purified by recrystallization from dimethyl sulfoxide and dried for 16 hr. at 100° (0.03 mm., mercury–phosphorus pentoxide).

Anal. Calcd. for $C_{12}H_{26}Br_6N_4$: C, 20.42; H, 3.71; Br, 67.93; N, 7.94. Found: C, 20.60; H, 3.79; Br, 67.89; N, 7.71.

Upon addition of water the tetrabromoethane is liberated. Hence the filter cake from above was dissolved in water and extracted with more pentane. The bulk of the pentane was carefully stripped from the combined filtrate and washings. The residue was analyzed quantitatively by gas chromatography. The compounds were identified by comparing their n.m.r. and infrared spectra with those of authentic materials.

Reaction of 1 with 1,1,1,4,4,4-Hexafluorotetrachlorobutane.—A mixture of 70 ml. of heptane, 2.55 g. (0.084 mole) of hexafluorotetrachlorobutane, and 1.7 g. (0.085 mole) of **1** was allowed to stand for 17 hr. at room temperature in a stoppered 125-ml. erlenmeyer flask. The mixture was then filtered in the closed system described above. The filtrate was analyzed by gas chromatography. 1,1,1,4,4,4-Hexafluorodichlorobutene-2 was identified by comparison of its infrared spectrum and gas chromatographic retention time with those of an authentic sample.

Reaction of 1 with 1,1,1-Trifluoropentachloropropane, Hexachloroethane, Carbon Tetrachloride, and Bromotrichloromethane.—Except for differences shown in Table I and others indicated below, the reactions of **1** with the above halocarbons are analogous to the reaction of **1** with 1,1,1,4,4,4-hexafluorotetrachlorobutane. Where necessary for identification purposes, the products were trapped for infrared spectral analysis. Reaction 6 required 4.8 g. of **1** and 90 ml. of carbon tetrachloride. Reactions 7–9 were quite exothermic. Therefore, a solution of one reactant was added dropwise into the stirred solution of the other, which was chilled with an ice–water bath. In reaction 7, 5.0 g. of bromotrichloromethane in 50 ml. of decane was added to 10.0 g. of **1** in 50 ml. of decane. In reaction 8 the addition order was reversed. Reaction 9 was carried out in the same way as 8 except for the substitution of cyclohexene for decane.

Reaction of 1 with Perfluoroheptyl Iodide.—A mixture of 6.7 g. of perfluoroheptyl iodide, 2.8 g. of **1**, and 50 ml. of heptane was allowed to stand at room temperature for 3 days before being filtered in the closed system. The filter cake was resuspended in about 25 ml. of heptane and refiltered. The combined filtrates (55.1 g.) were analyzed by gas chromatography on column C at 80°. The main product was 1-hydroperfluoroheptane, which was identified by its proton n.m.r. spectrum and by comparison of its infrared spectrum with that of the known material.[6] The other major product was an unidentified liquid, C_7F_{14}. Its infrared spectrum is very different from that of perfluoroheptene-1[7] and does not have absorption in the carbon–carbon double-bond region. A mass spectrographic analysis indicated a weak parent peak at mass 350. The material was isolated from the filtrate as follows. The original filtrate was partially distilled. All of the fluorocarbons distilled off first as azeotropes with heptane at 85–93° at atmospheric pressure. The two-phase distillate was fed through column B at 142° to remove the heptane and then through column C at 80° to separate $C_7F_{15}H$ from C_7F_{14}.

Anal. Calcd. for C_7H_{14}[8]: C, 24.02; H, 0.00; F, 75.98. Found: C, 23.79; H, 0.00; F, 76.01.

Several other minor peaks were evident by gas chromatography but were not investigated.

