, 11.01. Found: N, 10.92, 11.02.

Ruzicka[8] has prepared this compound, b. p. 120° (15 mm.), by the reaction of N-sodiocaprolactam and dimethyl sulfate, while Prochazka[2] states that only N-methylcaprolactam could be prepared by the action of dimethyl sulfate and caprolactam.

Method B.—By action of dimethyl sulfate on I: A solution of 25.4 g. (0.2 mole) of I, 1.9 ml. (0.02 mole) of dimethyl sulfate and 50 ml. of benzene was refluxed for six hours. The solution was shaken with excess 50% potassium carbonate, the organic layer separated and distilled. There was obtained 20.5 g. of N-methylcaprolactam, b. p. 128° (32 mm.), $n^{25}D$ 1.4812.

Method C.—Thermal rearrangement of I: O-Methylcaprolactim was heated in a steel bomb at 285° for ten hours. Distillation of the product gave a 67% yield of the N-methyl compound, b. p. 110–112° (10 mm.), $n^{25}D$ 1.4833.

N-Ethylcaprolactam.—O-Ethylcaprolactim (25 g.) was heated for two hours at 180–250° in an atmosphere of nitrogen. Distillation gave 23.4 g. (85% yield) of N-ethylcaprolactam, b. p. 97° (5.5 mm.), $n^{25}D$ 1.4777, d^{25}_4 0.9850.

Anal. Calcd. for $C_8H_{15}NO$: C, 68.04; H, 10.71; N, 9.92. Found: C, 68.42, 68.20; H, 10.85, 10.70; N, 9.48, 9.53.

Amidines.—The preparation of several cyclic amidines was achieved by heating I with the appropriate amine. The results are summarized in Table I. A typical example is given below.

A mixture of 25.4 g. (0.2 mole) of I and 24.6 g. (0.2 mole) of *p*-anisidine was heated at 175° for three hours, and the methanol continuously removed by distillation. The resulting 2-(*p*-anisidino)-1-aza-1-cycloheptene was crystallized from hexane–ether to give 36 g. (83% yield) of white needles, m.p. 85–87°. The analytical results are given in Table I.

2-(1′-Azacycloheptyl)-1-aza-1-cycloheptene. Method A.—A solution of 83.3 g. (0.657 mole) of I and 65 g. (0.657 mole) of hexamethylenimine was refluxed for nine hours and then the methanol was removed by distillation. The resulting product was fractionated through a 6″ Vigreux column to give 100 g. (78%) of the amidine, b. p. 165–170° (25–28 mm.), $n^{25}D$ 1.5242; methiodide, m. p. 194.5–196°.

Method B.—A solution of 50 g. (0.394 mole) of I in 125 ml. of absolute ethanol was shaken with platinum oxide catalyst under a hydrogen pressure of 20–30 lb./sq. in. for twenty-four hours. The total pressure drop corresponded to about 0.25 mole of hydrogen. The alcohol was removed by distillation and the product fractionated to give 27.3 g. of I, b. p. 33–35° (1 mm.) and 15.2 g. of the amidine, b. p. 98–105° (1 mm.) (87% yield at 45% conversion of I), $n^{25}D$ 1.5248, d^{25}_4 0.9956.

Anal. Calcd. for $C_{12}H_{22}N_2$: C, 74.17; H, 11.41; N, 14.42. Found: C, 73.77, 73.92; H, 11.29, 11.34; N, 14.18, 14.03.

Methiodide, m. p. 193.5–194.5°: a mixed m. p. of methiodides of the amidine prepared by Methods A and B, m. p. 194–196°.

Anal. Calcd. for $C_{13}H_{25}N_2I$: N, 8.33; I, 37.74. Found: N, 8.99, 8.70; I, 37.67, 37.73.

Hexamethylenimine.—O-Methylcaprolactim was hydrogenated at 150° and 2000–3000 lb./sq. in. hydrogen pressure using barium–copper chromite catalyst to give 70% yield of the imine, b. p. 134–137°, $n^{25}D$ 1.4645, d^{25}_4 0.8806 (literature values,[11] b. p. 138°, $n^{23}D$ 1.4654, d^{25}_4 0.8770). The imine was converted to its picrate, m. p. 144–145°, lit.[11] m. p. 146.5°, and *p*-toluenesulfonamide, m. p. 75–76°, lit.[12] m. p. 76.5°. The hydrogenation of I at 3000 lb./sq. in. using Raney nickel catalyst at 140° gave 49% of the imine, while the use of ruthenium catalyst at 125° gave 31% yield.

N-(β-Cyanoethyl)-caprolactam (III).—To a solution of 113 g. (1.0 mole) of caprolactam in 300 ml. of dioxane and 6 ml. of "Triton" B (trimethylbenzylammonium hydroxide) was added dropwise with stirring 56 g. (1.0 mole) of acrylonitrile over a period of thirty-five minutes with the temperature maintained at 30–35°. Stirring was continued for two hours and the reaction mixture allowed to stand at room temperature for sixty-three hours. The solution was made slightly acid with hydrochloric acid, the dioxane and unreacted acrylonitrile removed by distillation, and the product fractionated through an 8″ Vigreux column to give 108 g. (65% yield) of III, b. p. 153–158° (1.5–1.8 mm.), $n^{25}D$ 1.4903, d^{25}_4 1.074. On standing, the product crystallized to give white needles, m. p. 32–34°, readily soluble in water and most organic solvents.

