

TABLE I

Product	C, %		H, %		N, %		n_D^{20}	Mol wt		Nmr, ^a τ	Bp, °C (mm)	Yield, %
	Calcd	Found	Calcd	Found	Calcd	Found		Calcd	Found			
1 HC[N(CH ₃) ₂] ₂	57.9	57.9	13.2	13.3	28.9	29.3	1.4348	145	144 ^b	(s) 6.98, (s) 7.69 (1:18)	70 (50)	83
2 CH ₂ =C[N(CH ₃) ₂] ₂	63.1	62.7	12.4	12.1	24.5	24.3	1.4500	114	114	(s) 6.60, (s) 7.53 (1:6)	115 (744)	87
3 CH ₃ CH=C[N(CH ₃) ₂] ₂	65.5	65.2	12.7	12.8	21.8	21.5	1.4552	128	128	(q) 7.46, (s) 7.36, (s) 7.65, (d) 8.29 (1:6:6:3)	74 (80)	73
4 (CH ₃) ₂ C=C[N(CH ₃) ₂] ₂	67.5	67.3	12.8	12.9	19.7	19.5	1.4579	142	142	(s) 7.46, (s) 8.32 (2:1)	60 (30)	70
5 C ₆ H ₅ CH=C[N(CH ₃) ₂] ₂	75.8	75.6	9.5	9.2	14.7	14.1	1.5905	190	190	(m) 3.05, (s) 5.52 ^c (s) 7.34, (s) 7.40 (5:1:6:6)	80 (1)	88
6 Cl ₂ C=C[N(CH ₃) ₂] ₂ ^d	39.3	39.4	6.6	7.0			1.5903	183	183	(s) 7.59	54 (3)	68
7 {—CH=C[N(CH ₃) ₂] ₂ } ₂	63.7	63.4	11.6	11.3	24.8	24.6	1.5408	226	226	(s) 5.25, (s) 7.25 (s) 7.56 (1:6:6)	74 (1)	53

^a Benzene solvent, TMS internal standard. ^b By cryoscopy (all others by mass spectroscopy). ^c Carbon tetrachloride solvent, TMS internal standard. ^d Calcd for Cl: 38.8. Found: 39.1.

ether was prepared. To this solution was added dropwise with stirring 4.7 g (0.054 mole) of dimethylacetamide. The reaction mixture was allowed to stand overnight, then filtered, and the solvent removed. The residual oil was fractionally distilled yielding 4.8 g (78%) of vinylidenebisdimethylamine, bp 115° (749 mm).

Synthesis of Propenylidenebisdimethylamine.—A solution of 4.04 g (0.04 mole) of N,N-dimethylpropionamide (Eastman) in 20 ml of dry ether was prepared. To it was added dropwise with stirring a solution of 4.52 g (0.021 mole) of tetrakis(dimethylamino)titanium in 5 ml of dry ether. The reaction mixture was allowed to stand for 3 days, then filtered, and the solvent removed. The resulting oil was fractionally distilled yielding 3.74 g (73% yield) of propenylidenebisdimethylamine, bp 74° (80 mm).

Preparation of 2-Methylpropenylidenebisdimethylamine.—To 3.3 g (0.015 mole) of tetrakis(dimethylamino)titanium in a 25-ml round-bottom flask was added 3.25 g (0.028 mole) of N,N-dimethylisobutyramide. The reaction flask was placed in an oil bath kept at 90°. The flask was vented to the atmosphere through a tube of Drierite. After 16 hr in the bath the reaction mixture was a dark solid mass. It was cooled; ethyl ether was added; it was shaken vigorously and filtered. The ether was removed and the residual oil distilled yielding 2.8 g (70%) of 2-methylpropenylidenebisdimethylamine, bp 60° (30 mm).

Preparation of 2-Phenylvinylidenebisdimethylamine.—A solution of 4.89 g (0.030 mole) of N,N-dimethylphenylacetamide in 15

ml of dry ether was prepared. To this solution was added a solution of 3.36 g (0.015 mole) of tetrakis(dimethylamino)titanium in 5 ml of ether; 10 ml of ether was added to break up the precipitate which formed. The reaction mixture was allowed to stand overnight. The mixture was filtered and the solvent removed from the filtrate. The residual oil was distilled yielding 5.02 g (88% yield) of 2-phenylvinylidenebisdimethylamine, bp 80° (0.9 mm).

