of water was added dropwise with stirring, the temperature of the solution being kept below 5° with an ice bath. Stirring was continued for 5–10 min after addition of the sodium nitrite and then any excess nitrous acid was destroyed (starch–iodide test paper) by the addition of small portions of sulfamic acid.

The diazonium solution was added to a stirred solution of 0.95 g of **5** in 50 ml of 80% acetic acid at room temperature. The pH of the coupling mixture was brought to 4–5 by the addition of saturated sodium acetate solution. An immediate orange color developed. The extent of coupling was followed by periodic spot tests of the solution with resorcinol and tetrazotized dianisidine ("Fast Blue B Salt"). Coupling was complete after 3 hr. The solution was diluted slowly with 100 ml of water and the orange precipitate was collected by suction filtration and washed with water.

With most of the diazonium salts used in this work, the coupling reaction was complete within 5 hr. In a few cases (diazotized *p*-anisidine and other anilines bearing electron-donating groups) where slow reaction was observed, the coupling mixture was allowed to stand overnight in a refrigerator before dilution with water.

The crude O-acetylated dye was dissolved in 50 ml of methoxyethanol and stirred at room temperature for 30 min with 5 ml of 20% sodium hydroxide solution. The color rapidly changed from orange to deep red. The solution was then diluted with 5–6 times its volume of water and the precipitate was collected, washed with water, dried, and recrystallized from 80 ml of ethanol to give 0.79 g (62%) of dark needles.

1-Arylazo-2-naphthylamines were prepared as illustrated by the following procedure.

1-(*p*-Acetamido)phenylazo-2-naphthylamine.—The solution prepared by diazotizing 1.50 g of *p*-aminoacetanilide in 10 ml of water, 15 ml of acetic acid, and 4.5 ml of concentrated hydrochloric acid at 0–5° with 0.70 g of sodium nitrite was added to a solution of 1.43 g of β-naphthylamine in 120 ml of 80% acetic acid. The pH of the solution was brought to 4–5 by the addition of saturated sodium acetate solution. After 4 hr, the solution was diluted with 200 ml of water. The precipitated dye was collected by suction filtration, washed with water, dried, and recrystallized from 75 ml of ethanol to give 2.38 g (78%) of minute orange needles.

1-(*m*- and *p*-amino)phenylazo-2-amino-8-naphthols and 1-(*m*- and *p*-amino)-2-naphthylamines were prepared by hydrolysis of the corresponding N-acetyl compounds as illustrated by the following procedure.

1-(*p*-Amino)phenylazo-2-amino-8-naphthol (10).—A solution of 1.60 g of **11** in 25 ml of methoxyethanol containing 10 g of 50% sodium hydroxide solution was heated at 80° for 25 min, on a steam bath. After cooling to room temperature, the solution was diluted with 150 ml of water. The precipitated dye was recrystallized from 500 ml of carbon tetrachloride to give 0.99 g (71%) of dark crystals.

1-(*m*-Trifluoromethyl)phenylazo-8-acetoxy-2-naphthylamine.—To a solution of 2.38 g of **5** in 150 ml of 80% aqueous acetic acid was added the solution prepared by diazotizing, at 0–5°, 1.6 g of *m*-aminobenzotrifluoride in 15 ml of acetic acid, 10 ml of water, and 4.5 ml of concentrated hydrochloric acid with 0.70 g of sodium nitrite dissolved in 3 ml of water. Coupling began immediately. The pH was brought to 4–5 by the addition of saturated sodium acetate solution. The dye began to separate in microcrystalline form. Water (250 ml) was added in small portions over a period of 40 min at which time the reaction was complete. The product was collected, washed with water, and, after being dried *in vacuo* over potassium hydroxide, weighed 3.23 g (86.5%), mp 117–118.5°. An analytical sample, recrystallized from cyclohexane, had mp 134–135°, λ_{max} (benzene) 437 mμ (ε 9400). (See Figure 4.)

Anal. Calcd for $C_{19}H_{14}N_3O_2F_3$: C, 61.13; H, 3.78; N, 11.26; F, 15.27. Found: C, 61.41; H, 4.15; N, 10.99; F, 15.01.

Acknowledgments.—We wish to thank Dr. T. W. Milligan for considerable help in the planning and initiation of this work. A number of informative discussions were held with Dr. G. Bird and Drs. S. G. Cohen and D. H. R. Barton. Special thanks are due Mr. W. Legsdin and his associates for determining the many absorption curves. For preparing a useful program which enabled us to use a computer for our least-squares curve fitting, the help of Mr. S. Haskell is gratefully acknowledged.