Anal. Calcd. for $C_9H_{14}N_2O$: C, 65.03; H, 8.49; N, 16.85. Found: C, 64.97, 64.86; H, 8.49, 8.41; N, 17.11, 16.93.

N-(β-Cyanoethyl)-caprolactam was hydrolyzed to 4-azasebacic acid in 40% yield by refluxing with 25% sulfuric acid; m. p. 177–178° from 95% ethanol.

Anal. Calcd. for $C_9H_{17}NO_4$: C, 53.19; H, 8.43; N, 6.89. Found: C, 52.86, 52.93; H, 8.52, 8.56; N, 6.82, 6.77.

N-(1,1-Dioxotetrahydro-3-thienyl)-caprolactam (IV).—A mixture of 56.5 g. (0.5 mole) of caprolactam and 1 g. of potassium hydroxide was heated to 65° and 59 g. (0.5 mole) of 2,5-dihydrothiophene-1-dioxide added in 2-g. portions over a period of thirty minutes with constant stirring. The temperature rose to 70° and the mixture was heated and stirred at 65–75° for seven hours. The product was crystallized from ethanol and then from ethanol–ether to give 19 g. (16.5% yield) of white needles, m. p. 107–108°. An analytical sample melts at 108–109.5°.

Anal. Calcd. for $C_{10}H_{17}NO_3S$: C, 51.92; H, 7.41; N, 6.06; S, 13.86. Found: C, 51.81, 52.06; H, 7.48, 7.59; N, 6.04, 5.92; S, 13.82, 13.78.

N-Methylolcaprolactam (V).[13]—A mixture of 339 g. (3.0 moles) of caprolactam, 135 g. of paraformaldehyde,

(11) Müller and Sauerwald, *Monatsh.*, **48**, 727 (1927).

(12) Müller and Bleier, *ibid.*, **50**, 399 (1928).

(13) Prepared by Dr. Clarence E. Denoon; present address, Rohm & Haas Co., Philadelphia, Pa.

5 g. of sodium hydroxide and 500 ml. of 95% ethanol was stirred and heated at 140–150° for three hours. The mixture was filtered from a small amount of insoluble material and cooled in a Dry Ice–acetone-bath. There was obtained 184 g. of white, microcrystalline solid, V. Concentration of the filtrate yielded an additional 105 g. of V, m. p. 62–64°, total yield 289 g. (67%). Recrystallization from methanol gave an analytical sample, m. p. 65–66°.

Anal. Calcd. for $C_7H_{13}NO_2$: N, 9.78. Found: N, 9.98.

N-(Ethylthiomethyl)-caprolactam (VI).[13]—A mixture of 113 g. (1.0 mole) of caprolactam, 45 g. of paraformaldehyde, 3 g. of sodium hydroxide, and 250 ml. of 95% ethanol was stirred and heated at 40–50° for fourteen hours. The mixture was cooled, 40 ml. of concentrated hydrochloric acid added and the precipitated sodium chloride removed by filtration. To the filtrate was added 93 g. (1.5 moles) of ethyl mercaptan and the resulting mixture allowed to stand overnight. To the mixture was added 100 ml. of ether, the resulting organic layer washed with 5% sodium hydroxide and finally with water. The oil was dried over sodium sulfate and then distilled to give 122 g. (65% yield) of VI, b. p. 138–141° (5–6 mm.), $n^{25}D$ 1.5189, d^{25}_4 1.0689.

Anal. Calcd. for $C_9H_{17}NOS$: S, 17.12. Found: S, 17.30.

N-(Benzothiazolyl-2-thiomethyl)-caprolactam (VII).[13]—A mixture of 113 g. (1.0 mole) of caprolactam and 30 g. of paraformaldehyde was heated at 80–90° for one-half hour. To this hot mixture was added 167 g. (1.0 mole) of 2-mercaptobenzothiazole and the mixture heated at 130–140° for two additional hours. The resulting liquid was poured into 2 l. of 5% sodium carbonate and stirred to give a yellow crystalline mass. The yellow product was ground, extracted again with sodium carbonate and finally with 1500 ml. of 95% ethanol. The ethanol filtrate was decolorized with activated carbon, filtered and cooled to give 150 g. (51% yield) of crystalline solid, m. p. 150–155°. An analytical sample from methanol melts at 157°.

Anal. Calcd. for $C_{14}H_{16}N_2OS_2$: S, 21.93. Found: S, 22.21.

N-Acetylcaprolactam (VIII).—A mixture of 678 g. (6.0 moles) of caprolactam and 670 g. (6.65 moles) of acetic anhydride was refluxed for four hours. After removal of the unreacted anhydride and acetic acid, there was obtained 775 g. (83.5% yield) of N-acetylcaprolactam, b. p. 134–136° (26–27 mm.); $n^{25}D$ 1.4885, d^{25}_4 1.094.