Synthesis of 2,2-Dichlorovinylidenebisdimethylamine.—A solution of 3.12 g (0.02 mole) of N,N-dimethyl-2,2-dichloroacetamide in 20 ml of dry ether was prepared. A solution of 2.30 g (0.0103 mole) of tetrakis(dimethylamino)titanium in 10 ml of dry ether was added dropwise with stirring. The reaction mixture was allowed to stand overnight, then filtered, and the solvent removed. The resulting oil was fractionally distilled yielding 2.49 g (68% yield) of 2,2-dichlorovinylidenebisdimethylamine, bp 55° (3 mm).

Synthesis of 1,1,4,4-Tetrakis(dimethylamino)butadiene.—A solution of tetrakis(dimethylamino)titanium (7 g, 0.031 mole) in 40 ml of ethyl ether was prepared. To this solution was added dropwise with stirring a solution of 2 g (0.02 mole) of succinic anhydride in a minimum of warm dioxane. The reaction mixture was allowed to stand for 60 hr at room temperature; the precipitate was then filtered off and the filtrate removed by distillation. The residual oil was fractionally distilled to yield 2.6 g (58%) of 1,1,4,4-tetrakis(dimethylamino)butadiene, bp 74° (1 mm).

A Novel Synthesis of N-Carboxydehydro- α -amino Acid Anhydrides and Their Reactions

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New pseudoxazolones, 2-isopropylidene-4-isobutyl-3-oxazolin-5-one and 2-isopropylidene-4-isopropyl-3-oxazolin-5-one, were easily copolymerized with oxygen to give polyperoxides. By thermal decomposition of each polyperoxide, 4-isobutylidene-2,5-oxazolidinedione (dehydroleucine NCA) and 4-isopropylidene-2,5-oxazolidinedione (dehydrovaline NCA) were obtained in 28 and 16% yields, respectively. From these results, the structure of the polyperoxides was discussed. Dehydroleucine NCA and dehydrovaline NCA gave the corresponding α -keto acids by hydrolysis and anilides by reaction with aniline. In contrast to the saturated NCA, dehydroleucine NCA and dehydrovaline NCA did not give polypeptides by reaction with triethylamine. Hydrogenation of dehydroleucine NCA afforded poly-leucine.

As examples of unsaturated N-carboxy- α -amino acid anhydrides (NCA), allylglycine NCA¹ (4-allyl-2,5-oxazolidinedione) and propargylglycine NCA² (4-propargyl-2,5-oxazolidinedione) have been reported by Schlögl. Dehydroalanine NCA³ (4-methylene-2,5-

oxazolidinedione), in which the double bond was directly attached to the five-membered ring, has been synthesized by Sakakibara from benzyl carbamate and pyruvic acid. We have found that polyperoxides⁴ (IIa and IIb) are obtained by copolymerization of 2-

(1) K. Schlögl and H. Fabitschowitz, *Monatsh. Chem.*, **85**, 1060 (1954).

(2) K. Schlögl and H. Pelousek, *ibid.*, **91**, 227 (1960).

(3) S. Sakakibara, *Bull. Chem. Soc. Japan*, **32**, 13 (1957).

(4) F. Toda, *Bull. Tokyo Inst. Technol.*, **No 57**, 93 (1964); this will be reported separately in detail.

TABLE I
 ASSIGNMENT OF INFRARED BANDS

Compound	Mp, °C		cm ⁻¹				
			νC=O		νC=C		νN-H
IIIa	92-93	In Nujol	1840	1765	1700 ^a	1685	3250
IIIa		In THF	1862	1790	1700		
IIIb	138-139	In Nujol	1815	1755		1675	3170
IIIb		In THF	1825	1755	1685		
L-Leucine NCA	77-78 ^b	In Nujol	1855 ^a	1810	1755 ^b		3260
L-Leucine NCA		In THF	1855	1780			
D,L-Leucine NCA	47-48 ^b	In Nujol	1845	1785 ^a	1750		3250
Dehydroalanine NCA ^c	111-113	In Nujol	1840	1770		1675	3300
Dehydroalanine NCA (IIIc)		In THF	1855	1785			

^a Weak. ^b K. D. Kopple and J. J. Katy, *J. Am. Chem. Soc.*, **78**, 6199(1956). ^c Reference 3.

