

Central Research Laboratory, Allied Chemical Corporation

## New Derivatives of $\epsilon$ -Caprolactam

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The synthesis of  $\alpha$ -(carbethoxyvinyl)caprolactam (V) is reported. This synthesis involves condensation of  $\alpha$ -bromocaprolactam with diethyl malonate, semi-hydrolysis of the malonic ester derivative, and a Mannich reaction on the product of the latter reaction. All of the intermediate compounds and some of the by-products are new derivatives of  $\epsilon$ -caprolactam. Their infrared and n.m.r. spectra are recorded.

Exploratory studies in this laboratory have been concerned with the synthesis of compounds having the potential of forming both, condensation-type polymers by a ring opening mechanism, and addition polymers of the types that are derived from unsaturated monomers. Caprolactam may be considered the most prominent representative of the first class while the second group may be represented by the mono- and 1,1-disubstituted ethylenes. In this paper the synthesis of  $\alpha$ -(carbethoxyvinyl)caprolactam is reported.

Caprolactam (I) was converted into  $\alpha$ -bromocaprolactam (II) as described in the literature (1,2).

Reaction of II with sodium diethyl malonate gave  $\alpha, \alpha$ -(dicarbethoxymethyl)caprolactam (III). Semi-hydrolysis gave the  $\alpha$ -carboxy- $\alpha$ -carbethoxymethylcaprolactam (IV). The Mannich reaction on IV proceeded with the decomposition of the formed Mannich base and gave in fair yield directly the desired  $\alpha$ -(carbethoxyvinyl)caprolactam (V).

Total hydrolysis of the ester groups of III gave  $\alpha, \alpha$ -(dicarboxymethyl)caprolactam (VI) which was easily decarboxylated to the  $\alpha$ -(carboxymethyl)caprolactam (VII). Esterification with ethanol yielded  $\alpha$ -(carbethoxymethyl)caprolactam (VIII). This compound was identical with the one obtained by decarboxylation of IV.

Reaction with aqueous ammonia gave the  $\alpha$ -(carbamidomethyl)caprolactam (IX).

The structures of these compounds have been confirmed by infrared analysis. The spectra of all derivatives show bands in the 3020-3080  $\text{cm}^{-1}$  and 3175-3200  $\text{cm}^{-1}$  regions. Stemming from N-H stretching vibrations, these bands are typical for cyclic lactams. All spectra show the amide I band in the 1660-1670  $\text{cm}^{-1}$  region, which is characteristic for the carbonyl absorption of cyclic lactams consisting of unstrained rings of six or more carbon atoms. In case of the  $\alpha$ -(carboxymethyl)caprolactam this band occurs at 1630  $\text{cm}^{-1}$ . In the spectra of all compounds, except that of the  $\alpha$ -(carbamidomethyl)caprolactam, the so-called amide II band at 1600  $\text{cm}^{-1}$  is missing. Its occurrence in the spectrum of the latter compound was expected because of the presence of the primary amide group. All compounds absorb in the 1200-

1300  $\text{cm}^{-1}$  region causing the so-called amide III band. The spectra of the compounds III through VIII show an intense band in the 1730-1750  $\text{cm}^{-1}$  region which in case of the  $\alpha, \alpha$ -(dicarbethoxymethyl)caprolactam has been split into two bands at 1750 and 1725  $\text{cm}^{-1}$  (unsubstituted malonic acid absorbs at 1740 and 1710  $\text{cm}^{-1}$ ). Absorption in that region has been attributed to C=O stretching vibrations, while the bands in the 1020-1040  $\text{cm}^{-1}$  and 1200  $\text{cm}^{-1}$  region stem from C-O- stretching vibrations.

The spectrum of  $\alpha$ -(carbamidomethyl)caprolactam shows in addition to the amide II band a band at 1405  $\text{cm}^{-1}$  which may be assigned to C-N stretching absorption. This band is missing in N-substituted amides.

The spectrum of  $\alpha$ -(carboxymethyl)caprolactam shows a broad band at 2500  $\text{cm}^{-1}$  assigned to the OH stretching vibration. The spectrum of this compound exhibits another broader band at 1922  $\text{cm}^{-1}$  which is not present in the spectra of the other caprolactam derivatives. Absorption in this region has been observed for most amido acids (3).

For identification purposes the infrared spectrum of V is presented in Fig. 1. The structure of V has been further verified by its n.m.r. spectrum which is shown in Fig. 2.

