Tetrahedron. Vol 23, pp 3363 to 3373. Pergamon Press Ltd 1967. Printed in Great Britain

A NOVEL PREPARATION OF PSEUDOXAZOLONES

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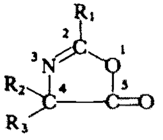
(*Received in Japan* 24 *October* 1966; *accepted for publication* 12 *December* 1966)

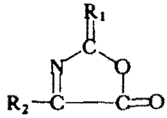
Abstract—2-Alkenyl-2-oxazolin-5-ones were prepared from N-Acryloyl- and N-methacryloyl-α-amino acids in excess acetic anhydride, while in the reaction with an equimolar amount of acetic anhydride in pyridine, new pseudoxazolones, 2-alkylidene-3-oxazolin-5-ones, were synthesized from the same N-acyl-α-amino acids in high yields. The 5-oxazolones were distinguished by IR, NMR, and UV spectroscopy. A structural relationship between the 5-oxazolones produced and the N-acyl-α-amino acids used as starting materials has been discussed.

5-OXAZOLONES are conveniently classified into a saturated type (I) and unsaturated types (II and III).[1-4]

Several preparative methods of 5-oxazolones from N-acyl-α-amino acids have been reported and it has been found that three types of 5-oxazolones may be obtained from the same N-acyl-α-amino acid.[5] Recently, 2-arylidenepseudoxazolones (IV) and 2-trifluoromethylpseudoxazolones (V) both examples of type II have been synthesized,[6,7] and an interesting study on the preparation of 2-alkylidene-pseudoxazolones from N-haloacyl-α-amino acids has been reported[8] but no 5-oxazolones have been synthesized from N-acryloyl- and N-methacryloyl-DL-α-amino acids. In this communication, a new method for the preparation of pseudoxazolones is



I



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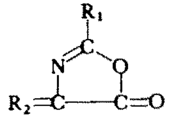

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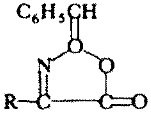

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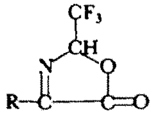

V

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[1] R. C. Elderfield, *Heterocyclic Compounds* Vol V; p. 298. Wiley, New York (1957).

[2] H. E. Carter, *Organic Reactions* Vol III; p. 199. Wiley, New York (1962).

[3] E. Baltazzi, *Quart. Rev.* **9**, 150 (1955).

[4] A. R. Katrizky, *Advances in Heterocyclic Chemistry* Vol IV; p. 75. Academic Press, New York (1965).

[5] Y. Iwakura, F. Toda and H. Suzuki, *J. Org. Chem.*, in press, Feb. (1967).

[6] R. Filler and E. J. Piasek, *J. Org. Chem.* **29**, 2205 (1964).