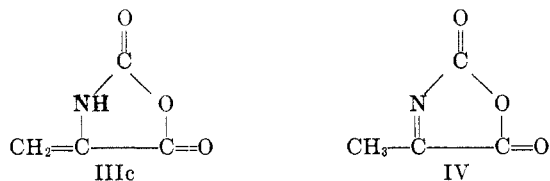
 TABLE II
 VALUES OF NCA

Compound	νN-H	νC-H				Solvents
		(CH ₃) ₂	9.09	9.20	CH=	
IIIa	0.63	(CH ₃) ₂	9.09	9.20	CH= 4.25 4.42	CDCl ₃
IIIb	0.87	(CH ₃) ₂	7.85	8.19		Dioxane
IIIc	-0.2				CH ₂ = 4.56 4.77	Acetone
L-Leucine NCA	2.57	(CH ₃) ₂	8.97	9.05	-CH-C=O 5.60 (triplet)	CDCl ₃

isopropylidene-4-isobutyl-3-oxazolin-5-one (Ia)⁵ and 2-isopropylidene-4-isopropyl-3-oxazolin-5-one (Ib) with oxygen. These polyperoxides are very unstable⁶ when isolated and even soft rubbing induces explosive decomposition to give resinous substances. However, when the thermal decomposition was carried out in inert solvents, dehydroleucine NCA (4-isobutylidene-2,5-oxazolidinedione) (IIIa) and dehydrovaline NCA (4-isopropylidene-2,5-oxazolidinedione) (IIIb) were obtained from the resinous products.

The benzene solution of IIa was added dropwise to a small quantity of refluxing benzene to carry out the thermal decomposition. After removal of benzene, IIIa was isolated in 28% yield from the residue. By the similar procedure, IIb was decomposed in toluene and IIIb was obtained in 16% yield. Formulas and structures were confirmed by elemental analyses and infrared spectra as shown in Table I.

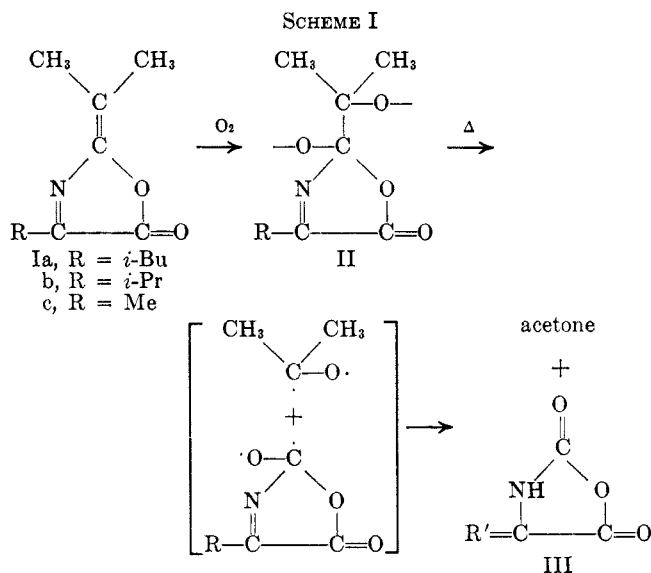
The fact that the position of the double bond in dehydroalanine NCA is *exo* to carbon-4 as IIIc and not as IV has already been determined by infrared spectral analysis. Nmr spectral analyses of IIIa and IIIb also led to the conclusion that the double bond is situated *exo* to carbon-4 and not between N and C as shown in Table II. Acetone was obtained from the recovered



solvents as 2,4-dinitrophenylhydrazine. These results make it reasonable to assume that polyperoxide⁷ formation proceeded in the manner depicted in Scheme I.

(5) H. E. Carter, *Org. Reactions*, **3**, 199 (1962). R. C. Elderfield, "Heterocyclic Compounds," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1957, p 298. A. R. Katritzky, *Advan. Heterocyclic Chem.*, **4**, 75 (1965). E. Baltazzi, *Quart. Rev.* (London), **9**, 150 (1955).

(6) H. Staudinger, *Ber.*, **58**, 1075 (1925).



In contrast to the saturated NCA, compounds of type III are unusually stable to moisture (especially IIIb).

