ε-Imido Esters. I. The Course of the Reaction between Phthalic Anhydride and Caprolactam

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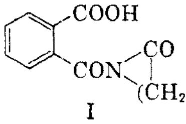
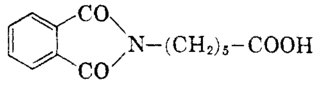
In the course of an investigation of the reaction of anhydrides with caprolactam we had occasion to condense the latter compound with phthalic anhydride. According to Benson and Cairns,[1] the compound formed by this reaction is *N*-phthaloyl-ε-caprolactam (I). However, G. M. van der Want[2] repeated this work and found the material to be ε-phthalimidocaproic acid (II). His proof of structure was based on the comparison of the latter's ultraviolet absorption curve with spectra from analagous compounds of known structure.



I



II

We have found by chemical means and by unequivocal syntheses of the possible structures, that the product formed by reaction of caprolactam with phthalic anhydride is the corresponding phthalimidocaproic acid (II) rather than the substituted *N*-acyl-ε-caprolactam (I).

This was accomplished by condensing caprolactam with phthalic anhydride at 180° to yield a substituted monocarboxylic acid which in turn was esterified with methyl alcohol. The product after distillation, solidified and had a melting point of 43.5–44.0°. Phthalic anhydride was then treated with methyl-6-isocyanatocaproate at 125° following the procedure of Hurd and Prapas[3] to yield methyl-ε-phthalimidocaproate which also solidified and melted at 43.5–44.0°. There was no depression of the melting point when the compounds prepared *via* the two methods were mixed. The infrared and ultraviolet absorption curves were identical for both compounds.

To elucidate further the course of the reaction between phthalic anhydride and caprolactam, the methyl ester of *N*-phthaloyl-ε-caprolactam (I) was prepared by an unequivocal synthesis. Thus, phthalic anhydride was esterified with methyl alcohol to yield methyl hydrogen phthalate which in turn was converted to the acid chloride with thionyl chloride. Finally, the acid chloride was condensed with caprolactam in the presence of triethylamine to give *N*-(*o*-carbomethoxybenzoyl)-ε-caprolactam which melted at 68–70°. The infrared and ultraviolet absorption curves were different from those of the phthalimido ester. This is conclusive evidence that the structure proposed by van der Want is correct.

EXPERIMENTAL

ε-Phthalimidocaproic acid. The compound was prepared following the procedure of Benson and Cairns.[1] Thus, a mixture of 113 g. (1.0 mol.) of caprolactam and 148 g. (1.0 mol.) of phthalic anhydride was heated to 180° and held there for 18 hr. Unreacted starting materials were removed by distillation and the residue was fractionally distilled to yield 169 g. (65%) of ε-phthalimidocaproic acid; b.p. 239–240°/3 mm.; m.p. 107–108°.

Methyl-ε-phthalimidocaproate. A. *From ε-phthalimidocaproic acid and methanol.* A mixture of 51 g. (0.20 mol.) of ε-phthalimidocaproic acid, 40 ml. of methanol, 100 ml. of benzene and 0.4 g. of *p*-toluenesulfonic acid was refluxed for 18 hr. The excess alcohol and the water formed during the esterification were removed by distillation following which the resultant benzene solution was washed with water, 5% aqueous sodium carbonate, again with water and finally dried over anhydrous sodium sulfate. The solvent was distilled off atmospherically and the residue was distilled in vacuo to yield 54 g. (84%) of methyl-ε-phthalimidocaproate; b.p. 182–183°/0.7 mm.; m.p. 43.5–44.0°.

Anal. Calcd. for $C_{15}H_{17}NO_4$: C, 65.5; H, 6.2; N, 5.1. Found: C, 66.0; H, 6.4; N, 5.0.

B. *From phthalic anhydride and methyl-6-isocyanatocaproate.* A mixture of 37 g. (0.25 mol.) of phthalic anhydride and 34.2 g. (0.20 mol.) of methyl-6-isocyanatocaproate was heated to 125° and held there for 18 hr. While on temperature evolution of carbon dioxide was apparent. The excess phthalic anhydride was distilled off following which the residue was distilled under vacuum to yield 48 g. (87%) of methyl-ε-phthalimidocaproate; b.p. 187°/0.9 mm.; m.p. 43.5–44.0°.