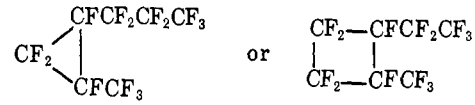
Relative Reactivities of Various Halocarbons toward 1.—About 5 g. of polytetrafluoroethylene with a high surface area[9] was placed in a large test tube and covered with **1**. The tube was sealed and heated at 200° for 1 hr. The mixture was removed and filtered. A portion of the filtrate was subjected to sodium fusion followed by the zirconium–alizarin test for fluoride ion. The test was negative. A water extract of the polytetrafluoroethylene also gave a negative fluoride test. About 1 g. each of the following was added to a solution of 1 ml. of **1** in 20 ml. of heptane: iodoform reacted immediately as evidenced by the formation of a voluminous, yellow precipitate; methylene iodide reacted rapidly but noticeably less rapidly than iodoform; methyl iodide reacted rather slowly but began to form a precipitate within a few minutes; chloroform reacted very slowly (the orange solution was stable in the absence of air for a long period of time, and after several days only a trace of precipitate was noticed); methylene chloride formed a yellow solution with **1** which was indefinitely stable in the absence of air. In the above experiments the products were not worked up except for the precipitate, which in each case was shown to contain **2**.

Acknowledgment.—The author is gratefully indebted to Mr. E. M. Bens, Dr. W. H. Urry, and Dr. Ronald A. Henry for their stimulating suggestions and to Mr. D. W. Moore for determining and interpreting n.m.r. spectra.

(6) J. H. Simons, "Fluorine Chemistry," Vol. 5, Academic Press Inc., New York, N. Y., 1954, p. 473.

(7) See ref. 6, p. 478.

(8) The n.m.r. spectrum of this material is complicated but gives an indication of two nonequivalent CF_3 groups, three nonequivalent CF_2 groups, and two nonequivalent CF groups. All of the data considered together indicate a possible cyclic structure, *e.g.*, as shown.



(9) Teflon-6 molding powder, E. I. du Pont de Nemours and Co., R. R. No. 1, Washington 1, W. Va.

Acetylenic Amines. XII. Some New Reactions of Acylaminoacetylenes

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A method for the conversion of secondary 3-alkyl-2-propynylamines to ketones is reported which consists of treating their N-acyl derivative with dry hydrogen chloride followed by hydrolysis. Treatment of the amides of 1,1-dialkyl-2-propynylamines with silver nitrate under various conditions was investigated also. The products were the ketoamide IX and/or the oxazoline X, and the amount of each was dependent upon the substituents on the propynylamines as well as the solvent employed.

It was reported[1] recently that attempts to hydrate N,N,1,1-tetramethyl-2-butynylamine by the usual procedure (mercuric sulfate, sulfuric acid) gave mesityl oxide instead of the desired 2-dimethylamino-2-methyl-3-pentanone. Since hydration[2] of N,N-diethyl-1,1-dimethyl-2-propynylamine gave the expected 3-diethylamino-3-methyl-2-butanone, the results observed by Kruse and Kleinschmidt[1] must be due to the effect of the terminal methyl group on the neighboring acetylenic function and not to the amine character.