Sakakibara obtained pyruvic acid as 2,4-dinitrophenylhydrazone⁴ by hydrolysis of IIIc in basic media. Hydrolysis of IIIa and b in 2% aqueous NaOH⁹ also afforded α -keto acids¹⁰ as 2,4-dinitrophenylhydrazone after addition of 2,4-dinitrophenylhydrazine to the reaction mixture (51% from IIIa and 31% from IIIb). Hydrolysis would proceed as shown in Scheme II.

IIIa reacted with aniline in ethyl acetate at 0 to -10° to give 4-methyl-2-oxovaleranyl in 59% yield after

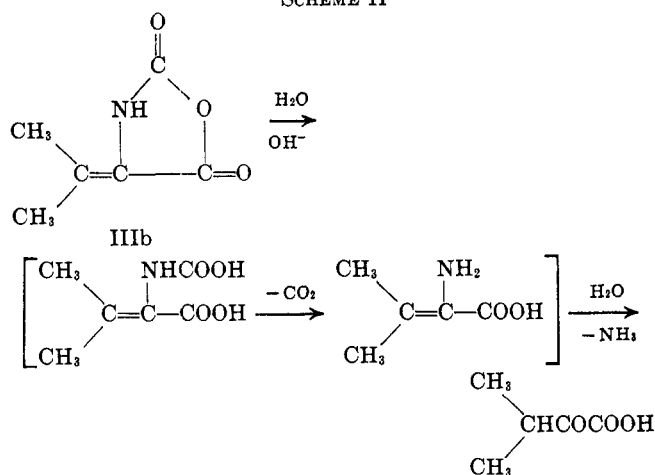
(7) We have found that these aliphatic pseudoxazolones copolymerized with oxygen forming polyperoxide. Filler⁸ reported that a pseudoxazolone dimerized by opening of the *exo* double bond at the 2 position under the effect of the light.

(8) R. Filler and E. J. Piasek, *J. Org. Chem.*, **29**, 2205 (1964). This will be reported at International Symposium on Makromolekulare Chemie, Tokyo, Japan, 1966.

(9) E. H. Rodd, "Chemistry of Carbon Compounds," Vol I-B, Elsevier Publishing Co., Amsterdam, The Netherlands, 1952, p 816.

(10) K. L. Waters, *Chem. Rev.*, **41**, 585 (1947).

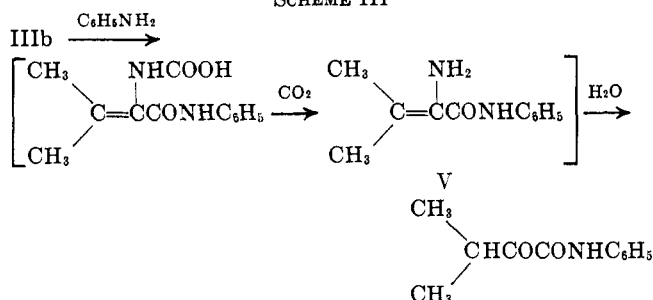
SCHEME II



1 day. IIIb appeared to be less reactive with aniline from the observation of the infrared spectra of the reaction mixture.

When IIIb and aniline were heated on a steam bath, 3-methyl-2-oxobutyranilide was obtained in 16% yield after evolution of CO_2 . Generally, the saturated NCA¹¹ gives polypeptide by reaction with primary amines. The lack of polymerization in the case of IIIa and IIIb is considered to be due to the lower reactivity of the amino group in V compared with that of the amino group in saturated compounds. (See Scheme III.)

SCHEME III

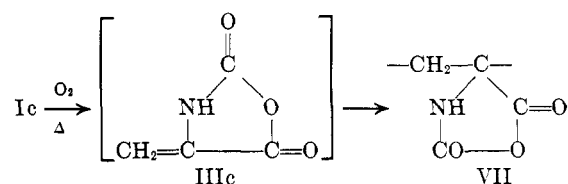


Catalytic hydrogenation of IIIa with palladium black was carried out in dioxane. Disappearance of $\text{C}=\text{C}$ bond in infrared spectra of the resulting solution was observed. An attempt to isolate the hydrogenated product was unsuccessful, presumably because the saturated NCA (4-isobutyl-2,5-oxazolidinedione) was rapidly polymerized by a trace of water in the course of removal of dioxane. Actually, polyleucine was obtained and after hydrolysis of the polymer, DL-leucine was detected by paper chromatography.¹²

