present in the 80% lactic acid (*ca.* 22 ml.) was removed rapidly, but the water resulting from dehydration of the amine lactate was formed at higher temperature and at a considerably slower rate. After removal of free water, 11 hours of refluxing at 154 to 166° was required to collect 18 ml. (1 mole) of water formed by dehydration of the salt. By using less entraining agent (50 ml. instead of 100 ml.) the reaction temperature was increased, and dehydration was completed considerably faster (7 hours instead of 11).

Upon completion of the reaction, the xylene was removed by distillation at 40–50 mm., and the dibutyllactamide was isolated by distillation at 5.0 mm.

The preparation of other substituted lactamides is summarized in Table I. The physical constants and analytical data were determined on redistilled or recrystallized samples. The solid lactamide derivatives were recrystallized from ether, except N-β-phenylethyllactamide, which was recrystallized from acetone. For purposes of comparison, N,N-dibutylpropionamide was also prepared.

Lactamides by Aminolysis of Methyl Lactate.—N-(α-methylbenzyl)-, N-(β-phenylethyl)-, N-3-hydroxypropyl- and N-(1-hydroxy-2-butyl)-lactamides were prepared by aminolysis of methyl lactate with an equivalent amount of α-methylbenzylamine, β-phenylethylamine, 3-aminopropanol and 2-amino-1-butanol, respectively. This method has been described previously.[3,6] The results are shown in Table I.

Boiling points of dibutyl, dihexyl, dioctyl and didecyl lactamides were determined at various pressures in the range of 0.1 to 10.0 mm. with a tensimeter still.[10] The results are shown in Fig. 1.

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(11) Mention of names, brands or companies should not be construed as a recommendation or endorsement by the Department of Agriculture over those not mentioned.

PHILADELPHIA 18, PENNA.

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Ester-amides of Lactic Acid

BY M. L. FEIN AND E. M. FILACHIONE

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Various esters of N-substituted lactamides, particularly dialkyl-, hydroxyalkyl- and di-(hydroxyalkyl)-lactamides, were prepared. Concurrent esterification and dehydration to produce satisfactory yields of esters of lactamides was accomplished by heating a mixture of the lactic acid–amine salt, fatty acid, and an entraining agent.

Because lactic acid contains both hydroxyl and carboxyl groups it is capable of being transformed into numerous derivatives which are simultaneously an ester and an amide. However, comparatively little information has been reported concerning these ester-amide derivatives of lactic acid. Earlier investigators have reported a few esters of lactamide, dimethyllactamide and lactanilide.[2–7]

More recently some acetates, acrylates and methacrylates of substituted lactamides have been reported.[8–11]

This paper reports various additional ester-amides of lactic acid particularly esters of the N,N-disubstituted lactamides and the hydroxyalkyl lactamides. The preparation of some of these ester-amides by simultaneous direct esterification and dehydration of the lactic acid–amine salt was also investigated.

The pure ester-amides were prepared by acylation of the lactamide with acid anhydrides or chlorides. Subsequently it was found practical to prepare at least some of these derivatives by direct esterification in which carboxylic acids were employed. The direct esterification of N,N-dibutyllactamide with lauric acid proceeded very slowly, and only approximately 40% esterification occurred as judged by the amount of water removed during the reaction. The yield of desired ester-amide was very poor. It was of interest that if the esterification was conducted with the lactic acid–amine salt in place of the lactamide the esterification proceeded satisfactorily with concurrent dehydration of the amine salt, and good yields of the ester of the substituted lactamide were obtained. Similarly a satisfactory yield of hydroxyethyllactamide dipelargonate was obtained by this method.