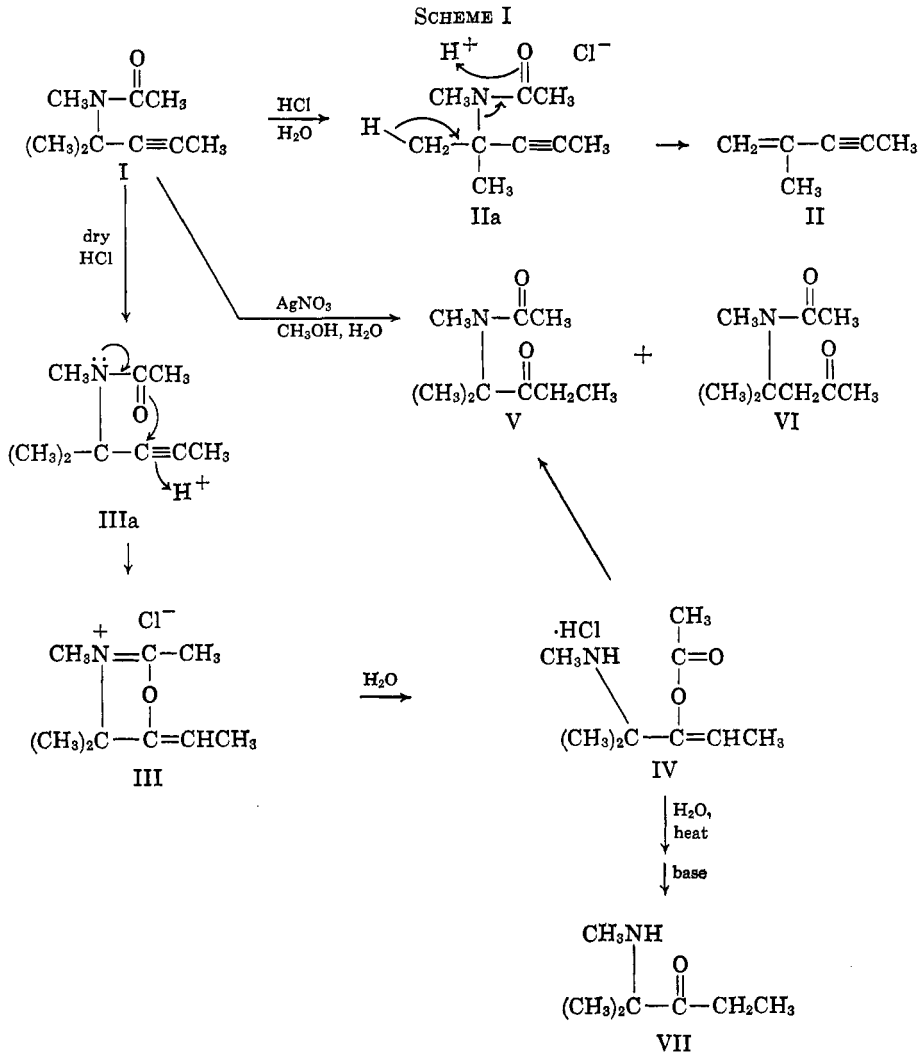
Because the hydration of 2-propynylamines *via* the amido derivatives has been shown[3] to involve a novel

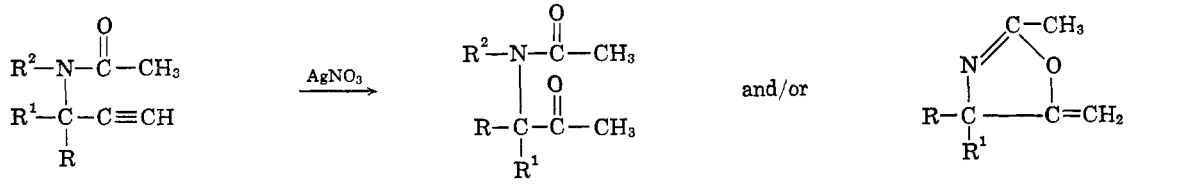
(1) C. W. Kruse and R. F. Kleinschmidt, *J. Am. Chem. Soc.*, **83**, 216 (1961).

(2) J. D. Rose and B. C. L. Weedon, *J. Chem. Soc.*, 782 (1949).

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

SCHEME I





VIIIa, R, R^1, R^2 = CH_3
b, R = CH_3; R^1 = $(CH_3)_2CH$; R^2 = H
c, R, R^1 = $-(CH_2)_5-$; R^2 = H

IXa, R, R^1, R^2 = CH_3
b, R = CH_3; R^1 = $(CH_3)_2CH$; R^2 = H
c, R, R^1 = $-(CH_2)_5-$; R^2 = H

Xb, R = CH_3; R^1 = $(CH_3)_2CH$
c, R, R^1 = $-(CH_2)_5-$

neighboring-group participation, it was of interest to investigate this method for hydrating 3-alkyl-2-propynylamines.