Acetylenic Amines. XIII. Syntheses of 3-Carboxy-3-pyrrolin-2-ones

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A new synthesis of 3-carboxy-3-pyrrolin-2-ones XVIII from oxazolidines VII has been investigated. The oxazolidines are readily available from the condensation of 2-propynylamines V and malonic esters. The conversion of VII to XVIII with acid or base involves a β-ketoamide intermediate XV which on cyclization readily hydrolyzes and dehydrates to XVIII. A general method for making 3-substituted 3-pyrrolin-2-ones XXIV from N-(1,1-dialkyl-2-propynyl)acetamides XXII involving the ketoamide intermediate has been made available.

The acid-catalyzed cyclization of acetylenic amides I to the oxazolinium salts II, together with metal-catalyzed cyclization to the oxazolines III, has been reported.[1,2] (See Scheme I.)

Preliminary attempts to prepare IV by treatment of the amides I where R^2 is alkyl either with acid followed by anhydrous base or with a metallic catalyst were unsuccessful. Compounds with substitution such as carbethoxy on the 2-methylene group of IV, which should stabilize the oxazolidine structure thus facilitating its isolation, were chosen for an extension of this study. In order to obtain the appropriate α-carbethoxyacetamides VI for cyclization, the condensation of secondary 2-propynylamines with malonic esters was investigated.

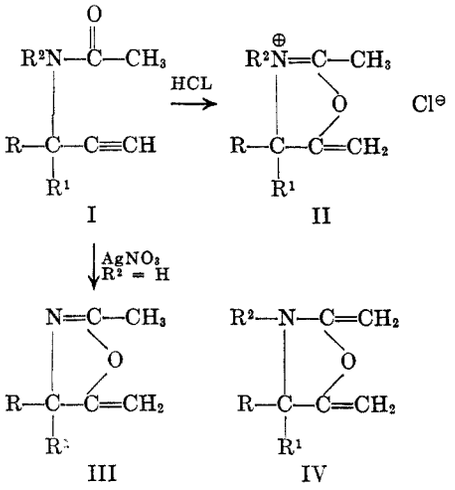
The reaction of N,1,1-trimethyl-2-propynylamine (Va) and malonic ester gave a product which was assigned the oxazolidine structure VIIa since its infrared spectrum had multiple absorptions in the carbonyl region and no acetylenic hydrogen absorption in the 3.02-μ region. A study of the nmr spectrum[3] substantiated the oxazolidine structure. There were two doublets centered at 282 cps and 255 cps (J = 3 cps) assigned to the *gem*-vinyl protons. A singlet at 240 cps was assigned to proton on the vinyl group containing the carbethoxy group. The remaining peaks

(1) N. R. Easton and R. D. Dillard, *J. Org. Chem.*, **28**, 2465 (1963).

(2) N. R. Easton, D. R. Cassady, and R. D. Dillard, *ibid.*, **30**, 3084 (1965).

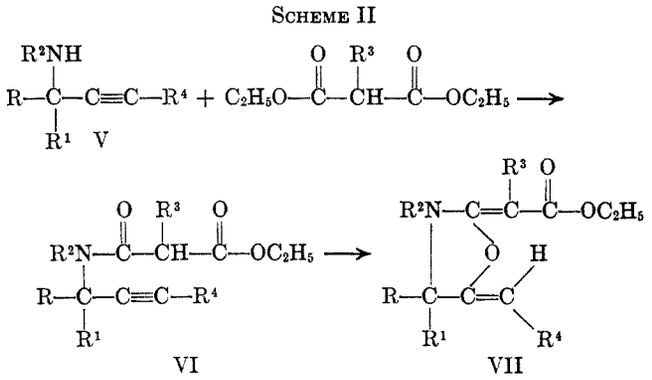
(3) The machine used was the Varian Associates Model HR-60, 60 Mc. Deuteriochloroform was used as the solvent and tetramethylsilane as the internal reference.

SCHEME I



of the nmr spectrum were consistent for the proposed structure. It seems likely that the acetylenic amide VI would be an intermediate, which under the reaction conditions would cyclize to VIIa (Scheme II).

SCHEME II



a, R = R^1 = R^2 = CH_3; R^3 = R^4 = H
b, R = R^1 = R^2 = CH_3; R^3 = C_2H_5; R^4 = H
c, R = R^1 = CH_3; R^2 = R^3 = R^4 = H

The oxazolidine structure VIIa was confirmed by the following chemical reactions. Catalytic semihydrogenation of VIIa gave VIII. Treating VIII with lithium aluminum hydride formed the known amino alcohol IX.[4] Reducing VIIa with 2 moles of hydrogen gave X which, upon reduction with lithium aluminum hydride, gave the dihydroxy compound XI (Scheme III). This compound was identical with the product obtained from the reduction of XII with sodium borohydride.