Experimental

Preparation of Lactamides.—Butyllactamide and the hydroxyalkyllactamides were prepared in almost quantitative yields by aminolysis of methyl lactate as previously described.[9–12] Lactanilide, *t*-octyllactamide and the dialkyllactamides were prepared in satisfactory yield by dehydration of the corresponding lactic acid–amine salt as reported recently.[13]

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

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TABLE I

PREPARATION AND PROPERTIES OF ESTERS OF LACTAMIDES

Lactamide ester	Yield %	B.p. °C.	B.p. Mm.	M.p., °C.	$n^{30}D$	d^{20}_4	Viscosity at 20°, cps.	Carbon, % Found	Carbon, % Calcd.	Hydrogen, % Found	Hydrogen, % Calcd.	Nitrogen, % Found	Nitrogen, % Calcd.
Lactamide, 2-ethylhexanoate	90[a]	107	0.2	....	1.4540	0.9999	612.1	61.45	61.36	9.87	9.83	6.36	6.51
Lactamide, laurate	94[a]			49-50[b]	....	....	....	66.58	66.38	10.70	10.77	5.08	5.16
N-Butyllactamide, 2-ethylhexanoate	69	139	1.0		1.4502	0.9492	119.7	66.27	66.38	10.96	10.77	5.20	5.16
N-Butyllactamide, laurate	85[a]	129	0.02	47.5–48.5[c]	....	....	....	...	...	...	...	4.34	4.28
N-*t*-Octyllactamide, acetate	74			83–86[d]	....	....	....	...	...	...	...	5.81	5.76
N-*t*-Octyllactamide, laurate	98[a]			66–67[d]	....	....	....	71.79	72.01	11.46	11.82	3.64	3.65
Lactanilide, 2-ethylhexanoate	93[a]			56[d]	....	....	....	70.16	70.07	8.44	8.65	4.87	4.81
Lactanilide, laurate	95[a]			106–107[e]	....	....	....	72.56	72.57	9.46	9.57	4.02	4.05
N,N-Dibutyllactamide, 2-ethylhexanoate	67	146	1.0	....	1.4526	0.9280	42.0	69.42	69.68	11.34	11.39	4.16	4.28
N,N-Dibutyllactamide, laurate	75	132	0.003	....	1.4558	0.9154	49.8	72.10	72.01	11.77	11.82	3.62	3.65
N,N-Dibutyllactamide, adipate	..	180–187	.005	....	1.4705	1.0201	2263	64.97	65.59	10.20	10.22	5.02	5.46
N,N-Di-*n*-octyllactamide, *n*-amyl carbonate	55	130–132	.009	....	1.4558	0.9339	87.6	70.05	70.21	11.84	11.55	3.13	3.28
N,N-Di-2-ethylhexyllactamide, 2-ethylhexanoate	75	119–124	.03		1.4590	.9122	112.5	73.66	73.75	12.16	12.15	3.11	3.19
N,N-Dibenzyllactamide, acetate	78	120–128	.003	....	1.5527	....	....	73.23	73.29	6.68	6.80	4.56	4.50
N,N-Di-*n*-decyllactamide, acetate	91	132	.005	....	1.4577	.9086	62.4	73.19	72.94	11.96	12.00	3.26	3.40
N-2-Hydroxyethyllactamide, diacetate	86	104–107	.13	44–46[f]	1.4558[g]	....	....	50.02	49.76	7.39	6.96	6.43	6.45
N-2-Hydroxyethyllactamide, dipropionate	..	104–105	.08	....	1.4546	....	....	53.49	53.86	7.91	7.80	5.66	5.71
N-2-Hydroxyethyllactamide, di-2-ethylhexanoate	83	133	.001(*ca.*)	....	1.4549	.9852	200	65.41	65.42	10.44	10.20	3.77	3.63
N-2-Hydroxyethyllactamide, dipelargonate	74	132	.007	58–62[b]	....	....	....	66.79	66.49	10.48	10.75	3.38	3.52
N-2-Hydroxyethyllactamide, bis-(*n*-hexyl carbonate)	90	125	< .012[h]	....	1.4531	1.0532	490	58.39	58.59	8.97	9.06	3.75	3.60
N-2-Hydroxyethyllactamide, dibenzoate	..	.....	...	107[e]	....	....	....	66.83	66.85	5.89	5.61	4.08	4.10
N-2-Hydroxypropyllactamide, diacetate	94	70–73	< .001	....	1.4536	1.1285	3195	51.72	51.94	7.37	7.41	6.08	6.06
N-2-Hydroxypropyllactamide, dipropionate	85	83	.001	....	1.4522	1.0818	394	55.80	55.58	8.17	8.16	5.33	5.40
N-2-Hydroxypropyllactamide, di-2-ethylhexanoate	83	124–127	.02	....	1.4532	0.9747	293	66.42	66.13	10.42	10.34	3.51	3.50
N-2-Hydroxypropyllactamide bis-(ethyl carbonate)	68[a]			51–53[f]	....	....	....	49.41	49.47	7.14	7.27	4.87	4.81
N-2-Hydroxypropyllactamide bis-(*n*-hexyl carbonate)	86	125	< .012[h]	....	1.4531	1.0532	490	58.39	58.59	8.97	9.06	3.75	3.60
N-3-Hydroxypropyllactamide, diacetate	..	69–71	.0005	....	1.4589	....	....	51.12	51.94	7.27	7.41	5.82	6.06
N-3-Hydroxypropyllactamide, di-2-ethylhexanoate	83	118–120	.0005	....	1.4562	0.9809	236	65.78	66.13	10.25	10.34	3.37	3.50
N,N-Di-(2-hydroxyethyl)-lactamide, triacetate	73	121–127	.01	....	1.4638	1.1806	1005	51.45	51.48	6.97	6.97	4.51	4.62
N,N-Di-(2-hydroxyethyl)-lactamide, tripropionate	64	132–140	.009	....	1.4602	1.1291	273	55.76	55.64	7.86	7.88	3.81	4.05
N,N-Di-(2-hydroxyethyl)-lactamide, trilaurate	95[a]	...	...	39–41[b]	....	....	....	70.63	71.32	11.36	11.27	1.63	1.93
N,N-Di-(2-hydroxyethyl)-lactamide, triheptanoate	71	193	.02		1.4593	1.0024	109	65.30	65.46	9.86	10.01	2.72	2.73
N,N-Di-(2-hydroxypropyl)-lactamide, triacetate	92	83	.001	....	1.4578	1.1275	1203(40°)	54.06	54.37	7.43	7.60	4.32	4.23
N,N-Di-(2-hydroxypropyl)-lactamide, tripropionate	..	102	.01	....	1.4558	1.0813	737	57.49	57.89	8.32	8.37	3.82	3.75
N,N-Di-(2-hydroxypropyl)-lactamide, tri-2-ethylhexanoate	80	136–138	.005	....	1.4559	0.9683	415	68.10	67.88	10.20	10.53	2.49	2.40