The compound, N-acetyl-N,1,1-trimethyl-2-butynylamine (I), was chosen for this investigation since it can be prepared readily by the acetylation of N,1,1-trimethyl-2-butynylamine which is available from the methylation of N,1,1-trimethyl-2-propynylamine.

Treatment of the amide I with dilute hydrochloric acid on the steam bath gave an oily, insoluble layer, which was isolated in 73% yield and was identified as 2-methyl-1-penten-3-yne[1] (II, see Scheme I). An infrared spectrum of the residue from concentration of the aqueous layer indicated the presence of 2-acetamido-N,2-dimethyl-3-pentanone (V). The N,1,1-trimethyl-2-butynylamine was recovered unchanged when it was treated in the same manner.

Treatment of an ether solution of the amide I with dry hydrogen chloride[3] gave a precipitate. The n.m.r. spectrum of this material showed a quartet (1H) centered at 305 c.p.s. (J = 7 c.p.s.) and unsplit signals at 217 (3H) and 177 c.p.s. (3H). This was in addition to two signals of different intensity in the C-methyl region (9H). Since this spectrum is closely related to that seen for the oxazolinium salts,[3] this material was assigned the structure III (5-ethylidene-2,3,4,4-tetramethyl-2-oxazolinium chloride). The infrared spectrum (bands at 5.88 and 6.00 μ) also supports this assignment. III could be readily converted to the enol acetate IV and thence to either the ketoamide V, by treating with base, or to the amino ketone VII by acid hydrolysis followed by neutralization. The amino ketone VII could be isolated in an 80% yield based on the starting amide.

The products obtained under the different reaction conditions can be explained by considering two possible mechanisms. Protonation of I on the oxygen could be followed or accompanied by the formal electron shifts

shown in IIa which would cause a cleavage of the N–C bond and give II. Protonation at the acetylenic group either followed or accompanied by the electron shifts shown in IIIa would give III.

It was then of interest to explore the possibilities of extending this reaction to the amides of primary 2-propynylamines. It was found that the N-acyl derivative of 1,1-dimethyl-2-propynylamine was not soluble in dilute hydrochloric acid nor did it react with dry hydrogen chloride in ether. However, this amide was soluble in concentrated hydrochloric acid and, after heating the solution, the presence of 3-amino-3-methyl-2-butanone was detected in the infrared spectrum of the dry reaction mixture. This did not appear to be a very practical method and it was not investigated further.

The treatment of N-acetyl-N,1,1-trimethyl-2-propynylamine (VIIIa) with an aqueous ethanolic solution of silver nitrate has been shown[4] to give a product presumed to be 3-acetamido-3-methyl-2-butanone. Examination of this product showed that this presumption was correct and further study indicated that this is a general method for hydration of these amides. This reaction proceeds smoothly and rapidly and gives good yields; it is particularly useful in the hydration of the acyl derivatives of the primary acetylenic amines which, as mentioned above, do not hydrate readily when treated with acid.

When the homologous compound VIIIb (R = CH_3; R^1 = $(CH_3)_2CH$; R^2 = H) was treated with silver nitrate, using aqueous methanol as the solvent, two products were produced. The higher boiling material was the expected ketoamide IXb. The n.m.r. spectrum of the lower boiling material showed doublets centered at 280 (1H), and 245 c.p.s. (1H), unsplit signals at 124 (3H) and 80 c.p.s. (3H), a multiplet between 80 and 124 c.p.s. (1H), and a pseudo-triplet[5] centered at 51 c.p.s. (6H). This spectrum indicates that the material is the oxazoline Xb. This assignment was also supported by the infrared spectrum (bands at 5.85 and 5.94 μ). The presence of the oxazoline in the reaction mixture indicated that the oxazoline could be an intermediate in the reaction. This interpretation appeared logical since a similar compound had been found as the intermediate in the acid-catalyzed cyclization.[3] When VIIIc (R, R^1 = $-(CH_2)_5-$) was treated with silver nitrate using anhydrous dimethylformamide as the solvent, the oxazoline Xc was formed, whereas use of aqueous methanol as the solvent produced only the ketoamide IXc. It would, therefore, appear that the oxazoline was the intermediate; the steric effect of the alkyl groups affected the amount of the oxazoline that was converted to the ketoamide when the reaction was run in a solution containing water. When no water was present, this second reaction could not proceed and only the oxazoline was produced.