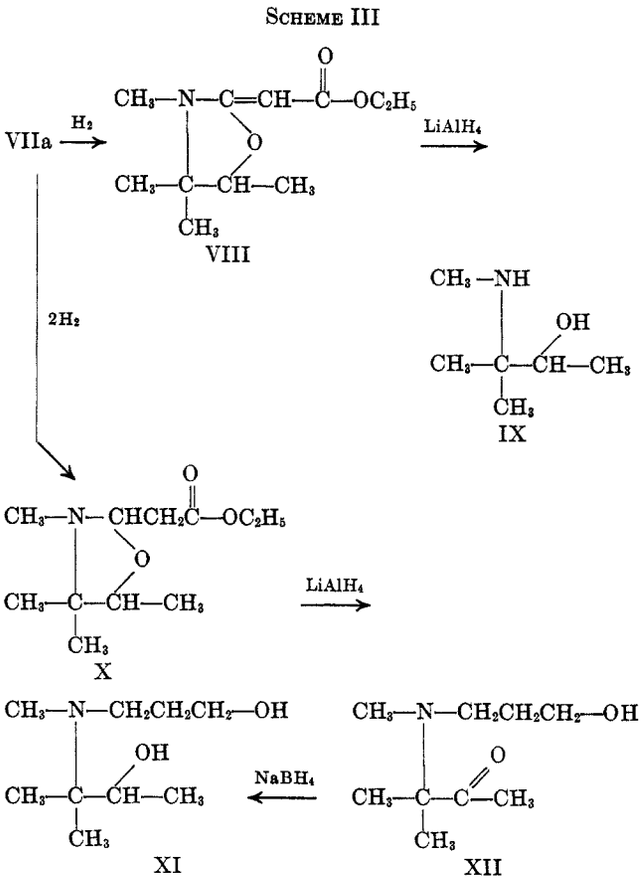
The condensation reaction was extended to other substituted 2-propynylamines and alkyl malonic esters. When the amine was secondary (R^2 = alkyl), the corresponding oxazolidine VII was obtained (see Table I). From the reaction of a primary 2-propynylamine with malonic ester, the acetylenic amide VI was isolated.

It has been shown that a compound of structure II was unstable under aqueous acidic conditions, giving an enol acetate salt that, on treatment with base, gave a ketoamide.[1]

The oxazolidine VIIa was treated with acid to form the oxazolinium salt XIIIa which was treated with water and base in an attempt to prepare the ketoamide

(4) N. R. Easton, D. R. Cassady, and R. D. Dillard, *J. Org. Chem.*, **29**, 1851 (1964).

SCHEME III



XVa. However, the product isolated upon acidification was the 3-carboxy-3-pyrrolin-2-one (XVIII) (Scheme IV). An intermediate such as XVa that cyclized to give XVIa, which underwent a facile hydrolysis and elimination of water, would explain the presence of XVIII. The structure of XVIII was confirmed by chemical reactions. The ester of XVIII and the decarboxylated product XIX were found to be identical with the two compounds isolated from the reaction of malonic ester with 3-methyl-3-methylamino-2-butanone (Scheme V).

Since acetylenic amides give oxazolinium salts when treated with acid, the amide VIc (R^2 = H) was treated with acid, base, and then acid to give 4,5,5-trimethyl-3-carboxy-3-pyrrolin-2-one. This compound was prepared also by the hydration of VIc with silver nitrate[2] followed by treatment with sodium ethoxide.

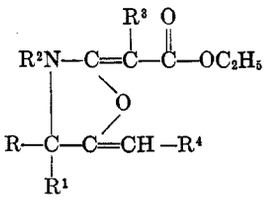
When the oxazolinium salt of VIIb, where R^2 = ethyl, was treated with water and dilute sodium hydroxide solution in the usual manner, the ketoamide XVb was obtained. Under these conditions, ring closure of XVb to XVIb was not effected. However, the reaction of XVb with sodium ethoxide in ethanol followed by distillation gave the 3-pyrrolin-2-one XXI.

In order to obtain the corresponding carboxylic acid, an alkaline hydrolysis of the oxazolidine VIIa was attempted. Surprisingly, treatment of VIIa with dilute sodium hydroxide followed by acidification with hydrochloric acid produced XVIII. An acyclic ketoamide intermediate was probably involved in the formation of the new ring system XVIII.