Anal. Calcd. for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03; sapn. eq., 155.2. Found: C, 62.20, 61.90; H, 8.75, 8.70, N, 9.36, 9.06; sapn. eq., 159, 158.

This compound has been prepared previously[2] but physical constants other than b. p. 130–131° (13 mm.) were not given.

N-(*o*-Carboxybenzoyl)-caprolactam (IX).—A mixture of 113 g. (1.0 mole) of caprolactam and 148 g. (1.0 mole) of phthalic anhydride was heated at 180–195° for eighteen hours. The product was distilled through a short column to give 231 g. of IX, b. p. 206–208° (0.20–0.25 mm.), m. p. 104.5–106.5°. Recrystallization from hexane–ethanol gave 210 g. (80% yield) of product, m. p. 105–107°. Further recrystallization from benzene gave m. p. 107.5–108°. The product is soluble in sodium bicarbonate solution.

Anal. Calcd. for $C_{14}H_{15}NO_4$: C, 64.35; H, 5.79; N, 5.36; neut. eq., 261.3. Found: C, 64.38, 64.44; H, 5.94, 5.97; N, 5.51, 5.46; neut. eq., 254.4, 253.6.

Prochazka[2] has reported that the above reaction using one-half mole of the anhydride per mole of lactam yields N-phthaloylcaprolactam, b. p. 279–282° (15 mm.), m. p. 108.5–109°; while a German report[7] states that only N-(*o*-carboxybenzoyl)-caprolactam, b. p. 250° (2–3 mm.), m. p. 109–110°, can be prepared. Since no analytical data were available and the reported physical constants are similar, it was necessary to repeat the reaction to determine the exact structure of the resulting compound. The directions of Prochazka were followed but only unchanged caprolactam and IX were obtained by distillation of the reaction mixture.

N-Methyl-ε-aminocaproic Acid Dihydrate.—A solution of 130 g. of concentrated sulfuric acid, 1170 ml. of water and 130 g. (1.025 mole) of N-methylcaprolactam was refluxed for ten hours. The hot solution was treated with a slight excess of barium hydroxide, filtered to remove the precipitated barium sulfate, the filtrate treated with solid carbon dioxide to remove the barium ions as barium carbonate and the solid removed by filtration. The resulting filtrate was concentrated by distillation to give a sirupy residue that was treated with benzene and heated to remove most of the remaining water. The resulting product was crystallized twice from absolute ethanol–ether to give a white, crystalline solid, m. p. 66–67°. The directions followed were those of Lukes and Smolek[9] who state that the product thus obtained was N-methyl-α-aminocaproic acid, m. p. 66°; however, Ruzicka[8] has stated that the hydrolysis of N-methylcaprolactam with concentrated hydrochloric acid yields N-methyl-ε-aminocaproic acid, m. p. 130–131°.

The product of m. p. 66–67° was identified as N-methyl-ε-aminocaproic acid dihydrate by analysis, dehydration to N-methyl-ε-aminocaproic acid, and ring closure to give N-methylcaprolactam.

Anal. Calcd. for $C_7H_{15}NO_2 \cdot 2H_2O$: C, 46.39; H, 10.57; N, 7.73; neut. eq., 181.23. Found: C, 46.95; 47.00; H, 10.44, 10.74; N, 7.37, 7.58; neut. eq., 180.4, 180.8.

To check the structure of the above compound, a weighed amount of the air-dried material was placed in a drying pistol, evacuated by means of a vacuum pump and heated by boiling alcohol for fifteen hours. The solid did not melt but the crystalline material slowly changed to an amorphous powder. A weighed sample (1.4868 g.) of the compound lost 0.3068 g.; the calculated loss for the dihydrate is 0.2956 g. In addition, the amorphous powder thus obtained melted at 129–131°, lit. m. p. 130–131° for N-methyl-ε-aminocaproic acid.[8]

The air-dried product was heated in a small distilling flask for fifteen minutes and most of the water collected. The temperature was raised and the major portion of the material distilled at 234°, $n^{25}D$ 1.4819. This is in good agreement with the values for N-methylcaprolactam, b. p. 234°, $n^{25}D$ 1.4818.

From the above data it is evident that the product obtained by Lukes and Smolek was the dihydrate of N-methyl-ε-aminocaproic acid rather than N-methyl-α-aminocaproic acid.

Summary

1. The reaction of caprolactam with dimethyl sulfate has yielded O-methylcaprolactim or N-methylcaprolactam depending on the amount of the sulfate used in the reaction. In addition, O-ethyl- and O-methylcaprolactim were rearranged thermally to the corresponding N-substituted derivatives.

2. The condensation of the methyl imino ether with amines yielded the corresponding cyclic amidines.

3. The reaction of caprolactam with active unsaturated compounds, with acid anhydrides and with formaldehyde gave other N-substituted compounds.

4. The hydrolysis of N-methylcaprolactam with 10% sulfuric acid was shown to yield the dihydrate of N-methyl-ε-aminocaproic acid rather than N-methyl-α-aminocaproic acid as previously reported.

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