LITERATURE CITED

(1) Barr, D.A., Haszeldine, R.N., *J. Chem. Soc.* **1955**, pp. 1881, 2532.

(2) *Ibid.*. **1956**, p. 3416.

(3) Christie, W.H., Tlumac, F.N., Dresdner, R.D., Young, J.A., Abstracts, p. 18m, 138th Meeting, ACS, New York, September 1960.

(4) Hauptschein, M., Braid, M., Lawlor, F.E., *J. Org. Chem.* **23**, 323 (1958).

(5) Petrov, K.A., Neimysheva, A.A., *J. Gen. Chem. (U.S.S.R.), (Engl. Transl.)* **29**, 2662-4); *CA* **54**, 10911h.

(6) Tullock, C.W., U. S. Patent **3,077,499**, Feb. 12, 1963.

(7) Young, J.A., Durrell, W.S., Dresdner, R.D., *J. Am. Chem. Soc.* **81**, 1587 (1959).

(8) Young, J.A., Simmons, T.C., Hoffmann, F.W., *Ibid.*, **78**, 5637 (1956).

(9) Young, J.A., Tsoukalas, S.N., Dresdner, R.D., *Ibid.*, **80**, 3604 (1958).

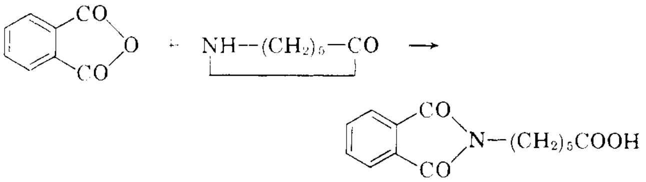
RECEIVED for review January 11, 1965. Accepted August 3, 1965.

ε-Imido Esters. The Reaction Between Anhydrides and ε-Caprolactam

BERNARD TAUB and HANS A. LEIPOLD[1]
National Aniline Division, Allied Chemical Corp., Buffalo, N. Y.

ε-Caprolactam reacts with cyclic anhydrides to yield the corresponding ε-imidocaproic acids which are converted to esters by normal esterification methods. ε-Imidocaproic acid esters, of the open-chain variety are prepared by condensing an acyclic anhydride with alkyl-6-isocyanatocaproates.

As previously shown (5), phthalic anhydride reacts with ε-caprolactam at elevated temperatures to yield ε-phthalimidocaproic acid instead of the expected corresponding *N*-acyl-ε-caprolactam derivative.



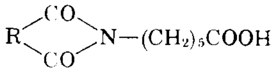
The utility of the esters of ε-phthalimidocaproic acid as plasticizers for both poly(vinyl chloride) and nylon molding resins, prompted an extension of the authors' investigation of the reaction between anhydrides and ε-caprolactam to include both cyclic and acyclic anhydrides.

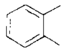
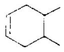
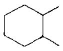
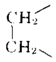
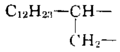
ε-Caprolactam was condensed with a variety of cyclic anhydrides (phthalic, hexahydrophthalic, tetrahydrophthalic, succinic, and dodecenylsuccinic anhydrides) to yield the corresponding ε-imidocaproic acids. The physical properties of the compounds are summarized in Table I. Attempts to prepare the ε-imidocaproic acid from maleic anhydride and ε-caprolactam resulted in the formation of polymeric products.

The ε-imidocaproic acids from the cyclic anhydrides were converted to esters by interaction with a variety of alcohols using conventional esterifying techniques. Table II lists the physical properties of the ε-imidocaproic acid esters.

The synthesis of ε-imidocaproic acids in which the imide structure is of the open-chain variety, could not be accomplished using the aforementioned technique. Thus, when ε-caprolactam was condensed with an acyclic anhydride—

Table I. ε-Imidocaproic Acids



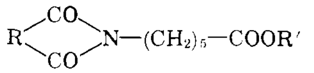
R	Yield, %	M.P., ° C.^{a}	B.P., ° C./Mm. Hg	Neut. Equiv.		Nitrogen, %	
				Calcd.	Found	Calcd.	Found
	70	107–108	239–240/3	261	265	5.4	5.5
	86	80	221–224/1	265	265	5.1	5.3
	62	. . .	235–239/3	267	271	5.2	4.9
	52	82–84	216–220/2	213	215	6.6	6.5
	28	. . .	247–252/2	379	384	3.7	3.6

^{a} Melting points are uncorrected.

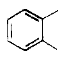
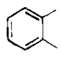
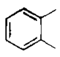
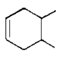
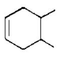
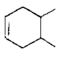
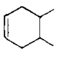
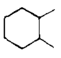
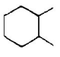
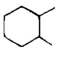
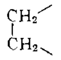
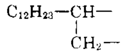
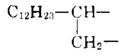
---

[1] Present address: Sinclair Oil Co., Chicago, Ill.