4-Methyl-3-oxazolin-5-one (Ic) also gave a polyperoxide as a result of polymerization with oxygen. Although thermal decomposition of the polymer was tried in benzene and chloroform, a yellowish resinous material (VI) remained after evaporation of solvents, and little 4-methylene-2,5-oxazolidinedione was obtained from VI. The infrared spectrum of VI resembled that of the polymer from IIIc by radical polymerization.¹³ Nitrogen contents of VI and its derivative

obtained by the reaction with dilute HCl indicated that VI was the polymer (VII) of IIIc.

The fact that not IIIc but VII was obtained might be due to the greater tendency of IIIc to polymerize by radical initiators.



It has been reported that IIIc polymerizes to the mixture of polypyrrolidone and unsaturated polypeptide¹⁴ in hot pyridine or hot toluene with a small quantity of triethylamine (TEA) giving off carbon dioxide, however, at a lower rate compared to that of the saturated NCA. In IIIa and IIIb polymerization was observed neither in pyridine nor in toluene with TEA. The reason might be that the active anionic species¹⁵ (IIIa⁻ and IIIb⁻), which are formed by proton abstraction from IIIa and IIIb, can not attack another molecule of III owing to the delocalization of the negative charge.

Experimental Section

Preparation of N-Methacryloyl-DL-alanine.—DL-Alanine (89 g) and 80 g of sodium hydroxide were dissolved in 200 ml of water. To this solution, 104.5 g of methacryloyl chloride was added dropwise under cooling with an ice bath. The temperature during reaction should not exceed 30°. Stirring was continued for an hour. The mixture was neutralized with 84 ml of concentrated HCl. The precipitated product was filtered by suction and recrystallized from benzene to give 115 g (73%) of the product, mp 117–118°.¹⁶

N-methacryloyl-DL-valine, mp 101–102°,¹⁷ and N-methacryloyl-DL-leucine, mp 105–106°, were prepared in the yield of 86 and 71%, respectively.

N-Methacryloyl-DL-alanine: *Anal.* Calcd for $\text{C}_7\text{H}_{11}\text{NO}_2$: C, 53.49; H, 7.05; N, 8.91. Found: C, 53.93; H, 6.96; N, 9.14.

N-Methacryloyl-DL-leucine: *Anal.* Calcd for $\text{C}_{10}\text{H}_{17}\text{NO}_2$: C, 60.28; H, 8.60; N, 7.03. Found: C, 60.60; H, 8.34; N, 7.16.

Preparation of 2-Isopropylidene-4-isopropyl-3-oxazolin-5-one (Ib).—A mixture of 37 g of N-methacryloyl-DL-valine and 100 ml of pyridine was heated to 90–100° on an oil bath. Acetic anhydride (21 g) was added with vigorous stirring. The mixture was kept at the same temperature for 2 hr. Pyridine and acetic acid were distilled off under reduced pressure. The fraction, boiling at 74–76° (1 mm), was collected as pure material weighing 21 g (64%). By the analogous procedure, Ic, 55° (1.5 mm), and Ia, 84–86° (1 mm), were prepared in the yield of 41 and 78%, respectively.

Ia: *Anal.* Calcd for $\text{C}_{10}\text{H}_{15}\text{NO}_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.07; H, 8.10; N, 7.91.

Ib: *Anal.* Calcd for $\text{C}_9\text{H}_{13}\text{NO}_2$: C, 64.65; H, 7.78; N, 8.38. Found: C, 64.16; H, 7.93; N, 8.88.

Ic: *Anal.* Calcd for $\text{C}_7\text{H}_9\text{NO}_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.28; H, 6.30; N, 10.01.

Isolation of 4-Isobutylidene-2,5-oxazolidinedione (IIIa).—In a 500 ml flask equipped with an inlet gas tube were placed 25.5 g of Ia and 200 ml of toluene. A dry air stream was bubbled into the mixture for 1 day. The mixture became viscous gradually as the result of polyperoxide formation. The viscous solution was poured into 1 l. of methanol. Polymer was obtained as white mass after filtration. The polymer was purified by reprecipitation from 50 ml of benzene to 1 l. of methanol. The polymer was dried thoroughly at room temperature and dissolved in 100 ml of benzene. The polymer solution was added dropwise to a small

(11) E. Katchalski and M. Sela, *Advan. Protein Chem.*, **13**, 243 (1958).