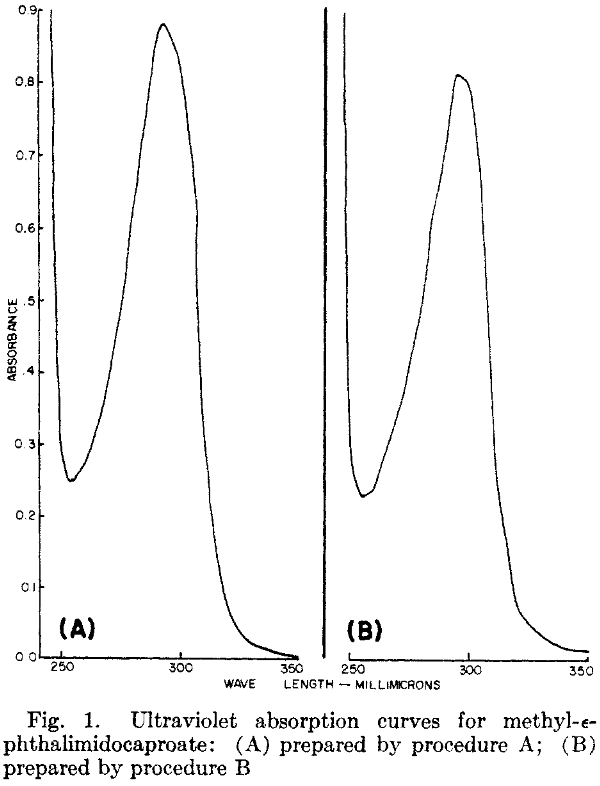


Fig. 1. Ultraviolet absorption curves for methyl-ε-phthalimidocaproate: (A) prepared by procedure A; (B) prepared by procedure B

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(1) R. E. Benson and T. L. Cairns, *J. Am. Chem. Soc.*, **70**, 2115 (1948).

(2) G. M. van der Want, *Rec. Trav. Chim.*, **71**, 1012 (1952).

(3) C. D. Hurd and A. G. Prapas, *J. Org. Chem.*, **24**, 388 (1959).

Anal. Calcd. for $C_{15}H_{17}NO_4$: N, 5.09. Found: N, 4.93.

The compound when mixed with the material from procedure A failed to show any depression in the melting point. The ultraviolet absorption curves for both compounds were identical, exhibiting a maximum at 293 mμ (Fig. 1, A and B). The infrared absorption curves for both compounds were also identical (Fig. 2, A and B).

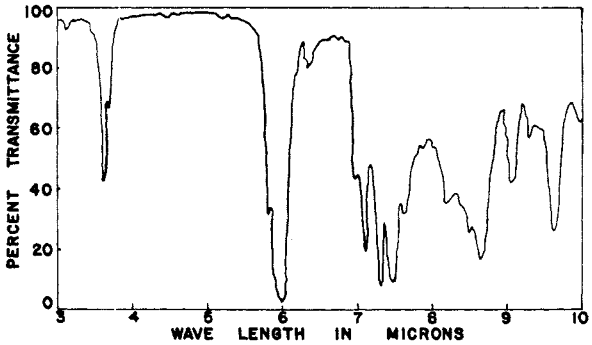

Fig. 2(A). Infrared absorption curve for methyl-ε-phthalimidocaproate prepared by procedure A

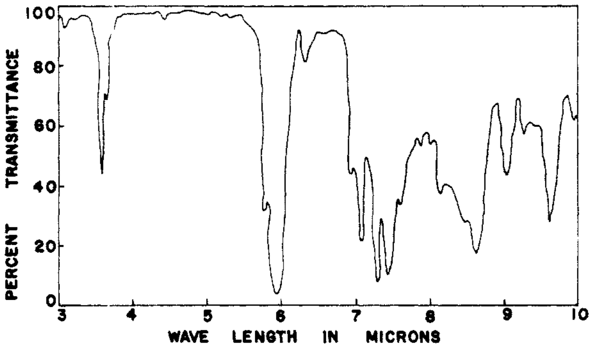

Fig. 2(B). Infrared absorption curve for methyl-ε-phthalimidocaproate prepared by procedure B