### EXPERIMENTAL (4)

#### $\alpha, \alpha$ -(Dicarbethoxymethyl)caprolactam (III).

Into a 3 l. three-necked flask equipped with a stirrer, dropping funnel, and a reflux condenser carrying a drying tube was placed 600 ml. of anhydrous ethanol. With frequent cooling 23 g. of sodium was added. The solution was heated under gentle reflux, and over a period of 1 hour 400 g. of redistilled diethyl malonate was added. The heating was continued for an additional 3 hours. After this time 192 g. of  $\alpha$ -bromocaprolactam dissolved in 300 ml. dry benzene was added. The reaction mixture was then heated under reflux for 5 hours and allowed to stand at room temperature overnight. The ethanol was then removed under an aspirator vacuum. The remaining solution was then diluted with 300 ml. ether and washed with 400 ml. of 10% aqueous hydrochloric acid solution. The aqueous phase was extracted several times with ether. The ether solutions were combined and washed first with a concentrated sodium bicarbonate solution and then with water. After the organic solution was dried over anhydrous sodium sulfate, the solvents and excess malonic ester were removed under vacuum, and the reaction product recrystallized from *n*-hexane. There was obtained 184 g. (68%) of product, m.p. 94-96°.

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{21}\text{O}_5\text{N}$ : C, 57.55; H, 7.80; N, 5.16. Found: C, 57.70; H, 7.76; N, 5.46.

#### $\alpha$ -Carboxy- $\alpha$ -carbethoxymethylcaprolactam (IV).

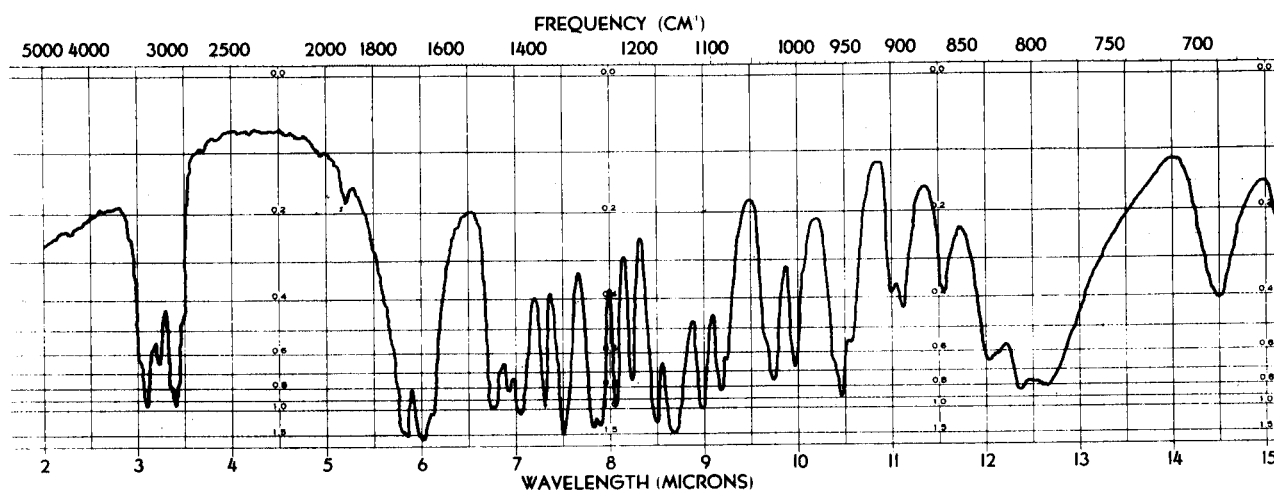
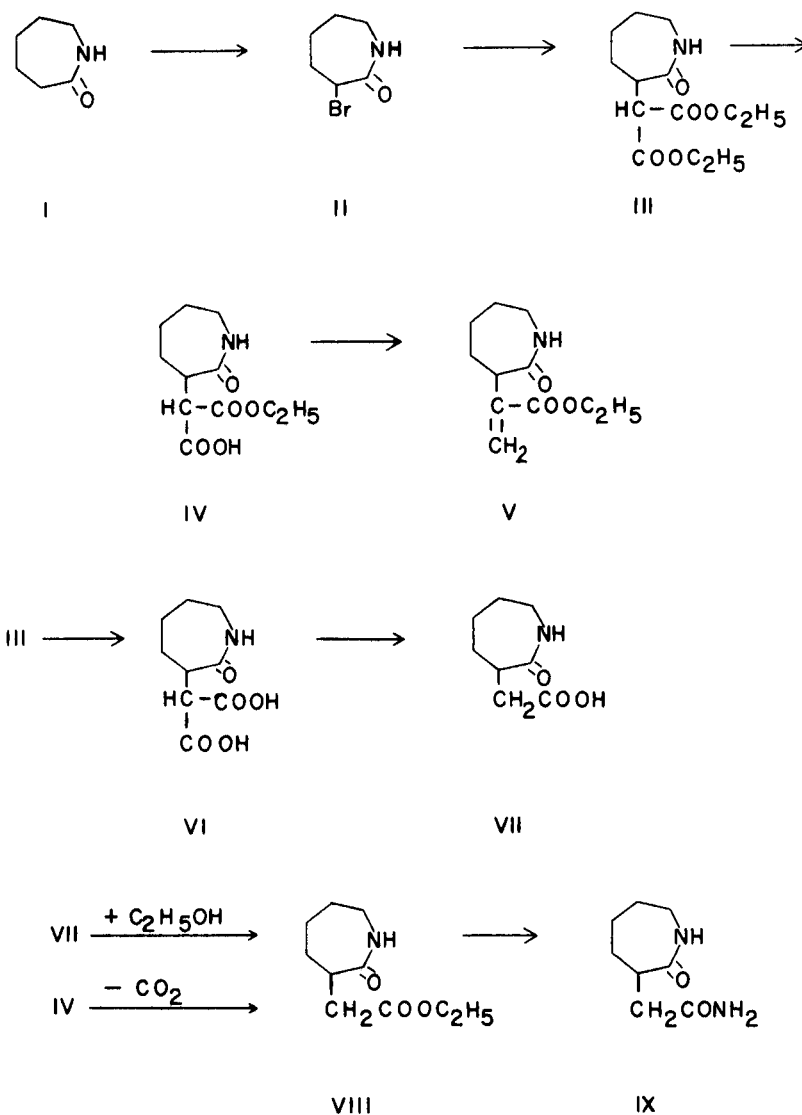