[a] Yield based on crude product. [b] Recrystallized from ethanol. [c] Recrystallized from acetone. [d] Recrystallized from hexane b.r. 63–70°. [e] Recrystallized from benzene. [f] Recrystallized from ether. [g] Supercooled liquid. [h] Distilled in a centrifugal molecular still.

Preparation of Esters of Lactamides.—These were prepared by acylation of the appropriate lactamide with acid anhydrides or chlorides. Acetic and propionic anhydrides were employed to obtain the acetates and propionates, and acid chlorides in conjunction with pyridine were used to prepare the remaining esters by standard procedures. The ester-amides were distilled in an alembic type still[14] at low pressure. Middle fractions or recrystallized materials in the case of solids were used for determination of properties and for analyses. It was necessary to distil the bis-(hexylcarbonate) of 2-hydroxyethyl- and 2-hydroxypropyllactamides in a centrifugal molecular still. The ester-amides prepared and their properties are shown in Table I. The boiling point curves for N-butyllactamide 2-ethylhexanoate and the 2-ethylhexanoate and laurate of N,N-dibutyllactamide are shown in Fig. 1.

Ester-amides by Simultaneous Esterification and Dehydration of Lactic Acid-Amine Salts.—Ethanolamine, 61 g. (1 mole), was added in portions to 112 g. of 80% lactic acid with occasional cooling to remove the heat of neutralization. Then 316 g. (2 moles) of pelargonic acid and 130 ml. of benzene were added to the reaction flask, and the mixture was refluxed under a Barrett-type water trap, which automatically separated water from the water-benzene azeotrope. After two hours, 29 ml. of water and 76 ml. of benzene had been removed from the trap, and the still-pot temperature had risen from 112 to 153°. An additional 40 ml. of water was separated from the reaction mixture as the pot temperature rose to 190° in the next six hours. The reaction mixture was transferred to a Vigreux still and freed of benzene by distillation at 10 mm., a water-bath being used for heating purposes. The ester-amide was then isolated by distillation in an alembic still under high vacuum. The yield of distilled product, N-2-hydroxyethyllactamide dipelargonate (which solidified in the receiver) was 74%.