When VIIIa, which has no hydrogen on the nitrogen, was treated with silver nitrate in anhydrous dimethylformamide and heated, only the starting material was isolated. However, as stated earlier, when VIIIa was treated with silver nitrate in the presence of water, hydration did take place and the ketoamide IXa was obtained. In this case, the N-acetyl group is still involved in a neighboring group effect to hydrate the triple bond, since treatment of N,1,1-trimethyl-2-propynylamine with silver nitrate using identical reaction conditions gave starting material and no hydration products. The reaction has been extended to a large variety of acetylenic amines (see Table II) and appears to be of considerable synthetic value.

Extension of this reaction to the nonterminal acetylene derivative I was of interest. When the reaction was run with silver nitrate in aqueous methanol, two products were isolated. One of these, about 30% of the mixture, was the ketoamide V. The n.m.r. spectrum of the other product showed unsplit signals at 85 (6H), 122 (6H), 178 (3H), and 196 c.p.s. (2H). This material was assigned the structure VI. Further proof of structure was obtained by the formation of N-methylacetamide and mesityl oxide on treatment of VI with aqueous acid.

The formation of VI from this reaction indicates that attack at the triple bond can occur at either carbon atom when the acetylene function is nonterminal.

Other metallic salts also catalyze this hydration; especially useful are the salts of copper, iron, and mercury.

Experimental

The 60-Mc. n.m.r. spectra were obtained on a Varian Associates Model HR-60 spectrometer in deuteriochloroform with tetramethylsilane as an internal standard. Melting points were taken in open capillary tubes.

N,1,1-Trimethyl-2-butynylamine.—To a solution of 1 mole of sodamide in 1.5 l. of liquid ammonia, there was added, dropwise with stirring, a solution of 1 mole of N,1,1-trimethyl-2-propynylamine in 100 ml. of anhydrous ethyl ether. After the addition had been completed, a solution of 1 mole of methyl iodide in 100 ml. of anhydrous ether was added dropwise and the liquid ammonia was replaced with ether over a 5-hr. period. After this time 1 l. of water was added, the layers were separated, and the organic layer was dried over magnesium sulfate and distilled. The N,1,1-trimethyl-2-butynylamine (61 g., 55%) had b.p. 129°, $n^{25}D$ 1.4389.

Anal. Calcd. for $C_7H_{13}N$: C, 75.62; H, 11.79. Found: C, 75.65; H, 11.76.

N-Ethyl-1,1-dimethyl-2-butynylamine had b.p. 89° (130 mm.).

Anal. Calcd. for $C_8H_{15}N$: C, 76.74; H, 12.06. Found: C, 77.00; H, 12.29.

Preparation of N-Acyl-2-propynylamines.—To a solution of 0.5 mole of the 2-propynylamine, 3–4 moles of triethylamine, and 200 ml. of chloroform, there was added slowly with stirring 0.55 mole of acyl chloride (excess acyl chloride was added to react with any alcohol present in the chloroform); the reaction mixture was kept below 35° with external cooling. Additional chloroform was added as necessary to maintain fluidity. After all of the acyl chloride had been added, some methanol was added (to decompose any excess acyl chloride) followed by water. The layers were separated, and the organic layer was dried over magnesium sulfate and concentrated at reduced pressure. The amides were isolated by distillation or by recrystallization. See Table I for physical constants and analytical data.