Fig. 1

Infrared Spectrum of  $\alpha$ -(Carboxyvinyl)caprolactam

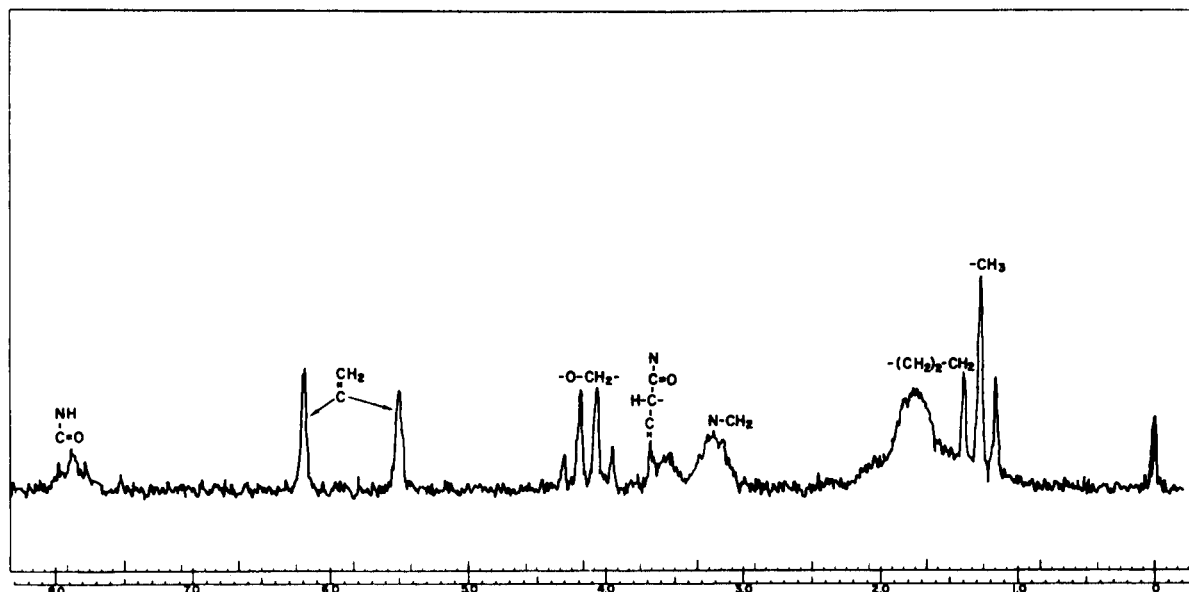


Fig. 2

n.m.r. Spectrum of  $\alpha$ -(Carbomethoxyvinyl)caprolactam

To a solution containing 27.13 g. of III in 75 ml. of anhydrous ethanol solution was added 5.6 g. of potassium hydroxide dissolved in 60 ml. anhydrous ethanol. The resulting solution was held at room temperature until the pH of the solution was 7. At this point the solution was heated under reflux for 1 hour, filtered, and the ethanol distilled under vacuum. To the residue was added ethyl ether. The salt which formed was removed by filtration, washed with ether, and dried in vacuum. The salt amounted to 24.9 g. (85%). The salt was dissolved in 150 ml. of chloroform and this solution cooled below 0°. An equivalent amount of hydrochloric acid was added and the chloroform distilled under reduced pressure after the solution had been filtered. The temperature was not allowed to exceed 35°. The residue was treated with *n*-hexane and dried in a vacuum desiccator. By this procedure a yield of 19.3 g. (94%) was obtained. Attempts to purify this material by recrystallization from chloroform-ether were not successful. Infrared analysis showed the presence of -NHCO-, -COOH, and -COOC<sub>2</sub>H<sub>5</sub> groups. A small sample was decarboxylated by heat and recrystallized from *n*-hexane to yield  $\alpha$ -(carbomethoxymethyl)caprolactam (VIII), m.p. 76-77°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>17</sub>O<sub>3</sub>N: C, 60.28; H, 8.60; N, 7.03. Found: C, 60.32; H, 8.86; N, 6.97.

 $\alpha$ -(Carbomethoxyvinyl)caprolactam (V).

A solution containing 6.1 g. of IV in 3 ml. of water was neutralized with 1.83 g. of diethylamine while cooled to 0°. Then 1.5 g. of formaldehyde was added in form of a 37% aqueous solution. The resulting solution was heated under reflux with stirring for 24 hours. The pH of the solution was adjusted to 9 by the addition of potassium hydroxide and the solution was then extracted with chloroform. The residue from the chloroform extract solidified after standing for a few days at room temperature. Recrystallization from *n*-hexane yielded 2.3 g. (44%) of product, m.p. 87-88°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>17</sub>O<sub>3</sub>N: C, 62.54; H, 8.11; N, 6.63. Found: C, 62.32, 62.43; H, 8.16, 8.30; N, 6.96, 6.10.

 $\alpha, \alpha$ -(Dicarbomethoxy)caprolactam (VI).