Methyl hydrogen phthalate. Methyl hydrogen phthalate was prepared following the procedure of Eliel and Burgstahler.[4] Thus, 74 g. (0.50 mol.) of phthalic anhydride and 50 ml. of methanol were refluxed for 2 hr. The excess methanol was distilled off, 25 ml. of benzene was added and the distillation continued to insure the complete removal of the excess alcohol. The residual oil was dissolved in 200 ml. of benzene following which 300 ml. of Skellysolve B was added. Upon cooling in an ice-salt bath, the product crystallized following which it was filtered, washed with more Skellysolve B and finally dried in vacuo. There was obtained 80 g. (89%) of methyl hydrogen phthalate; m.p. 80–82°; lit. val. 82°.[4]

o-Carbomethoxybenzoyl chloride. A mixture of 36 g. (0.2 mol.) of methyl hydrogen phthalate and 100 ml. of thionyl chloride was refluxed for 1 hr. on a steam bath. The excess thionyl chloride was removed under reduced pressure following which dry benzene (two 50-ml. portions) was added and distilled away from the acid chloride *in vacuo* two times, to complete the removal of unreacted thionyl chloride. The acid chloride, a pale yellow oily liquid was used as such in the following experiment without any further purification.

N-(o-Carbomethoxybenzoyl)-ε-caprolactam. Into a flask equipped with an agitator, thermometer, dropping funnel and reflux condenser was placed a solution of 22.6 g. (0.20 mol.) of caprolactam in 100 ml. of dry dioxane. While stirring, a solution of the *o*-carbomethoxybenzoyl chloride (from the previous experiment) in 100 ml. of dioxane was added dropwise over a period of 30 min. The mixture was next cooled to 10° and a solution of 20.2 g. (0.20 mol.) of triethylamine in 200 ml. of dioxane was added dropwise, maintaining the temperature below 20°. After the addition was complete, the mixture was refluxed for 3 hr., cooled to room temperature and filtered to remove the triethylamine hydrochloride.

The salt was washed with two 50-ml. portions of fresh dioxane following which the combined filtrates were subjected to a vacuum distillation to remove the dioxane. The residue was distilled at reduced pressures to yield 31 g. (57%) of *N*-(*o*-carbomethoxybenzoyl)-ε-caprolactam; b.p. 190–194°/0.8 mm. The compound crystallized on standing. After recrystallizing from Skellysolve B, the compound melted at 68–70°.

Anal. Calcd. for $C_{15}H_{17}NO_4$: C, 65.46; H, 6.18; N, 5.09. Found: C, 65.39; H, 5.51; N, 4.97.

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[4] E. L. Eliel and A. W. Burgstahler, *J. Am. Chem. Soc.*, **71**, 2251 (1949).

Benzyllithium from Triphenylbenzyltin and Phenyllithium

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In a recent communication to this journal procedures were described for the direct preparation of benzyllithium by cleavage reactions.[1] An attempt was made to list all types of procedures that had been described for the synthesis of benzyllithium. However, a method involving a metal-metal interconversion or exchange was not included.[2] This involves the following reaction:

$$(C_6H_5)_3SnCH_2C_6H_5 + C_6H_5Li \longrightarrow C_6H_5CH_2Li + (C_6H_5)_4Sn$$

The yield of phenylacetic acid obtained subsequent to carbonation was 39%; and the yield of tetraphenyltin was as high as 91.8%. This exchange reaction between organotin and organolithium compounds is one which has been employed broadly for some time,[3] and a particularly effective use of it was described recently by Seyferth and Weiner[4] for a neat preparation of vinyllithium from tetravinyltin and phenyllithium.

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(1) H. Gilman, H. A. McNinch, and D. Wittenberg, *J. Org. Chem.*, **23**, 2044 (1958).

(2) S. D. Rosenberg, Doctoral Dissertation, Iowa State College, 1952.

(3) H. Gilman, F. W. Moore, and R. G. Jones, *J. Am. Chem. Soc.*, **63**, 2482 (1941). See, also, R. G. Jones and H. Gilman, *Chem. Revs.*, **54**, 835 (1954) on the preparation of organometallic compounds.

(4) D. Seyferth and M. A. Weiner, *Chem. & Ind.* (*London*), 402 (1959).