N-Acetyl-N,1,1-trimethyl-2-butynylamine (I) with Aqueous Hydrochloric Acid.—A mixture of 20 g. (0.13 mole) of the amide, 15 ml. of concentrated hydrochloric acid, and 30 ml. of water was heated gently with stirring. The mixture became cloudy and a mixture of water and 2-methyl-1-penten-3-yne distilled. The organic layer was dried over potassium carbonate (7.5 g., 73%). This material exploded on attempted analysis as had been reported for this compound. The infrared spectrum agreed with the published data[1] and the n.m.r. spectrum confirmed the structure assignment. Infrared analysis of the residue obtained by concentrating the aqueous layer showed that a small amount of the ketoamide was present.

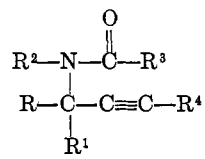
2-Methylamino-2-methyl-3-pentanone.—An excess of dry hydrogen chloride was bubbled into a mixture of 40 g. (0.26 mole) of N-acetyl-N,1,1-trimethyl-2-butynylamine in 500 ml. of

(4) Personal communication from Dr. William Hargrove (unpublished work).

(5) This triplet was apparently produced by overlapping of doublets of nonequivalent methyls of the isopropyl group.

TABLE I

AMIDES

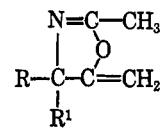


R	R¹	R²	R³	R⁴	B.p. (mm.) or m.p., °C.	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
CH_3	CH_3	CH_3	CH_3	CH_3	80–82 (5 mm.)	$C_9H_{15}NO$	[a]			
CH_3	CH_3	C_2H_5	CH_3	CH_3	92–94 (5 mm.)	$C_{10}H_{17}NO$	71.81	10.25	71.76	10.38
CH_3	$(CH_3)_2CH$	H	CH_3	H	89–91	$C_9H_{15}NO$	70.55	9.87	70.25	9.69
CH_3	C_6H_5	C_2H_5	H	H	146–148 (6 mm.)	$C_{13}H_{15}NO$	77.57	7.51	77.36	7.68
$(CH_3)_2CH$	$(CH_3)_2CH$	H	CH_3	H	98–100	$C_{11}H_{19}NO$	72.88	10.56	72.71	10.53
$-(CH_2)_5-$		H	CH_3	H	109–111	$C_{11}H_{17}NO$	73.70	9.56	73.87	9.35
CH_3	CH_3	CH_3	C_6H_5	H	38–40	$C_{13}H_{15}NO$	77.58	7.51	77.69	7.57

[a] Calcd.: N, 9.14. Found: N, 9.39.

TABLE II

OXAZOLINES

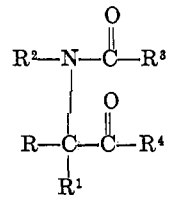


R	R¹	B.p., °C. (mm.)	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
CH_3	$(CH_3)_2CH$	92–93 (85 mm.)	$C_9H_{15}NO$	[a]			
CH_3	$(CH_3)_2CH$	174–176	$C_9H_{16}ClNO$[b]	56.98	8.50	57.06	8.80
C_2H_5	C_2H_5	98 (100 mm.)	$C_9H_{15}NO$	70.55	9.87	70.91	9.80
$(CH_3)_2CH$	$(CH_3)_2CH$	50–51 (4 mm.)	$C_{11}H_{19}NO$	72.88	10.56	72.64	10.71
$-(CH_2)_5-$		69 (4 mm.)	$C_{10}H_{15}NO$	72.69	9.15	72.60	9.03

[a] Converted to hydrochloride for analyses. [b] Hydrochloride.