In a similar manner, the alkaline hydrolysis of VIIb produced 1,4,5,5-tetramethyl-4-hydroxy-3-carboxy-2-pyrrolidone (XVIIb). Since in this example there is

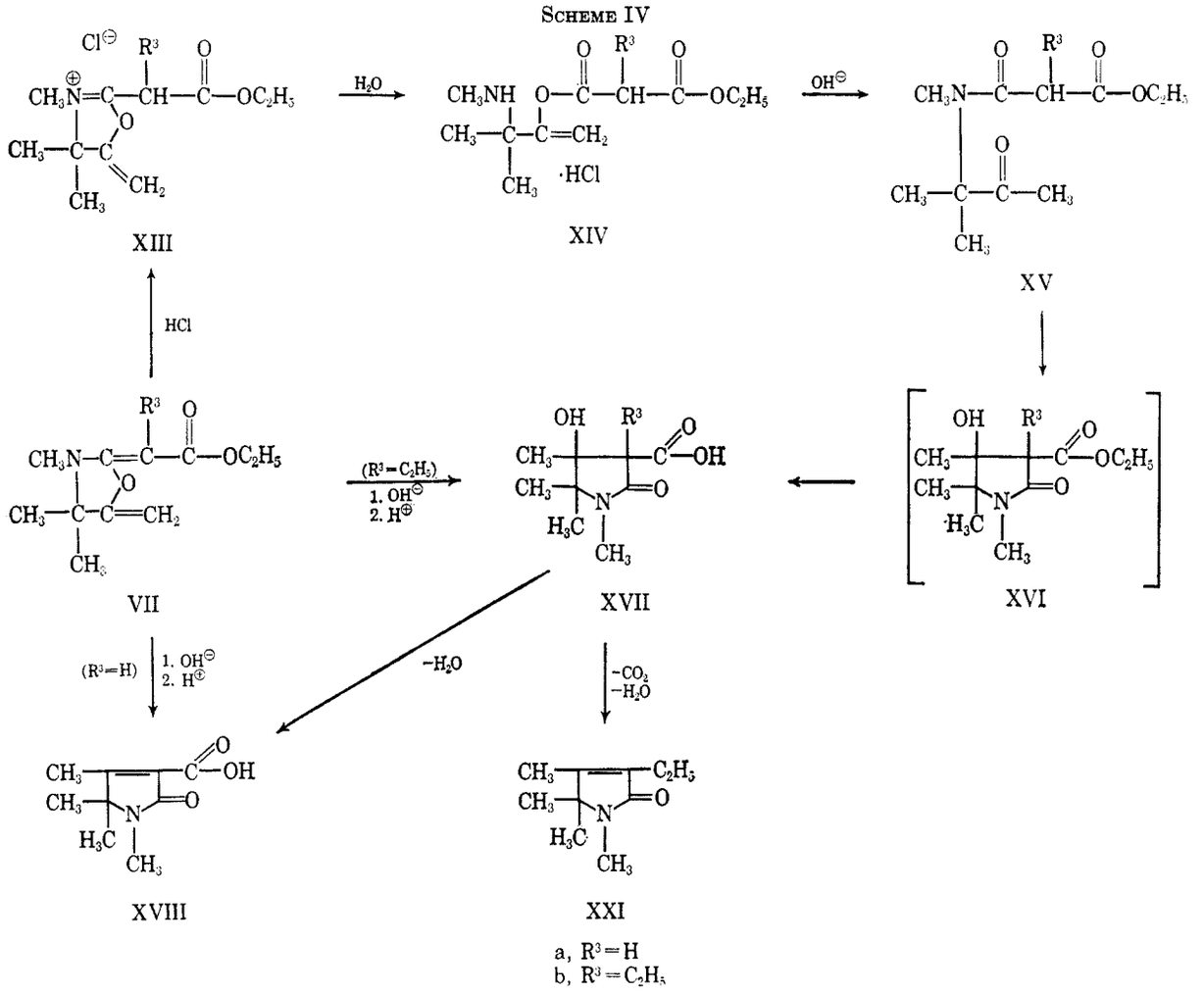
TABLE I

OXAZOLIDINES VII



R	R¹	R²	R³	R⁴	Bp (mm), °C	Formula	C, % Calcd	C, % Found	H, % Calcd	H, % Found
CH_3	CH_3	CH_3	H	H	124–125 (0.1)	$C_{11}H_{17}NO_3$	62.52	62.34	8.11	8.28
CH_3	CH_3	CH_3	C_2H_5	H	81–82 (0.02)	$C_{13}H_{21}NO_3$	65.27	65.47	8.85	8.87
CH_3	C_2H_5	CH_3	H	H	115–120 (0.05)	$C_{12}H_{19}NO_3$	63.97	64.02	8.50	8.58
CH_3	CH_3	CH_3	H	CH_3	110–115 (0.05)	$C_{12}H_{19}NO_3$	63.97	63.86	8.50	8.62

