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STUDIES ON POLYMERIZATION AND RING FORMATION. VIII. AMIDES FROM ε-AMINOCAPROIC ACID

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ε-Aminocaproic acid on being heated reacts with itself and yields two products—the corresponding 7-membered lactam, 20–30%, and an undistillable material of approximately the same composition, 80–70%.[1] The following related facts are of interest. δ-Aminobutyric acid and ε-aminovaleric acid readily lose water and yield the corresponding 5- and 6-membered lactams.[2] No corresponding polymers are formed or known. The reaction of ζ-aminoheptoic acid with itself is apparently exclusively intermolecular, for it leads to an undistillable product quite different in its properties from the known 8-membered lactam.[3] Similar relationships are found among the hydroxy acids: γ- and δ-hydroxy acids yield lactones; ε-hydroxy acids yield both lactones and polyesters,[4] and the higher ω-hydroxy acids yield only the polyesters,[5] although many of the higher lactones are known.[6] Polyesters have now been studied in some detail,[7] but (except for polypeptides) little attention has been devoted to the polyamides. In this paper we record some observations concerning the polyamide derived from ε-aminocaproic acid.

Water is rapidly evolved when ε-aminocaproic acid is heated above its melting point (*e. g.*, to 210–220°). The polymer and the lactam which result are readily separated by allowing the latter to distil under diminished pressure, or by extracting it with boiling alcohol. In different experiments the yield of lactam was 20–30% and the polymer 80–70%. The same products were obtained by gradually heating the ethyl ester of the acid from 160 to 200° during six hours, and the yield of lactam was about 38%.

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[1] V. Braun, *Ber.*, **40**, 1840 (1907); Gabriel and Maas, *ibid.*, **32**, 1266 (1899)

[2] Gabriel, *ibid.*, **22**, 3338 (1889); Schotten, *ibid.*, **21**, 2240 (1888).

[3] V. Braun, *ibid.*, **40**, 1834 (1907); Wallach, *Ann.*, **312**, 205; **309**, 18 (1899); Manasse, *Ber.*, **35**, 1367 (1902).

[4] Baeyer and Seuffert, *ibid.*, **32**, 3619 (1899); Blaise and Koehler, *Compt. rend.*, **148**, 1772 (1909); Marvel and co-workers, THIS JOURNAL, **46**, 2838 (1924).

[5] (a) Blaise and Koehler, Ref. 4; (b) Chuit and Hauser, *Helv. Chim. Acta*, **12**, 4634 (1929); (c) Lycan and Adams, THIS JOURNAL, **51**, 625, 3450 (1929); (d) Blaise and Marcilly, *Bull. soc. chim.*, **31**, 308 (1904).

[6] Ruzicka and Stoll, *Helv. Chim. Acta*, **11**, 1159 (1928).

[7] (a) Lycan and Adams, THIS JOURNAL, Ref. 5c; (b) Carothers and Arvin, *ibid.*, **51**, 2560 (1929); (c) Carothers and Van Natta, *ibid.*, **52**, 314 (1930); (d) Carothers and Dorough, *ibid.*, **52**, 711 (1930); (e) Carothers, Dorough and Arvin, *ibid.*, **52**, 3292 (1930); (f) Chuit and Hauser, Ref. 5b; (g) Blaise and Marcilly, Ref. 5d; (h) Bougault and Bourdier, *J. pharm. chim.*, [6] **29**, 561 (1909); [6] **30**, 10 (1909).

The polymer is a hard gray wax, insoluble in most organic solvents, but soluble in hot formamide, from which it separates as a microcrystalline powder melting at 212–214°. Its analytical composition agrees very closely with that required for the structural unit $\text{—NH—(CH}_2)_5\text{CO—}$.

Anal. Calcd. for $C_6H_{11}ON$: C, 63.71; H, 9.73. Found: C, 63.35, 63.62; H, 9.93, 10.07. A product from another preparation gave: C, 63.35, 63.45; H, 9.56, 9.43.

It is quantitatively hydrolyzed in six hours by boiling concentrated hydrochloric acid to ϵ-aminocaproic acid (identified by conversion to the *p*-toluenesulfonyl derivative, melting point and mixed melting point, 105–106°).