TABLE III

KETOAMIDES



R	R¹	R²	R³	R⁴	B.p. (mm.) or m.p., °C.	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
H	$(CH_3)_2CH$	CH_3	CH_3	CH_3	89–91 (4 mm.)	$C_9H_{17}NO_2$	63.12	10.00	63.45	10.02
CH_3	CH_3	C_2H_5	CH_3	C_2H_5	122 (7 mm.)	$C_{10}H_{19}NO_2$	64.83	10.34	64.81	10.24
CH_3	$(CH_3)_2CH$	H	CH_3	CH_3	84–85	$C_9H_{17}NO_2$	63.12	10.00	63.33	10.1
CH_3	C_6H_5	C_2H_5	H	CH_3	170–172 (4 mm.)	$C_{13}H_{17}NO_2$	71.20	7.83	71.33	7.61
$-(CH_2)_5-$		H	CH_3	CH_3	133–135	$C_{10}H_{17}NO_2$	65.54	9.35	65.94	9.53
CH_3	CH_3	C_2H_5	CH_3	CH_3	139–141[a]	$C_9H_{18}ClNO_2$	52.04	8.74	52.32	8.75
CH_3	CH_3	CH_3	C_6H_5	CH_3	48–50	$C_{13}H_{17}NO_2$	71.20	7.82	71.53	8.08

[a] Hydrochloride.

ethyl acetate. The mixture was concentrated to dryness at reduced pressure and the residue was taken up in a solution of 200 ml. of water and 50 ml. of concentrated hydrochloric acid. The mixture was refluxed for 3 hr., cooled, and saturated with potassium carbonate. The organic layer was separated, dried over magnesium sulfate, and distilled. The yield was 27 g. (80%), b.p. 96–98° (70 mm.).

Anal. Calcd. for $C_7H_{15}NO$: C, 65.07; H, 11.70. Found: C, 64.89; H, 11.60.

Other solvents can be substituted for the ethyl acetate. Ether and ethanol have been used with equal success.

5-Ethylidene-2,3,4,4-tetramethyl-2-oxazolinium Chloride (III).—Excess anhydrous hydrogen chloride was bubbled into an ether-solution of 3 g. (0.02 mole) of N-acetyl-N,1,1-trimethyl-2-butynyl amine and the solvent and excess hydrogen chloride were removed at reduced pressure. The resulting white crystalline residue (3.6 g., 95% yield) melted at 184–186°. Any exposure of the product to the moisture of the air resulted in the addition of 1 mole equiv. of water to give the enol acetate IV, making recrystallization of the product very difficult.

Anal. Calcd. for $C_9H_{16}ClNO$: C, 56.98; H, 8.50. Found: C, 56.40; H, 8.45.

Treatment of N-Acetyl-N,1,1-trimethyl-2-butynylamine with Silver Nitrate.—To a well-stirred solution of 13 g. of the amide in 40 ml. of methanol there was added a solution of 4 g. of silver nitrate in 15 ml. of water. The mixture became warm and turned dark, and a silver mirror formed. When the temperature reached 70°, 20 ml. of methanol was added. After the mixture returned to room temperature, an excess of sodium chloride solution was added and the mixture was filtered. The filtrate was made basic and extracted with ether; the ether layer was dried over magnesium sulfate and concentrated. The residue was distilled and the portion boiling at 80–120° (10 mm.) was collected, 7.5 g. The n.m.r. spectra indicated a mixture of two parts of 4-acetamido-N,4-dimethyl-2-pentanone and one part of 2-acetamido-N,2-dimethyl-3-pentanone. Distillation through a spin-

ning-band column gave pure 4-acetamido-N,4-dimethyl-2-pentanone, b.p. 47° (4 mm.).

Anal. Calcd. for $C_9H_{17}NO_2$: C, 63.12; H, 10.00; N, 8.18. Found: C, 63.03; H, 10.24; N, 8.00.

Silver Nitrate Catalyzed Reaction. A. In Dimethylformamide.—To a well-stirred solution of 10 g. of the acetylenic amide in 30 ml. of dimethylformamide there was added a solution of 2 g. of silver nitrate in 3 ml. of dimethylformamide. The mixture became warm and, after it had returned to room temperature, it was poured with stirring into a mixture of ether, salt, ice, and water. The mixture was stirred vigorously and the layers were separated; the ether layer was dried, filtered, and concentrated. The oxazoline was then distilled. See Table II.