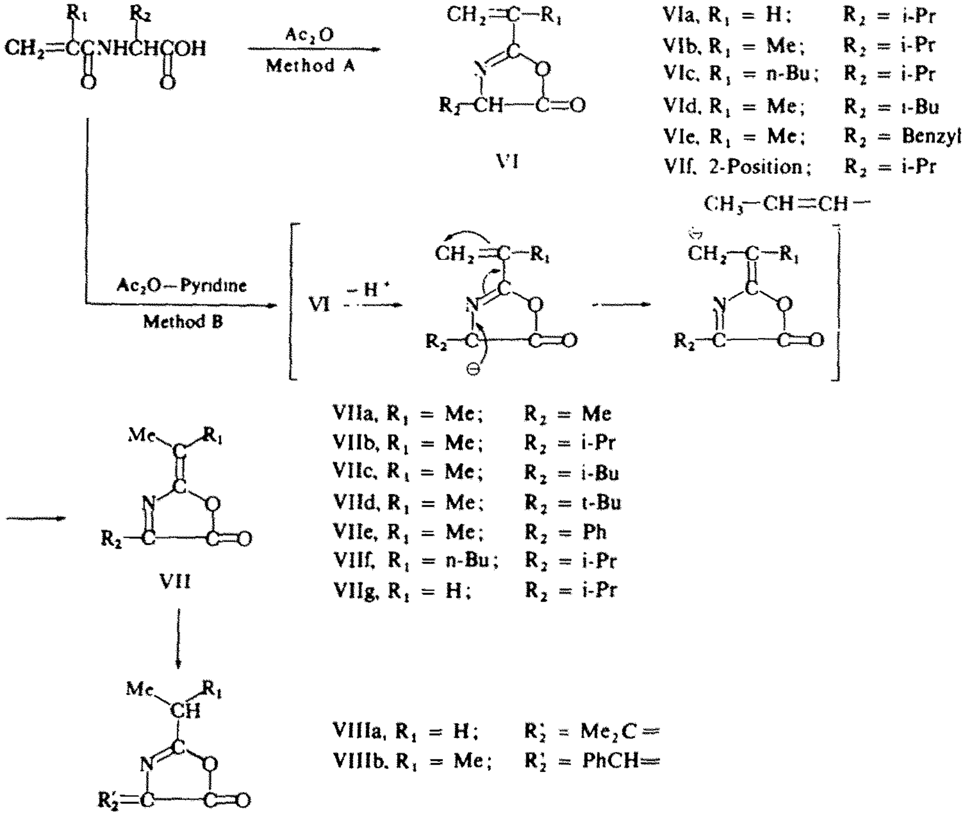
[7] F. Weygand, W. Steglich and H. Tanner, *Liebigs Ann.* **658**, 128 (1962).

[8] W. Steglich and R. Hurnaus, *Tetrahedron Letters* No. 4, 383 (1966).

recorded and the relationship between the types of 5-oxazolones produced and the starting materials investigated.

RESULTS AND DISCUSSION

The cyclodehydration of N-acryloyl- and N-methacryloyl-DL-α-amino acids was achieved either (1) by the action of excess acetic anhydride (Method A),[9] or (2) by the action of acetic anhydride in pyridine (Method B).[10]



VI

VIa, R_1 = H; R_2 = i-Pr
VIb, R_1 = Me; R_2 = i-Pr
VIc, R_1 = n-Bu; R_2 = i-Pr
VId, R_1 = Me; R_2 = i-Bu
VIe, R_1 = Me; R_2 = Benzyl
VIf, 2-Position; $CH_3-CH=CH-$ R_2 = i-Pr

VII

VIIa, R_1 = Me; R_2 = Me
VIIb, R_1 = Me; R_2 = i-Pr
VIIc, R_1 = Me; R_2 = i-Bu
VIId, R_1 = Me; R_2 = t-Bu
VIIe, R_1 = Me; R_2 = Ph
VIIf, R_1 = n-Bu; R_2 = i-Pr
VIIg, R_1 = H; R_2 = i-Pr

VIII

VIIIa, R_1 = H; R_2' = $Me_2C=$
VIIIb, R_1 = Me; R_2' = $PhCH=$

Method A. 2-Vinyl-4-isopropyl-2-oxazolin-5-one (VIa, 20% yield), VIb (51%),[11] VIc (47%), VId (50%), VIe (20%), and VIf (43%) were synthesized from the corresponding N-acyl derivatives of DL-valine, DL-leucine, and DL-phenylalanine by heating in acetic anhydride for 5 min at 100°.[12] The structure of VI as 2-oxazolin-5-one[13] was based on IR and NMR spectra and its reaction with aniline. Compound VI

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[9] C. S. Cleaver and B. C. Pratt, *J. Am. Chem. Soc.* **77**, 1544 (1955).

[10] H. E. Carter, P. Handler and C. M. Stevens, *J. Biol. Chem.* **138**, 619 (1941).

[11] W. Lynn, *J. Org. Chem.* **24**, 1030 (1959).