SCHEME IV



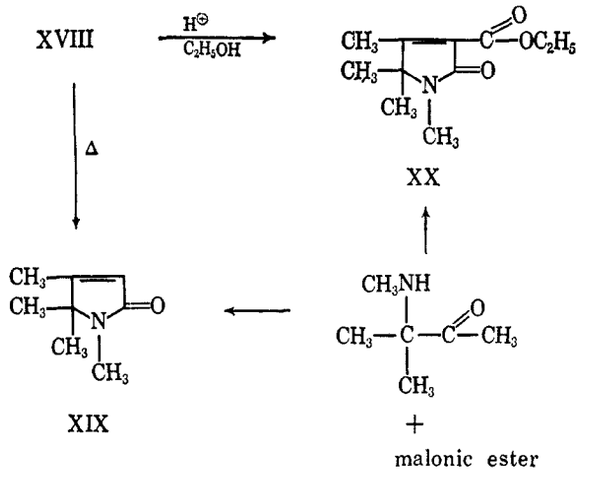
no proton α to the carboxy group, the facile elimination of water could not occur.

Since a method for making ketoamides from acetylenic amides had been devised[1,2] and the ketoamides have been found to be intermediates for the formation of 3-pyrrolin-2-ones, a general procedure was available for making a large number of substituted 3-pyrrolin-2-ones. Hydration of the acetylenic amides XXII with acid or metallic catalysts produced the ketoamides XXIII. Treatment of these intermediates with strong base (sodium ethoxide in ethanol) gave good yields of the 3-pyrrolin-2-ones XXIV (Scheme VI). The R^5 substituent could be a wide variety of groups, such as phenyl, phenoxy, phenylthio, and benzyl. A specific example of this method is given in the Experimental Section. The pharmacological testing results of a large number of these compounds and their intermediates will be reported elsewhere.

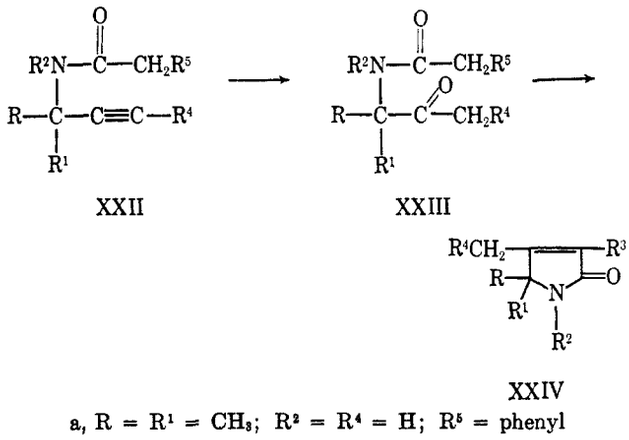
Since there are two available methylene groups, cyclization of a ketoamide of type XXVI could give a five- or six-membered ring product. A study of this reaction was undertaken. Treatment of XXVI with sodium ethoxide followed by acidification gave the five-membered ring XXVII (Scheme VII); again facile hydrolysis took place.

Although it was questionable that an analysis of the nmr spectrum of the product could differentiate XXVII from XXVIII, the difference in acidity of an acetic acid XXVII and an acrylic acid XXVIII should be helpful in the product assignment. pK_a' values (de-

SCHEME V



SCHEME VI



a, R = R^1 = CH_3; R^2 = R^4 = H; R^5 = phenyl

termined in 66% DMF) of acrylic acid and a related compound, XVIII, were found to be 6.65 and 6.50, respectively. The pK_a' of the product in question was 6.98 which was close to the value of 7.00 for acetic acid measured in 66% DMF. On this basis structure XXVII was favored over XXVIII.

Experimental Section[5]

3,4,4-Trimethyl-5-methylene-2-carbethoxymethyleneoxazolidine (VIIa).—A solution of 194 g (2.0 moles) of N,1,1-trimethyl-2-propynylamine Va and 420 g (2.6 moles) of diethyl malonate was heated at 200° for 16 hr in an autoclave. The reaction mixture was distilled and the fraction boiling at 124° (0.1 mm) was collected, giving 302 g (73.5%) of clear oil, $n^{25}D$ 1.5229 (see Table I).

Other 2-propynylamines and malonic esters were allowed to react as described above and the results are reported in Table I.