Table II. ϵ-Imidocaproic Acid Esters

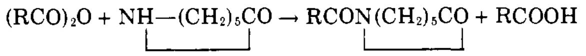


$R\langle(CO)_2\rangle N-(CH_2)_5-COOR'$

Product		Yield, %	B.P., °C./Mm. Hg	Carbon, %		Hydrogen, %		Nitrogen, %	
R	R′			Calcd.	Found	Calcd.	Found	Calcd.	Found
	CH_3—	84	182-183/0.7	65.44	65.36	6.22	6.15	5.09	4.96
	C_4H_9—[a]	88	214-216/2	...	...	...	...	4.41	4.62
	C_8H_{17}—[b]	88	243-246/3	...	...	...	...	3.75	3.70
	CH_3—	88	182-183/1	64.49	64.06	7.58	7.37	5.01	4.80
	C_2H_5—	79	197-200/2	...	...	...	...	4.78	4.85
	C_4H_9—[a]	85	203-205/2	...	...	...	...	4.36	4.51
	C_8H_{17}—[b]	72	234-237/2	...	...	...	...	3.71	3.65
	CH_3—	60	170-171/0.4	64.03	64.14	8.24	8.15	4.98	4.98
	C_2H_5—	68	197-200/2	...	...	...	...	4.74	4.87
	C_8H_{17}—[b]	72	220-225/1.3	...	...	...	...	3.69	3.60
	CH_3—	52	172-176/2.5	58.14	57.87	7.54	7.36	6.16	5.81
 $C_{12}H_{23}-\underset{CH_2-}{\underset{\vert}{CH}}-$	CH_3—	80	223-225/3	70.19	70.27	9.99	9.94	3.56	3.44
 $C_{12}H_{23}-\underset{CH_2-}{\underset{\vert}{CH}}-$	C_3H_{17}—[b]	55	251-253/2	...	...	...	...	2.85	2.95

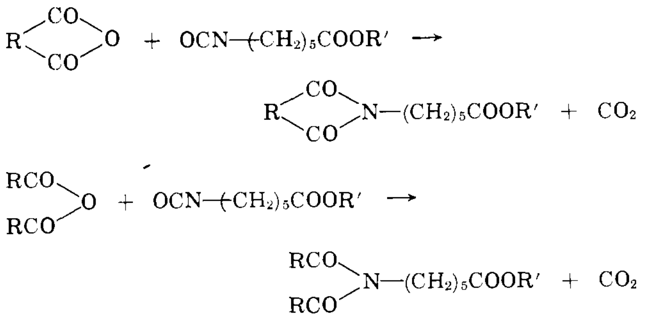
[a] -*n*-butyl. [b] 2-ethylhexyl.

e.g., acetic, propionic, etc.—only N-acyl-ϵ-caprolactam was obtained (*1*).



$$(RCO)_2O + \underbrace{NH-(CH_2)_5CO} \rightarrow RCO\underbrace{N(CH_2)_5CO} + RCOOH$$

The ϵ-imidocaproic acid esters of the open-chain type were prepared via an alternate route. Hurd and Prapas (*3*) reported that isocyanates react with cyclic anhydrides to form the corresponding cyclic imides. The authors confirmed this work and extended it to the reaction of isocyanates with acyclic anhydrides, obtaining acyclic imides. Thus, alkyl-6-isocyanatocaproates when condensed with either cyclic or acyclic anhydrides yield the desired ϵ-imidocaproic acid esters—i.e.,



$$R\langle(CO)_2\rangle O + OCN(CH_2)_5COOR' \rightarrow R\langle(CO)_2\rangle N-(CH_2)_5COOR' + CO_2$$

$$(RCO)_2O + OCN(CH_2)_5COOR' \rightarrow (RCO)_2N-(CH_2)_5COOR' + CO_2$$

The ϵ-imidocaproic acid esters prepared via this route are listed in Tables III and IV. The alkyl-6-isocyanatocaproates are prepared following the procedure described by Taub and Hino (*4*).

EXPERIMENTAL

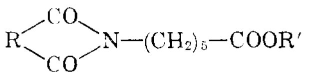
ϵ-Imidocaproic Acids. A mixture of 1.0 mole of ϵ-caprolactam and 1.0 mole of a cyclic anhydride is heated to 200° and held there for 18 hours. Unreacted ϵ-caprolactam and anhydride are removed by distillation, following which the ϵ-imidocaproic acid is isolated and purified by fractional distillation at reduced pressures. Yield data and physical constants are reported in Table I.

ϵ-Imidocaproic Acid Esters (Via Esterification). A solution of 0.25 mole of an ϵ-imidocaproic acid, 1.0 mole of an alcohol, 200 ml. of toluene, and 1 gram of p-toluenesulfonic acid is refluxed for 18 hours while water formed during the reaction is removed through a Dean-Stark trap. The reaction mixture is filtered, and the filtrate is washed with four 50-ml. portions of a 5% aqueous sodium carbonate solution, again with four 50-ml. portions of water, and then dried over anhydrous sodium sulfate. The toluene and excess alcohol are removed by distillation, and the alkyl-ϵ-imidocaproic acid esters are isolated by fractionation under vacuum. Yields and physical data are reported in Table II.