N,N-Dibutyllactamide laurate was prepared by a similar procedure from one mole each of lactic acid, dibutylamine and lauric acid, with xylene as the entraining agent, in 70% yield.

Acknowledgment.—The authors are indebted to Mary Jane Welsh and Ruth Kelly for the ultimate analyses, E. H. Harris, Jr., for assistance in several preparations, and H. B. Knight for the distillation of two products in a centrifugal molecular still.

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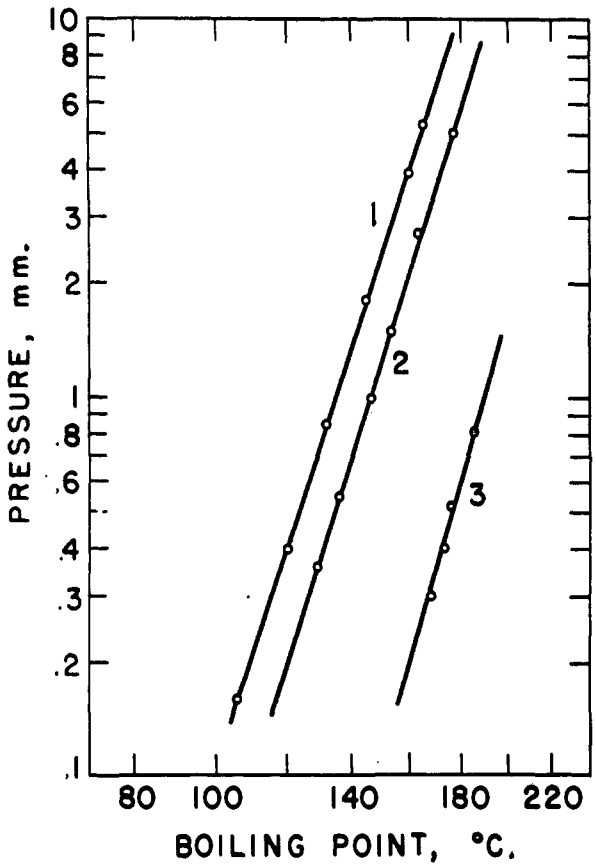

Fig. 1.—Boiling points of lactamide esters: 1, N-butyllactamide, 2-ethylhexanoate; 2, N,N-dibutyllactamide, 2-ethylhexanoate; 3, N,N-dibutyllactamide, laurate.

PHILADELPHIA 18, PENNA.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, PHOSPHATE DIVISION, MONSANTO CHEMICAL COMPANY]

The Preparation of Isocyanates by the Thermal Decomposition of Substituted Ureas[1]

BY WILLIAM B. BENNET, J. H. SAUNDERS AND EDGAR E. HARDY

RECEIVED DECEMBER 15, 1952

Isocyanates have been prepared in 57–71% yields by the vapor-phase reaction of *sym*-disubstituted ureas with hydrogen chloride. Lower yields were obtained from the vapor-phase reaction of amines and urea or cyanuric acid with hydrogen chloride, and from N-phenylurea with hydrogen chloride.

The thermal dissociation of substituted ureas into the corresponding amines and isocyanates, according to equation 1

$$RNHCONHR' \rightleftarrows RNCO + R'NH_2 \quad (1)$$

has been demonstrated qualitatively both in the liquid phase[2] and in solution.[3] Isocyanates have been identified among the products obtained by the distillation of molten substituted ureas,[4] and by the treatment of molten ureas with phosphorus pentoxide[5] or with dry hydrogen chloride.[6] As a preparative method for isocyanates, however, the process has been limited to certain trisubstituted ureas which decomposed on heating into a low-boiling isocyanate and a relatively nonvolatile secondary amine,[7] as in equation 2, or to

$$(C_6H_5)_2NCONHCH_3 \longrightarrow (C_6H_5)_2NH + CH_3NCO \quad (2)$$

ureas containing as the only substituent a large tertiary alkyl group, such as the neopentyldimethylcarbinyl group.[8] The recombination of the

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