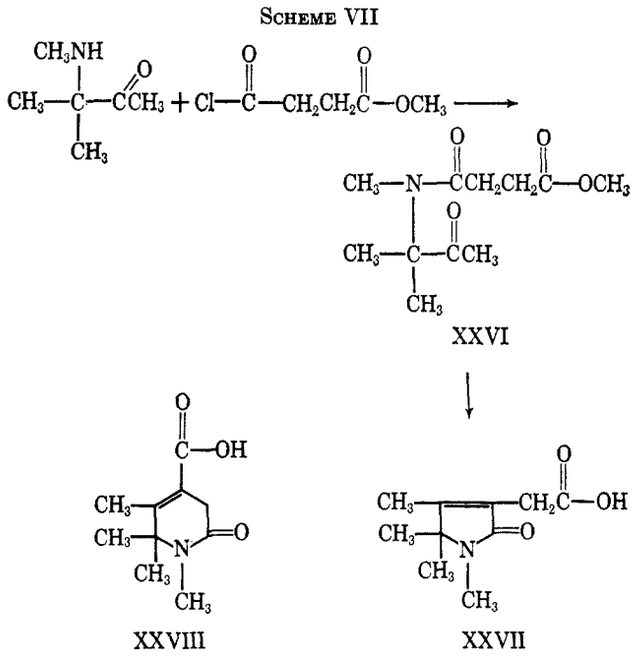
3,4,4,5-Tetramethyl-2-carbethoxymethyleneoxazolidine (VIII).—An ethanolic solution of 37 g (0.175 mole) of VIIa was shaken with a pressure of 40 psi of hydrogen using palladium on carbon as catalyst until 1 mole equiv of hydrogen was taken up. The catalyst was filtered and the filtrate distilled. The fraction boiling at 136° (0.12 mm) was collected giving 33 g (88%) of VIII.

Anal. Calcd for $C_{11}H_{19}NO_3$: C, 61.94; H, 8.98. Found: C, 61.70; H, 9.10.

Reduction of VIII with Lithium Aluminum Hydride.—A solution of 16 g (0.075 mole) of VIII in 50 ml of ether was added dropwise to 500 ml of ether containing 15.2 g (0.4 mole) of lithium aluminum hydride and the resulting mixture was stirred for 16 hr. After decomposing the reaction mixture with dilute sodium hydroxide solution, the ether solution was separated and dried. Distillation yielded 5 g (57%) of **3-methyl-3-methylamino-2-butanol (IX)** boiling at 41–42° (4 mm). The infrared spectrum of this product was identical with that of an authenic sample.[4]

(5) All melting points were taken in open capillary tubes.

SCHEME VII



3,4,4,5-Tetramethyl-2-carbethoxymethyloxazolidine (X).—An ethanolic solution of 52.25 g (0.25 mole) of VIIa was hydrogenated for 16 hr using palladium on carbon as catalyst with a pressure of 40 psi of hydrogen. The catalyst was filtered and the filtrate distilled. A fraction was collected at 90–96° (4 mm) (24 g) and a higher boiling material was obtained at 136–137° (0.1 mm) (10 g), unidentified (probably VIII). The lower boiling fraction was redistilled and the product collected at 95–96° (4 mm) (20 g).

Anal. Calcd for $C_{11}H_{21}NO_3$: C, 61.36; H, 9.83; N, 6.51. Found: C, 61.14; H, 9.85; H, 6.34.

Reaction of X with Lithium Aluminum Hydride.—An ethereal solution of 20 g (0.093 mole) of X was added dropwise to 500 ml of ether containing 11.4 g (0.3 mole) of lithium aluminum hydride at 0° and the mixture stirred at 0° for 2 hr. After decomposing with dilute base, the ether solution was separated, dried, and distilled, giving 10 g (62%) of **N,3-dimethyl-3-(3-hydroxypropylamino)-2-butanol (XI)** boiling at 126–127° (4 mm).

Anal. Calcd for $C_9H_{21}NO_2$: C, 61.67; H, 12.08. Found: C, 61.87; H, 12.37.

An authenic sample of XI was prepared by reducing N,3-dimethyl-3-(3-hydroxypropylamino)-2-butanone XII with sodium borohydride in methanol. The two products were identical in all respects.

α-Carbethoxy-N-(1,1-dimethyl-2-propynyl)acetamide (VIc).—A solution of 83 g (1.0 mole) of 1,1-dimethyl-2-propynylamine and 208 g (1.3 moles) of diethyl malonate was heated at 120° for 16 hr in an autoclave. The reaction mixture was distilled and 72 g (37%) of VIc was collected at 110–115° (5 mm). The distillate solidified and after recrystallizing from ether–petroleum ether (low boiling, bp 35–60°) the material melted at 59–61°.

Anal. Calcd for $C_{10}H_{15}NO_3$: C, 60.89; H, 7.66. Found: C, 61.08; H, 7.66.