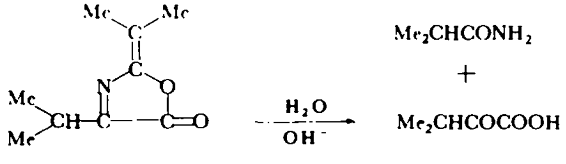
[12] Y. Iwakura, F. Toda and Y. Torii, *J. Polymer Sci.* **4**, A-1, 2649 (1966).

[13] Y. Iwakura, F. Toda and Y. Torii, *Bull. Chem. Soc. Japan* in press, Jan (1967). The identification of the structures of 5-oxazolones by NMR spectroscopy.

absorbed at 1825 (ν C=O), 1655 (ν C=N), and 1610–1620 cm^{-1} (ν C=C) in liquid film.[14] In the NMR spectrum of VIb, the Me protons of the isopropenyl group at C-2 and the terminal methylene protons were shown at $\delta = 2{\cdot}03$; 5·91 and 5·67. The proton at C-4 gave a doublet (δ 4·12, $J = 4{\cdot}2$ c/s). The 6 protons of two Me groups of the isopropyl substituent at C-4 gave two pairs of doublets of 7·2 c/s centered at δ 0·98 and 1·11, respectively. Differences in the conformational populations caused magnetic nonequivalence of the isopropyl groups close to the center of molecular asymmetry.[15] The same splitting was seen in the spectra of VIb and VIc. Compounds of type VI could not be obtained from either N-acryloyl- and N-methacryloyl-DL-alanine or N-acryloyl-DL-phenylalanine by Method A due to polymerization in the course of reaction.

Method B. 2-Isopropylidene-4-methyl-3-oxazolin-5-one (VIIa, 41% yield), VIIb (64%), VIIc (78%), VIId (69%), VIIe (14%), VIIf (58%), and VIIg (42%) were obtained by the dehydration of N-acyl-α-amino acids with acetic anhydride in pyridine at 100° for 2 hr as shown in the equation.[16] The products were found to be pseudoxazolone on the basis of IR and NMR spectra:[13] the ν C=O and C=N vibrations in the region of 1775 and 1680 cm^{-1} are due to the increased conjugate system and the ν C=C band has disappeared due to improved symmetry. In the NMR spectrum of VIIb, two Me groups of the isopropylidene substituent at C-2 induce two singlets at δ 2·11 and 2·02. The 6 protons of two Me groups of isopropyl substituent at C-4 result in a doublet (δ 1·28, $J = 6{\cdot}6$ c/s) and the tertiary proton produces a septet at δ 2·97.[17] Only 2-isopropenyl-4,4-dimethyl-2-oxazolin-5-one (type VI compound) which lacks a labile hydrogen at 4-position was obtained in 56% yield from N-methacryloyl-α-aminoisobutyric acid by Method B.

The structure of VIIa was confirmed by synthesis[18] from N-(α-bromoisobutyryl)-DL-alanine in 65% yield. Compound VIIb was hydrolysed with dilute alkali to isobutyramide and 3-methyl-2-oxobutyric acid in 9 and 93% (in the form of 2,4-dinitrophenylhydrazone), respectively.[19]



VIIb

Filler[21] reported that IV (R = Me) undergoes photodimerization, when exposed to the UV radiation, but VIIe does not show this tendency to dimerize in UV light in the solid state although the copolymerization of VII with oxygen in the air has been reported.[20]

[14] Y. Shimodoi, K. Masuda and N. Murata, *Kogyo Kagaku Zasshi* **65**, 1664 (1962).

[15] A. T. Bottini and R. L. VanEtten, *J. Org. Chem.* **30**, 575 (1965). Optically active VIb was obtained from N-methacryloyl-L-valine: $[\alpha]_D^{20}$ + 3·8°/benzene. M. Goodman and W. J. McGahren, *J. Am. Chem. Soc.* **88**, 3028 (1966).

[16] Y. Iwakura, F. Toda and Y. Torii, *Tetrahedron Letters* No. 37, 4427 (1966).

[17] F. Weygand, W. Steglich, D. Mayer and V. von Philipsborn, *Chem. Ber.* **97**, 2023 (1964).