(12) S. Akabori, "Chemistry of Protein," Vol. I, Kyoritsu Publishing Co., Tokyo, 1954, p 144.

(13) S. Sakakibara, *Bull. Chem. Soc. Japan*, **34**, 174 (1961).

(14) S. Sakakibara, *ibid.*, **33**, 814 (1960).

(15) M. Goodman and J. Hutchison, *J. Am. Chem. Soc.*, **87**, 3524 (1965).

(16) R. K. Kulkarni and H. Morawetz, *J. Polymer Sci.*, **64**, 491 (1961).

(17) J. W. Lynn, *J. Org. Chem.*, **24**, 1030 (1959). A report on the radical polymerization of oxazolones was submitted for publication.

volume of refluxing benzene in a 500-ml flask fitted with a dropping funnel and a reflux condenser. After addition, the solution was maintained at 80° for 15 min in order to decompose the peroxide perfectly. Benzene was removed under reduced pressure, and the residue was dissolved in 10 ml of ethyl acetate. After addition of 300 ml of petroleum ether (bp 40–80°), the mixture was left in a refrigerator overnight. IIIa, mp 92–93°, obtained in the form of needles, was collected by filtration and recrystallized from an ethyl acetate–petroleum ether mixture. It weighed 6 g (28% from Ia).

Anal. Calcd for $C_7H_9NO_3$: C, 54.19; H, 5.85; N, 9.03. Found: C, 53.99; H, 5.81; N, 9.02.

By the analogous procedure, 63 g of Ib was polymerized with oxygen. Polyperoxide was decomposed in boiling toluene. After recrystallization from an ethyl acetate–petroleum ether mixture, 6 g of IIIb, mp 138–139°, was obtained in the yield of 16%.

Anal. Calcd for $C_6H_7NO_3$: C, 51.06; H, 5.00; N, 9.93. Found: C, 51.45; H, 5.23; N, 9.99.

Polymerization of Ic.—Polymerization of Ic was carried out in benzene and as polymerization proceeded, the resulting polyperoxide was precipitated from benzene. The polymer was separated by filtration and purified by reprecipitation from chloroform to petroleum ether. The polyperoxide was decomposed in benzene or chloroform. After evaporation of the solvent under reduced pressure, a small amount of resinous product remained which showed infrared absorptions at 1850 and 1780 cm^{-1} .

Anal. Calcd for $C_4H_5NO_3$: N, 12.39. Found: N, 12.60.

The resinous material was treated with dilute HCl. Resulting substance exhibited a strong absorption at 1700 cm^{-1} in place of $\nu_{C=O}$ at 1850 and 1780 cm^{-1} .

Anal. Calcd for $C_3H_5NO_2$: N, 16.09. Found: N, 15.35.

Hydrogenation of IIIa.—A sample of 500 mg of IIIa was dissolved in 10 ml of dioxane; 50 mg of palladium black was added. The suspension was stirred by magnetic stirrer while hydrogen gas was passed into it at room temperature. About 2 hr later, reaction was stopped, the catalyst was separated by filtration, and the solvent was removed at 30 mm. Infrared absorptions of the white polymer (polyleucine, mp >260°) obtained quantitatively, were as follows: NH 3280, amide I 1645, amide II 1530 cm^{-1} (lit.,¹⁹ for poly-DL-leucine, NH 3280, amide I 1652, amide II 1531 cm^{-1}).

Anal. Calcd for $C_6H_{11}NO$: N, 12.39. Found: N, 12.10.

Hydrolysis of Polyleucine.—In an ampoule of 10 ml, 500 mg of the polyleucine and 3 ml of concentrated HCl were added and heated in an oil bath at 150° 1 hr. Excess HCl was evaporated to dryness on a steam bath; the residue was dissolved in water and neutralized with dilute NaOH to pH 7. The solution was concentrated to 1 ml. Leucine was obtained after cooling, which was compared with the authentic sample by paper chromatog-

(18) We have found that Ia, Ib, and Ic had the structure of pseudoxazolones by nmr and infrared spectra. Report on the relationship between the structure of pseudoxazolones and nmr spectra was submitted to the *Bull. Chem. Soc. Japan* in detail. Nmr spectra of aliphatic pseudoxazolones were also reported: F. Weygand, W. Steglich, D. Mayer, and W. Von Philipsborn, *Chem. Ber.*, **97**, 2023 (1964); W. Steglich and R. Hurnaus, *Tetrahedron Letters*, No 4, 383 (1966).