By partial hydrolysis, polyaminocaproylaminocaproic acids are formed. Thus, a sample of the polyamide was heated to boiling for one hour in concentrated hydrochloric acid solution, and the solution was diluted with water to precipitate the unchanged polymer (about 50%). The material remaining in solution, on being treated with alkali and *p*-toluenesulfonyl chloride, gave a solid product which, after repeated crystallization, showed a neutral equivalent corresponding with the formula $C_7H_7\text{-}SO_2\text{-[NH(CH}_2)_5\text{CO]}_3\text{-NH(CH}_2)_5\text{COOH}$ (calcd., 607; found, 601). The structure of the polymer may, therefore, be represented by the formula

$$?\ \text{—NH(CH}_2)_5\text{CO—[NH(CH}_2)_5\text{CO]}_x\text{—NH(CH}_2)_5\text{CO—}\ ?$$

It is a true condensation polymer and is formed directly from the amino acid by intermolecular reaction. This is proved by the fact that the lactam does not polymerize under the conditions of formation of the polyamide either in the presence or absence of catalysts. Moreover, no lactam can be obtained from the polyamide by heating it to high temperature in high vacuum. Thus there is no such reversible relationship between lactam and polyamide as is found[7c,e] to exist between six-membered cyclic esters and corresponding polyesters. Lactam and polyamide result from the amino acid by two independent and simultaneous processes. The lactam incidentally is really the 7-ring $\underline{\ulcorner \text{NH(CH}_2)_5\text{CO} \urcorner}$.[8] This was proved by identifying its hydrolytic product with ϵ-aminocaproic acid through its *p*-toluenesulfonyl derivative by means of a mixed melting point.

The polyamide is sufficiently soluble in phenol to permit a determination of molecular weight by cryoscopy. Values obtained ranged from 800 to 1200, and since the errors of this method are such as to lead to low results it may be assumed that at least 10 molecules of the amino acid must have participated in the formation of a single molecule of the polyamide.

The question of the nature of the groups at the ends of the polyamide

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[8] The shifting of a functional group down a chain in attempts to prepare large rings by bifunctional reactions has been reported by various investigators. See, for example. Blaise and Koehler, Ref. 4.

chains cannot yet be answered. The formation of large rings is very improbable on theoretical grounds,[9] and in the formation of polyesters ring formation is known not to occur—the hydroxyl or carboxyl groups still persist at the ends of the polyester chain.[7b,c,d,5c] However, no certain evidence of the presence of terminal amino or carboxyl group in the molecule of the polyamide could be obtained. The polyamide dissolves readily in cold concentrated hydrochloric acid, but when the solution is diluted with water it separates unchanged and free from more than traces of halogen. It is not soluble in hot or cold aqueous sodium hydroxide nor does it form any sodium salt. It reacts with molten *m*-bromobenzoic anhydride and, in hot pyridine, with *p*-bromobenzene-sulfonyl chloride. The products contain bromine in amounts which correspond with derivatives of minimum molecular weights about 1100 and 1500, respectively, but in view of the failure of other reactions these cannot be accepted as evidence of the presence of free amino groups in the polyamide. At present we are inclined to assume that the amino and carboxyl groups which would normally be present at the ends of the polyamide chains are lost by pyrolysis. (The evolution of carbon dioxide during the formation of the polyamide could not be detected, but the vapors evolved had a strong amine odor.)

Summary

ε-Aminocaproic acid (or its ethyl ester) on being heated reacts with itself both intra- and intermolecularly and yields the 7-ring lactam (*ca.* 30%) and a polyamide (*ca* 70%). The formation of a molecule of the latter probably involves at least ten molecules of the amino acid.

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NOTES

A Method for the Determination of Molecular Weights in Liquid Ammonia.—Very recently Schwarz[1] and Signer[2] have published a new method for the determination of molecular weights. This method makes use of the principle that two solutions in the same solvent confined with a common vapor phase will come to the same molecular concentration by diffusion of the vapor.

The advantages of the method are that it enables the molecular weights of substances of low solubility and large molecular weight to be determined accurately; it makes possible molecular weight determinations in the same solvent at different temperatures; and it is adaptable to micro-manipulation.

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[9] Carothers, THIS JOURNAL, **51**, 2556 (1929).

[1] Schwarz, *Monatsh.*, **53, 54**, 926 (1929).

[2] Signer, *Ann.*, **478**, 246 (1930).