[18] M. Bergmann and F. Stern, *Liebigs Ann.* **448**, 20 (1926).

[19] *Dictionary of Organic Compounds* Vol III; p. 149. Eyre & Spotiswoode, London (1953).

[20] Y. Iwakura, F. Toda and Y. Torii, *J. Org. Chem.* **31**, 2875 (1966).

[21] R. Filler and E. J. Piasek, *J. Org. Chem.* **28**, 221 (1963).

If instead of N-methacryloyl derivatives, N-acryloyl-DL-valine was treated in accordance with Method B, a crude product, b.p. 60–95°/12 mm, consisting mainly of VIIg (74·5–78·50/11 mm) was isolated. Careful distillation of the residue gave a small fraction b.p. 88·5–91·5°/11 mm, the NMR spectrum of which indicated that this fraction was mainly VIIIa, as shown in Fig. 1. Compound VIIg shows ν C=O and ν C=N frequencies at 1780 and 1680 cm^{-1}, while VIIIa exhibits in addition to the above peaks, new strong absorptions at 1620 (ν C=C), 1275, and 880 cm^{-1}.

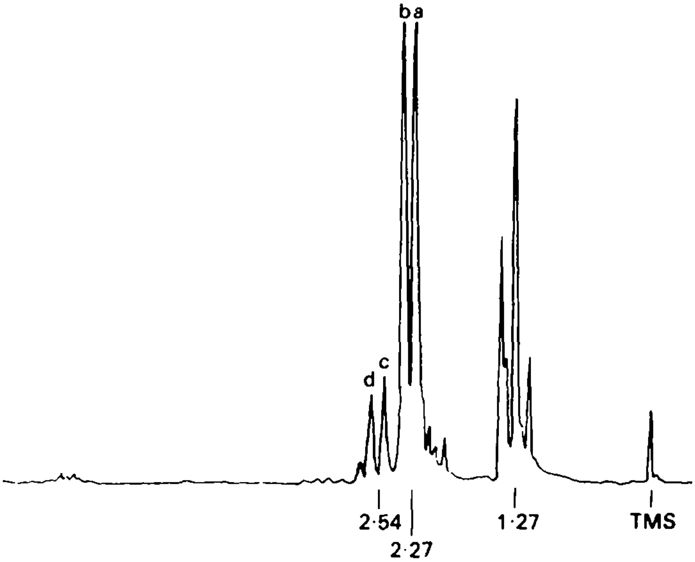
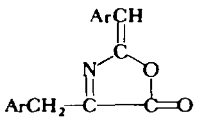
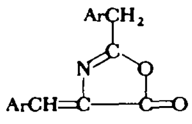


FIG. 1. The NMR spectrum of VIIIa.
a, b: Two singlets of methyl protons of VIIIa.
c, d: A quartet of methylene protons of VIIIa.

Bergmann suggested that a tautomeric equilibrium between 2-arylidene-3-oxazolin-5-one (IX) and 4-arylidene-2-oxazolin-5-one (X) is easily established, so that each preparative reaction of IX and X will produce whichever form happens to be the more stable.[22] In the reaction of N-acryloyl-DL-valine, a mixture of VIIg and



IX



X

VIIIa was obtained with Method B. In view of the experimental evidence that VIIg rearranges to VIIIa with trace acetic acid in pyridine, the reaction should proceed from N-acryloyl-DL-valine via VIIg to VIIIa (cross conjugated formula). N-Methacryloyl-DL-phenylalanine gave only VIIIb on treatment according to Method B, which permits the most extended conjugation with the Ph group. On the other

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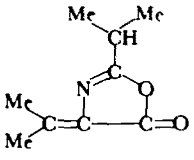
[22] E. Baltazzi, *Quart. Rev.* **9**, 154 (1955).

hand, a product consisting mainly of type VII compound, b.p. 75°/4 mm, was obtained in 25% yield from N-acryloyl-DL-leucine.