(19) S. Akabori, "Chemistry of Protein," Vol. V, Kyoritsu Publishing Co., Tokyo, 1957, p 41.

raphy with 1-butanol–acetic acid–water mixture (4:2:1) at R_f 0.64 (lit.¹² 0.69).

Hydrolysis of IIIa and IIIb.—To 10 ml of 2% aqueous NaOH 272 mg of IIIa was added and the mixture was allowed to stand 2 days at room temperature. It was neutralized with 2% HCl to pH 4, an equimolar amount of 2,4-dinitrophenylhydrazine was added, and the mixture was warmed on a water bath. Reaction was completed when the color of the solution was changed from orange to yellow. After cooling, the precipitate was collected by filtration and washed with water. 2,4-Dinitrophenylhydrazone of 4-methyl-2-oxovaleric acid (280 mg 51%) was obtained by recrystallization from benzene, mp 155–156° (lit.²⁰ mp 155–156°).

Anal. Calcd for $C_{12}H_{14}N_4O_6$: C, 46.45; H, 4.55; N, 18.06. Found: C, 46.86; H, 4.45; N, 18.05.

IIIb was so stable that it could be recrystallized from water. IIIb (300 mg) was boiled in 2% NaOH for 10 min. The resulting mixture was treated by the same procedure. The product (199 mg) was obtained as the 2,4-dinitrophenylhydrazone of 3-methyl-2-oxobutyric acid, mp 191–192° (lit.²¹ mp 189–191°, 199 mg, 31%) after recrystallization.

Anal. Calcd for $C_{11}H_{12}N_4O_6$: C, 44.60; H, 4.08; N, 18.91. Found: C, 44.78; H, 4.13; N, 18.98.

Methanolysis of IIIa.—About 500 mg of IIIa was dissolved in 10 ml of methanol with a few drops of concentrated HCl and boiled for 10 min. Into the mixture an equivalent amount of 2,4-dinitrophenylhydrazine was added and warmed for 10 min. After cooling, the resulting crystals were separated by filtration as 2,4-dinitrophenylhydrazone of methyl 4-methyl-2-oxovalerate (mp 104–106°).

Anal. Calcd for $C_{13}H_{16}N_4O_6$: C, 48.15; H, 4.97; N, 17.28. Found: C, 48.23; H, 5.11; N, 17.44.

Reaction of IIIa with Aniline.—In 50 ml of ethyl acetate, 249 mg of IIIa and 1072 mg of aniline were added and the mixture was allowed to stand in a refrigerator for 1 day. The mixture was washed with 10 ml of 5% HCl and then with 20 ml each of water for three times successively. The solution was dried with sodium sulfate. After removal of ethyl acetate, 4-methyl-2-oxovaleramide (mp 67°) was obtained in the yield of 59% (194 mg).

Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.45; H, 7.40; N, 6.81.

2,4-Dinitrophenylhydrazone of anilide, mp 200–201°: *Anal.* Calcd for $C_{13}H_{19}N_5O_6$: C, 56.10; H, 4.97; N, 18.17. Found: C, 56.12; H, 5.16; N, 17.96.

A sample of 1 g of IIIb and 5 ml of aniline were heated on a steam bath for 3 hr. The mixture was dissolved in 20 ml of ethyl acetate and treated by the same procedure as above. After two recrystallizations from aqueous ethanol, 212 mg of the anilide was obtained in the yield of 16% (mp 57–59°).

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33. Found: C, 69.04; H, 6.83; N, 6.88.

2,4-Dinitrophenylhydrazone of the anilide, mp 236–238°: *Anal.* Calcd for $C_{17}H_{17}N_5O_6$: C, 54.98; H, 4.61; N, 18.86. Found: C, 55.16; H, 4.77; N, 18.73.

(20) "Dictionary of Organic Compounds," Vol. III, Eyre and Spottiswoode Ltd., London, 1965, p 2280.

(21) Reference 20, p 2274.