1,4,5,5-Tetramethyl-3-carboxy-3-pyrrolin-2-one (XIII).—Concentrated hydrochloric acid, 25 g, was added to a solution of 53 g (0.25 mole) of VIIa in 250 ml of ethyl acetate. After concentration at reduced pressure to remove the ethyl acetate, 200 ml of water was added and the aqueous solution was made basic with excess 20% sodium hydroxide. No material was extractable with chloroform. Upon acidification with hydrochloric acid, a chloroform extraction yielded a material that was recrystallized from benzene. Thirty-four grams (74%) of XIII, mp 165–167°, was thus obtained.

Anal. Calcd for $C_9H_{13}NO_3$: C, 59.00; H, 7.15. Found: C, 59.30; H, 7.42.

In a similar manner, 25 g of 3,4-dimethyl-4-ethyl-5-methylene-2-carbethoxymethylene-oxazolidine was converted to 12 g (55%)

of **1,4,5-trimethyl-5-ethyl-3-carboxy-3-pyrrolin-2-one**, melting at 106–108°, after crystallizing from ethylcyclohexane.

Anal. Calcd for $C_{10}H_{15}NO_3$: C, 60.89; H, 7.66. Found: C, 61.05; H, 7.90.

1,4,5,5-Tetramethyl-3-pyrrolin-2-one (XIX).—Sixty grams (0.33 mole) of XIII was heated at 200° for 90 min and the resulting liquid on distillation was collected at 92–93° (4 mm), $n^{25}D$ 1.4852, giving 35 g (76%) of XIX.

Anal. Calcd for $C_8H_{13}NO$: C, 69.03; H, 9.41. Found: C, 69.13; H, 9.29.

1,4,5,5-Tetramethyl-3-carbethoxy-3-pyrrolin-2-one (XX).—Concentrated sulfuric acid, 20 g, was added to an ethanolic solution of 34 g (0.186 mole) of XIII; the reaction mixture was refluxed for 3 hr and was concentrated to approximately 100 ml at reduced pressure. After diluting with water, a chloroform extraction yielded on distillation 25 g (61%) of XX boiling at 111° (0.06 mm).

Anal. Calcd for $C_{11}H_{17}NO_3$: C, 62.54; H, 8.11. Found: C, 62.17; H, 8.15.

Reaction of 3-Methyl-3-methylamino-2-butanone with Diethyl Malonate.—A solution of 0.3 mole of 3-methyl-3-methylamino-2-butanone and 0.4 mole of diethyl malonate was heated in an autoclave at 200° for 16 hr. Distillation of the reaction product gave 18.5 g (44%) of XIX and 12.5 g (20%) of XX.

4,5,5-Trimethyl-3-carboxy-3-pyrrolin-2-one. A. Acid Catalysis.—Twenty grams of VIc was converted by the procedure described for XIII to 4,5,5-trimethyl-3-carboxy-3-pyrrolin-2-one, which melted at 204–206° after recrystallizing from benzene. Two grams (11%) of product were obtained.

Anal. Calcd for $C_8H_{11}NO_3$: C, 56.79; H, 6.55. Found: C, 56.93; H, 6.66.

B. Metal Catalysis.—Two grams of silver nitrate dissolved in 10 ml of water was added to a solution of 19.7 g (0.1 mole) of VIc in 300 ml of ethanol and the mixture heated at reflux temperature for 1 hr. After cooling, 100 ml of saturated sodium chloride solution was added and the mixture, after adding 500 ml of water, was extracted with chloroform. The chloroform solution was dried and the solvent removed at reduced pressure. The residue was added to 300 ml of ethanol in which previously 5 g of sodium had reacted and the mixture refluxed 1 hr. After cooling, the reaction mixture was made acidic with dilute hydrochloric acid and was extracted with chloroform. After drying, the chloroform was removed and the residue crystallized from benzene, giving 10 g (59%) of product which was identical with that prepared by method A.

α-Carbethoxy-N-methyl-N-(1,1-dimethyl-2-propynyl)butyramide (XVb).—Excess anhydrous hydrogen chloride was added to a solution of 25 g (0.105 mole) of VIIb in 250 ml of methyl ethyl ketone; the solvent and excess hydrogen chloride were removed at reduced pressure. The residue was dissolved in water and made basic with excess sodium hydroxide solution. The mixture was extracted with chloroform, the chloroform solution dried over magnesium sulfate and filtered, and solvent removed at reduced pressure. Distillation of the residue gave 17.5 g (67%) of product boiling at 110–113° (0.05 mm).

Anal. Calcd for $C_{13}H_{23}NO_4$: C, 60.68; H, 9.01. Found: C 61.00; H, 8.97.