A condensation product obtained in 11% yield from the reaction of N-isobutyrylglycine and acetone by Erlenmeyer's method[23] was decided to have structure XI by the NMR spectrum which has two singlets (δ 2·32, 2·22), a doublet (δ 1·28, J = 6·6 c/s), and a septet (δ 2·81) and shows a C=C band at 1620 cm^{-1}. Compounds VIIb and XI are probably isomeric as they are not interconvertible in boiling pyridine with a small amount of acetic acid.



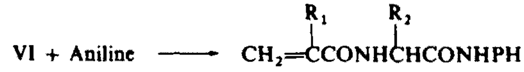
XI

Three types of 5-oxazolones may be distinguished on the basis of UV spectra as shown in Table 1. A bathochromic shift of λ_{max} in the UV region is characteristic of pseudoxazolones.

TABLE 1. λ_{max} OF 5-OXAZOLONES (IN CYCLOHEXANE)

VIa	225	VIIa	305 (ε = 17000)	VIIIa	271 mμ
VIb	218 (ε = 18800)	VIIb	305 (ε = 17300)	XI	270
VIc	220	VIIc	305		
		VIId	305		
		VIIe	352		
		VIIf	305		
		VIIg	292		

2-Alkenyl-5-oxazolones reacted with aniline in benzene or toluene analogous to 2-alkyl-5-oxazolones and afforded the corresponding anilides as depicted below:



$$\text{VI} + \text{Aniline} \longrightarrow CH_2{=}\overset{R_1}{\overset{|}{C}}CONH\overset{R_2}{\overset{|}{C}}HCONHPH$$

Compound VI could be polymerized and had the ability to react with amines through vinyl polymerization.

EXPERIMENTAL

Preparation of α-n-butylacryloyl chloride. To α-n-butylacrylic acid (38 g) in a flask cooled with ice-water PCl_5 (65g) was added portionwise and after 1 hr the mixture was distilled under reduced press yielding the acid chloride (44 g), b.p. 71–74°/28 mm (lit.[24] 62°/19 mm).

Preparation of N-methacryloyl-DL-alanine. DL-alanine (89 g) and NaOH (80 g) were dissolved in 200 ml water and 104·5 g methacryloyl chloride was added dropwise under cooling with an ice bath (the temp should not exceed 30°) and stirring continued for 1 hr. The mixture was neutralized with 84 ml conc HCl aq, the ppt was filtered off by suction and recrystallized from benzene to give 115 g (73%) of the product

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[23] G. R. Ramage and J. L. Simonsen, *J. Chem. Soc.* 532 (1935).

[24] Y. Iwakura, M. Sato and Y. Matsuo, *Nippon Kagaku Zasshi* **80**, 502 (1959).

(m.p. 117–118°). N-Methacryloyl-DL-valine (m.p. 101–102°, lit.[11] 99–100°) and N-methacryloyl-DL-leucine (m.p. 105–106°) were prepared in 86 and 71 %, respectively.[12] By the analogous method the following compounds were synthesized and are summarized in Table 2.

*Preparation of α-bromoisobutyryl-*DL*-alanine.* Into a soln of DL-alanine (19·3 g) and NaOH (9 g) in water (50 ml), α-bromoisobutyryl bromide and NaOH aq (9 g NaOH in 20 g H_2O) were added dropwise separately under cooling from two dropping funnels. The resulting mixture was stirred for ½ hr, then neutralized with conc HCl aq (19 ml). The solid was removed by filtration and recrystallized from water–acetone, m.p. 113–115°; ν_{max} 3380 (N–H), 1720 (C=O), 1650 cm^{-1} (C=O). (Found: C, 36·79; H, 5·18. $C_7H_{12}NO_3Br$ requires: C, 35·30; H, 5·04 %).