To a solution containing 67.5 g. of potassium hydroxide dissolved in 250 ml. of 99.8% ethanol was added 135.6 g. of III dissolved in 150 ml. ethanol. The resulting solution was heated under reflux for 20 hours. After cooling the precipitated dipotassium salt was collected and washed first with ethanol and then with ether. There was obtained 141.7 g. (97.5%) of product. The dipotassium salt was dissolved in 100 ml. of water, the solution extracted with ether, cooled below 0°, and acidified with concentrated hydrochloric acid solution while the temperature was maintained at 0°. The precipitate was collected and washed with a small quantity of cool methanol and ether. Recrystallization from methanol yielded 110 g. (85%) of product decomposing

about 160°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>15</sub>O<sub>3</sub>N: C, 50.23; H, 6.09; N, 6.51. Found: C, 50.28; H, 6.13; N, 6.33, 6.50.

 $\alpha$ -(Carboxymethyl)caprolactam (VII).

A solution was prepared by adding 21.52 g. of VI in small portions to 150 ml. of *o*-dichlorobenzene at 160-165°. The resulting clear solution was filtered hot to remove resinous by-products. Upon cooling, 11.4 g. (67%), of the acid derivative crystallized. After recrystallization from hot *o*-dichlorobenzene the material melted at 176-177°.

*Anal.* Calcd. for C<sub>8</sub>H<sub>13</sub>O<sub>3</sub>N: C, 56.13; H, 7.65; N, 8.18. Found: C, 56.05; H, 7.57; N, 8.26.

 $\alpha$ -(Carbomethoxymethyl)caprolactam (VIII).

In a mixture containing 120 ml. of ethanol, 20 ml. of benzene and 2 ml. of concentrated sulfuric acid, 34.24 g. of VII was dissolved. This solution was refluxed in an esterification apparatus for 4 hours. The excess solvent was removed by distillation and the residue dissolved in ether. The ether solution was washed with saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. The ether was removed in vacuum and the crystalline residue recrystallized from *n*-hexane. There was obtained 29.3 g. (74%) of product, m.p. 76.5-77.5°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>17</sub>O<sub>3</sub>N: C, 60.28; H, 8.60; N, 7.03. Found: C, 60.29; H, 8.65; N, 7.00.

 $\alpha$ -(Carbamidomethyl)caprolactam (IX).

A solution containing 19.93 g. of VIII dissolved in 150 ml. of concentrated aqueous ammonium hydroxide was allowed to stand for 48 hours at room temperature, then distilled under vacuum. Upon recrystallizing the residue from ethanol, 11.1 g. (65%) of product m.p. 202° was obtained.

*Anal.* Calcd. for C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>N<sub>2</sub>: C, 56.45; H, 8.29; N, 16.46. Found: C, 57.34; H, 8.49; N, 16.01.

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