1,4,4,5-Tetramethyl-3-ethyl-3-pyrrolin-2-one (XXI).—An ethanolic solution of 0.27 mole of XVb and sodium ethoxide prepared from 0.6 mole of sodium was refluxed 2 hr. After dilution with water, the reaction mixture was extracted with chloroform and the chloroform solution dried. On distillation, 20 g (44.5%) of product which boiled at 96° (4 mm) was obtained.

Anal. Calcd for $C_{10}H_{17}NO$: C, 71.81; H, 10.25. Found: C, 71.53; H, 10.17.

Hydrolysis of VIIa with Sodium Hydroxide Solution.—A solution of 30 g of sodium hydroxide in 150 ml of water was added to 21 g (0.1 mole) of VIIa in 100 ml of ethanol and the mixture heated at reflux for 16 hr. Most of the ethanol was removed at reduced pressure and the concentrate was made acidic with excess hydrochloric acid. Extraction with chloroform gave after recrystallization from benzene 10 g (55%) of product, mp 165–167°, identical with XVIII.

Anal. Calcd for $C_9H_{13}NO_3$: C, 59.00; H, 7.15. Found: C, 59.16; H, 7.36.

Using the same reaction conditions as above, 0.146 mole of 3,4,4-trimethyl-5-methylene-2-(1-carbethoxypropylidene)oxazolidine VIIb was converted to **1,4,5,5-tetramethyl-3-ethyl-5-hydroxy-3,carboxy-2-pyrrolidone (XVIIb)**, giving 10 g (30%), mp 142–144°, of product.

Anal. Calcd for $C_{11}H_{19}NO_4$: C, 57.62; H, 8.35. Found: C, 57.90; H, 8.36.

α-Phenyl-N-(1,1-dimethyl-2-propynyl)acetamide (XXIIa).—Phenylacetyl chloride (0.5 mole) was added dropwise to a solution of 0.5 mole of 1,1-dimethyl-2-propynylamine and 1.0 mole of triethylamine in 1000 ml of chloroform and the reaction mixture stirred overnight at room temperature. After washing with water and removing the chloroform at reduced pressure, the crude product was recrystallized from benzene to give 61 g (60%) of XXIIa melting at 135–137°.

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51. Found: C, 77.73; H, 7.62.

3-(α-Phenylacetamido)-3-methyl-2-butanone (XXIIIa).—To an ethanolic solution (200 ml) of 0.1 mole of XXIIa there was added 3 g of silver nitrate dissolved in 20 ml of water and the resulting mixture heated at reflux temperature for 0.5 hr. After cooling 200 ml of saturated sodium chloride solution was added, the mixture was stirred 0.5 hr, diluted with water, and extracted with chloroform. After drying and filtering, the chloroform was removed at reduced pressure and the residue crystallized from benzene–ether, giving 16 g (73%) of XXIIIa which melted at 128–130°.

Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.20; H, 7.82. Found: C, 71.04; H, 7.83.

4,5,5-Trimethyl-3-phenyl-3-pyrrolin-2-one (XXIVa).—A solution of 0.073 mole of XXIIIa and sodium ethoxide, from 5 g of sodium, was heated at reflux temperature for 2 hr, diluted with water, and extracted with chloroform. After removing the chloroform, the residue was crystallized from benzene. The product XXIVa melted at 179–181° and a 68% yield was obtained.

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51. Found: C, 77.69; H, 7.73.

3-Methoxycarbonyl-N-methyl-N-(1,1-dimethylacetonyl)propionamide (XXVI).—Using the procedure described for XXIIa, 0.2 mole of 3-methyl-3-methylamino-2-butanone was treated with 0.2 mole of β-carbethoxypropionyl chloride and distillation of the crude product gave 29 g (69%) of XXVI boiling at 125–127° (0.05 mm).

Anal. Calcd for $C_{11}H_{19}NO_4$: C, 57.62; H, 8.35. Found: C, 57.65; H, 7.94.

Reaction of XXVI with Sodium Ethoxide.—Sodium ethoxide (from 0.2 mole of sodium) and 0.1 mole of XXVI in ethanol was heated at reflux for 2 hr. The reaction mixture was diluted with water and made acidic with excess hydrochloric acid. Extraction of this mixture with chloroform gave **3-carboxymethyl-1,4,5,5-tetramethyl-3-pyrrolin-2-one (XXVII)**. The product was purified by crystallization from benzene to give 9 g (46%) of white crystalline material melting at 122–124°.

Anal. Calcd for $C_{10}H_{15}NO_3$: C, 60.89; H, 7.67. Found: C, 60.94; H, 7.85.

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