Preparation of 2-isopropenyl-4-isopropyl-2-oxazolin-5-one (VIb). About 200 ml Ac_2O was preheated to 100° (oil bath) and 25 g N-methacryloyl-DL-valine added as quickly as possible and the mixture kept at 100° for an additional 5 min. AcOH and excess Ac_2O were removed under reduced press and the residue after fractionation *in vacuo* yielded 11·5 g (51 %) b.p. 100–103°/20 mm[13]; n_D^{20} 1·4641 (lit.[11] 81°/10·5 mm; n_D^{30} 1·4550). By the analogous procedure the following compounds were obtained as shown in Table 3.

Preparation of 2-isopropylidene-4-methyl-3-oxazolin-5-one (VIIa). An equimolar amount of Ac_2O was added to a soln of N-methacryloyl-DL-alanine in pyridine and the mixture heated to 100° for 2 hr.[12] After removal of pyridine (red. press), the residue was fractionally distilled *in vacuo* yielding a product, b.p. 54–56°/1·5 mm; m.p. 31–32°. By an analogous method the following pseudoxazolones were prepared as shown in Table 4.

Preparation of 2-isopropylidene-4-phenyl-3-oxazolin-5-one (VIIe). N-Methacryloyl-DL-phenylglycine (40 g) was dissolved in pyridine (200 ml) and heated to 100°. Ac_2O (20 g) was added dropwise and the mixture kept at 100° for 2 hr. About half the pyridine was removed *in vacuo* and the resulting red-brown crystals were filtered off and recrystallized from benzene (200 ml), yield 5 g (14 %) of red crystals, m.p. 138°; ν_{max} 1765 (C=O), 1670 cm^{-1} (C=N).

(Found: C, 71·26; H, 5·70; N, 6·90. $C_{12}H_{11}NO_2$ requires: C, 71·62; H, 5·51; N, 6·96 %).

Preparation of 2-ethylidene-4-isopropyl-3-oxazolin-5-one (VIIIa). N-Acryloyl-DL-valine (22 g) was dissolved in pyridine (100 ml) and heated to 95°. Ac_2O (10 g) was added dropwise and the soln kept at 95° for 3 hr. Pyridine and AcOH were distilled off under reduced press and by the distillation of the residue a crude fraction, b.p. 60–95°/12 mm was obtained in 50 % yield. Redistillation of the crude fraction gave a product, b.p. 74·5–78·5°/11 mm; ν_{max} 1775 (C=O), 1680 cm^{-1} (C=N); n_D^{22} 1·5030.

Preparation of 2-isopropyl-4-isopropylidene-2-oxazolin-5-one (XI). A mixture of N-isobutyrylglycine (66 g), acetone (204 g), Ac_2O (153 g), and AcONa (41 g) was heated under reflux at 110° for 20 hr. After excess acetone, Ac_2O and AcOH were removed under reduced press, the residue was distilled at 76–78°/2·5 mm (8 g, 11 % yield). ν_{max} 1780 (C=O), 1675, 1620 cm^{-1} (C=N, C=C); n_D^{20} 1·4903.

(Found: 64·46; H, 8·02; N, 8·68. $C_{12}H_{11}NO_2$ requires: C, 64·65; H, 7·84; N, 8·38 %).

Preparation of 2-isopropenyl-4,4-dimethyl-2-oxazolin-5-one. N-Methacryolyl-α-aminoisobutyric acid (10 g) was cyclized by the Method B using benzoic anhydride in order to avoid the formation of an azeotropic mixture with the product. About 5 g (56 % yield) of the product, b p 75–76°/19 mm was obtained; ν_{max} 1825 (C=O). 1660 (C=N). 1615 cm^{-1} (C=C); δ1·51 (6H), 2·15 (3H), 6·37 (1H), 6·06 (1H); n_D^{20} 1·4580.

(Found: C, 62·66; H, 7·31; N, 8·77. $C_8H_{11}NO_2$ requires: C, 62·72; H, 7·24; N, 9·14 %).