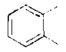
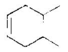
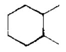
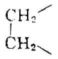
Methyl-6-isocyanatocaproate. ϵ-AMINOCAPROIC ACID HYDROCHLORIDE. ϵ-Caprolactam is converted to ϵ-aminocaproic acid hydrochloride following the procedure outlined by Eck (*2*).

METHYL-ϵ-AMINOCAPROATE HYDROCHLORIDE. A mixture of 167 grams (1.0 mole) of ϵ-aminocaproic acid hydrochloride and 160 grams (5.0 moles) of methanol is refluxed for 18 hours. The excess alcohol is removed by distillation

Table III. Cyclic ε-Imidocaproic Acid Esters (Via Anhydrides and Isocyanate Esters)

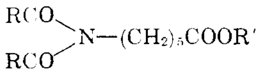


$$R\langle(CO)_2\rangle N-(CH_2)_5-COOR'$$

Product[a]		Yield, %	B.P., ° C./Mm. Hg	Carbon, %		Hydrogen, %		Nitrogen, %	
R	R′			Calcd.	Found	Calcd.	Found	Calcd.	Found
	CH_3-	88	187-188/0.9	65.44	65.62	6.22	6.15	5.09	4.93
	CH_3-	71	189-190/1.3	64.49	64.61	7.58	7.51	5.01	5.15
	CH_3-	66	174-175/0.5	64.03	63.90	8.24	8.11	4.98	5.20
	CH_3-	63	161-164/0.6	58.14	58.09	7.54	7.36	6.16	5.76
$C_{12}H_{23}-CH-$ CH_2-	CH_3-	54	214-216/0.7	. . .	. . .	. . .	. . .	3.56	3.25

[a] Products had identical IR spectrums with those compounds prepared via esterification of the ε-imidocaproic acids (Table II).

Table IV. Acyclic ε-Imidocaproic Acid Esters (Via Anhydrides and Isocyanate Esters)



$$(RCO)_2N-(CH_2)_5COOR'$$

Product		Yield, %	B.P., ° C./Mm. Hg	Carbon, %		Hydrogen, %		Nitrogen, %	
R	R′			Calcd.	Found	Calcd.	Found	Calcd.	Found
CH_3-	CH_3-	69	130-131/0.4	57.62	57.43	8.35	8.53	6.11	5.72
CH_3CH_2-	CH_3-	78	136-137/0.2	60.67	60.51	9.01	9.12	5.44	5.45
$CH_3(CH_2)_2$	CH_3-	82	158-159/0.7	63.13	63.10	9.53	9.30	4.91	5.31
CH_3 CH_3-CH-	CH_3-	73	156-157/1.5	63.13	63.40	9.53	9.18	4.91	5.13
$CH_3(CH_2)_4-$	CH_3-	69	186-187/0.7	66.83	66.42	10.33	10.30	4.10	4.50
C_6H_5-	CH_3-	75	204-205/0.5	71.37	71.04	6.56	6.80	3.96	3.86

at atmospheric pressure. The water formed during the esterification is removed by heating on a steam bath under reduced pressures. The yield is 163 to 181 grams (90 to 100%) of methyl-ε-aminocaproate hydrochloride which can be used without further purification.

Phosgenation. A mixture of 181 grams (1.0 mole) of methyl-ε-aminocaproate hydrochloride and 1000 ml. of chlorobenzene is heated to 100°, and then phosgene is bubbled in until no more hydrogen chloride is evolved (about 4 hours). The solution is purged with nitrogen to remove the last traces of phosgene, the solution is stripped of chlorobenzene at reduced pressure, and the residue is distilled under vacuum. The yield is 134 to 154 grams (80 to 90%) of methyl-6-isocyanatocaproate; b.p. 111-112°/6 mm.

ε-Imidocaproic Acid Esters (Via Isocyanate-Anyddride Reaction). A mixture of 0.21 mole of anhydride and 0.20 mole of methyl-6-isocyanatocaproate is heated at 190° to 220° for 20 hours. Carbon dioxide evolution is pronounced at the onset of the reaction and slower towards the end. Excess anhydride is removed by distillation and the methyl-ε-imidocaproate is isolated and purified by fractionation under vacuum. Yield data and physical properties are reported in Tables III and IV.

LITERATURE CITED

(1) Benson, R.E., Cairns, T.L., *J. Am. Chem. Soc.* **70**, 2115 (1948).
(2) Eck, J.C., *Org. Syn.* **17**, 7 (1937).
(3) Hurd, C.D., Prapas, A.G., *J. Org. Chem.* **24**, 288 (1959).
(4) Taub, B., Hino, J.B., J. Chem. Eng. Data **9**, 106 (1964).
(5) Taub, B., Leipold, H.A., Hino, J.B., *J. Org. Chem.* **24**, 2062 (1959).

Received for review February 3, 1965. Accepted May 5, 1965.