Rearrangement of XI *to* VIIb. A mixture of XI (2 ml) and pyridine (10 ml) was kept at 100–110° in a sealed tube for 5 hr. Similarly, a mixture of XI (2 ml), Ac_2O (1 ml), AcOH (1 ml) in pyridine was also kept under the same conditions. After removal of AcOH, Ac_2O and pyridine, both oxazolone fractions were subjected to measurement of UV spectra in cyclohexane

Rearrangement of VIIb *to* VIIIa. Rearrangement was carried out by the same method to that of XI. VIIb was converted to VIIIa under the influence of AcOH in pyridine, which was noted by the change of λ_{max} from 292 to 271 mμ in cyclohexane.

Hydrolysis of 2-isopropylidene-4-isopropyl-3-oxazolin-5-one (VIIb). A mixture of VIIb (5·5 g) and 10 % NaOH aq (20 ml) was heated on a water bath kept at 80° for 5 min, (uniform soln). The soln was cooled and extracted with three 30 ml portions of ether. The combined ether extracts were evaporated and the residue recrystallized from ether yielding 219 mg (9 %) of isobutyramide; m.p. 126° (lit.[26] 128°).

(Found: C, 55·33; H, 10·32. C_4H_9NO requires: C, 55·14; H, 10·41 %).

The water layer was acidified with dil HCl aq to pH 4. After addition of an equimolar amount of 2,4-

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[25] M. N. Gavrilov, A. W. Kopèrina and M. Klutcharova, *Bull. Soc. Chim. Fr.* **12**, 778 (1945).

[26] *Dictionary of Organic Compounds* Vol III; p. 73. Eyre & Spotiswoode, London (1953).

TABLE 2. N-ACYL-α-AMINO ACIDS

Compound	m.p.	Yield	Solvent for crystallization	Formula	Analysis						IR absorption maximum
					Found			Required			
					C	H	N	C	H	N	
N-Acryloyl-DL-valine	149–150°	66%	Ethyl acetate	$C_8H_{13}NO_3$	55·95	7·45	8·42	56·12	7·65	8·18	1720, 1700 1650, 1620 cm^{-1}
N-Methacryloyl-DL-pseudoleucine	172–173°	79%	Water	$C_{10}H_{17}NO_3$	60·21	8·49	6·84	60·28	8·60	7·03	1715, 1650, 1610 cm^{-1}
N-Methacryloyl-DL-phenylglycine	102–103°	69%	Toluene	$C_{12}H_{13}NO_3$	65·58	6·09	6·25	65·74	5·98	6·39	1710, 1650, 1610 cm^{-1}
N-Isobutyrylglycine[25]	103–104°	40%	Acetone–Benzene	$C_6H_{11}NO_3$	49·77	7·63	9·89	49·64	7·64	9·65	
N-(α-n-butylacryloyl)-DL-valine	63°	62%	Benzene	$C_{12}H_{21}NO_3$	63·30	9·18	6·19	63·41	9·31	6·16	1725, 1650, 1610 cm^{-1}
N-Crotyl-DL-valine	168–170°	58%	Water	$C_9H_{15}NO_3$	58·36	7·89	7·80	58·36	8·16	7·56	1720, 1665, 1620 cm^{-1}
N-Methacryloyl-α-amino-isobutyric acid	159–160°	37%	Water	$C_8H_{13}NO_3$	56·29	7·67	8·01	56·12	7·65	8·18	1720, 1650, 1595 cm^{-1}

TABLE 3. 2-OXAZOLIN-5-ONES

Compound	b.p.	Yield	Formula	Analysis						IR absorption maximum
				Found			Required			
				C	H	N	C	H	N	
VIa	53–55°/3 mm	20%	$C_8H_{11}NO_2$	61·90	7·35	8·58	62·72	7·24	9·14	1825 cm^{-1} (C═O) 1655 (C═N) 1610 (C═C)
VIc	95–96°/2 mm	47%	$C_{12}H_{19}NO_2$	68·93	9·32	6·79	68·86	9·15	6·69	1825 (C═O) 1655 (C═N) 1615 (C═C)
VID	70°/2 mm	50%	$C_{10}H_{15}NO_2$	65·74	7·85	8·04	66·27	8·34	7·73	1825 (C═O) 1655 (C═N) 1610 (C═C)
VIf	83–88°/3 mm	43%	$C_9H_{13}NO_2$	64·11	7·65	8·33	64·65	7·84	8·38	1825 (C═O) 1675 (C═N) 1620 (C═C)

TABLE 4. 3-OXAZOLIN-5-ONES

Compound	b.p.	Yield	Formula	Analysis						IR absorption maximum
				Found			Required			
				C	H	N	C	H	N	
VIIa	54–56°/1·5 mm n_D^{40} = 1·5437	41%	$C_7H_9NO_2$	60·28	6·30	10·01	60·42	6·52	10·07	1775 cm^{-1} (C=O) 1680 (C=N)
VIIb	74–76°/1 mm n_D^{20} = 1·5191	64%	$C_9H_{13}NO_2$	64·16	7·93	8·88	64·65	7·84	8·38	1775 (C=O) 1680 (C=N)
VIIc	84–86°/1 mm n_D^{20} = 1·5159	78%	$C_{10}H_{15}NO_2$	66·07	8·10	7·91	66·27	8·34	7·73	1775 (C=O) 1680 (C=N)
VIId	73–74°/1 mm n_D^{20} = 1·5051	69%	$C_{10}H_{15}NO_2$	65·81	8·24	7·35	66·27	8·34	7·73	1770 (C=O) 1680 (C=N)
VIIf	86–88°/0·7 mm n_D^{20} = 1·5036	58%	$C_{12}H_{19}NO_2$	68·84	8·96	6·53	68·86	9·15	6·69	1775 (C=O) 1675 (C=N)

(Large refractive indexes are characteristic of pseudoxazolones.)

TABLE 5. ANILIDES OF 2-OXAZOLIN-5-ONES

Compound	m.p.	Yield	Solvent for crystallization	Formula	Analysis Found C	Found H	Found N	Required C	Required H	Required N	IR absorption maximum
Anilide of VIa	188–189° *	24%	Toluene	$C_{14}H_{18}N_2O_2$	69·31	7·59	11·20	68·27	7·37	11·37	1685 cm^{-1} 1655 1625
VIb	174–175°	55%	EtOH	$C_{15}H_{20}N_2O_2$	69·65	7·07	10·79	69·20	7·74	10·76	1685 1650 1620
VIc	97–98°	71%	MeOH	$C_{18}H_{26}N_2O_2$	71·22	8·43	9·07	71·49	8·67	9·26	1670 1645 1605
VId	175°	—	Benzene	$C_{16}H_{22}N_2O_2$	69·03	7·60	10·57	70·04	8·08	10·21	1680 1650 1605
VIf	210–211°	—	EtOH-Water	$C_{15}H_{20}N_2O_2$	69·53	7·84	10·35	69·20	7·74	10·76	1660 1620
2-Isopropenyl-4,4-dimethyl-	135–136°	89%	EtOH-Water	$C_{14}H_{18}N_2O_2$	68·34	7·38	11·29	68·27	7·37	11·37	1675 1615 1595

dinitrophenylhydrazine the mixture was refluxed for 15 min and cooled. The crude 2,4-dinitrophenylhydrazone was filtered off and recrystallized from 300 ml water-EtOH (8·25 g, 93% yield); m.p. 191–192° (lit.[19] 189–191°).

(Found: C, 44·45; H, 4·04; N, 18·96. $C_{11}H_{12}N_4O_6$ requires: C, 44·60; H, 4·08; N, 18·91%).

Reaction of VI *with aniline.* To a soln of VIb (2·10 g) in toluene (5 ml) aniline (1·28 g) was added dropwise in an ice-bath and the mixture allowed to stand for 2 hr. The resulting solid was filtered off and recrystallization from EtOH gave a product (1·79 g, 55% yield). By an analogous procedure, anilides of VI type were obtained as summarized in Table 5.

Acknowledgement—We express thanks to the Ajinomoto Co. Inc. for a generous gift of each amino acid.