B. In Aqueous Methanol.—To a well-stirred solution of 10 g. of the acetylenic amide in 20 ml. of methanol there was added a solution of 2 g. of silver nitrate in 2–3 ml. of water. The temperature of the mixture usually rose to 50–60°. After the reaction mixture had returned to room temperature, a solution of sodium chloride was added followed by 100 ml. of chloroform. The mixture was filtered and the layers were separated. The organic layer was dried and concentrated. The product was purified either by distillation or by recrystallization. Mixtures were obtained in most cases where R and R^1 of VIII were larger than methyl. See Table III for the ketoamides and Table II for the oxazolines.

Use of Other Catalysts.—Silver nitrate, ferric chloride, and cupric acetate gave better than 90% conversions. The reactions were run in aqueous methanol as above and the residues from the concentration of the chloroform solution were analyzed by vapor phase chromatography. The yields of the products were not calculated, but the per cents of conversion were approximated.

Hydration Using Cupric Acetate as Catalyst.—To a stirred solution containing 15 g. of N-acetyl-N,1,1-trimethyl-2-propynylamine, 50 ml. of methanol, and 15 ml. of water was added a slurry of 2.0 g. of cupric acetate in 5 ml. of water. The temperature at the time of addition of the catalyst was 20°. After 5 min. the temperature had risen to a maximum of 60° and after 20 min. was 25°. At this time a mixture of 10 g. of NaOH in 50 ml. of cold water and 200 ml. of ether was added. The layers were separated and the organic layer was dried over $MgSO_4$; the per cent of ketoamide was determined by v.p.c. (100% conversion). Distillation of the product yielded 11.0 g. (66%) of the ketoamide IXa.

Acknowledgment.—The microanalyses were performed by Messrs. William Brown, Howard Hunter, George Maciak, and Alfred Brown. Many of the starting materials were prepared by Dr. Dwight Morrison and Mr. Lawrence White. The infrared spectra were obtained by Mrs. Doris Stephens and Miss Martha Hofmann and the n.m.r. spectra by Mr. John Klemmn. The authors wish to thank especially Dr. Harold Boaz and Messrs. Paul Landis and Donald Woolf, Jr., for their invaluable services in interpreting and compiling the infrared and n.m.r. data.

Potential Antiradiation Agents.[1] Preparation and Polymerization of S-Vinyl-N-vinylthiocarbamates[2,3]

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Three S-vinyl-N-vinylthiocarbamates (IV) have been prepared by dehydrochlorination of the respective S-2-chloroethyl-N-2-chloroethylalkylthiocarbamates (III). The monomers were polymerized under a variety of conditions in an attempt to prepare linear, high molecular weight polymers containing a predominant amount of the tetrahydro-1,3-thiazin-2-one moiety along the backbone of the polymer chain. Free-radical-initiated polymerization was found to favor the formation of poly-S-vinyl recurring units, while cationic initiation favored the formation of repeating poly-N-vinyl units. Cyclopolymerization was favored by high dilution and decreasing size of the alkyl substituent. Attempts to isolate polymeric α-amino γ-thiols (VIII) formed on hydrolysis of the resultant "terpolymers" (VII) proved unsuccessful.

The investigation of various compounds as protective agents against ionizing radiation has been considerable since the discovery by Patt,[6] *et al.*, in 1950 that mice could be protected by cysteine from otherwise lethal doses of radiation by X-rays. The most promising agents to date appear to be 2-aminoethanethiol and 2-aminopropanethiol and several of the S-substituted derivatives.[7,8] None of the radiobiological protectants now known, however, satisfy the criterion of being highly active over a period of long duration. We have therefore undertaken the preparation of compounds with possible latent effects,[9] *i.e.*, low activity and toxicity during transport of the drugs to the tissues where the formation of more active agents may take place, as well as polymeric analogs of 2-mercaptoethylamine[10] and 3-mercaptopropylamine (reported herein). In the case of the latter two, the assumption is made that their relatively high molecular weights would make of them long-lasting radioprotective agents.

It has recently been established that nonconjugated di- and triolefinic monomers can be polymerized to yield linear, high molecular weight polymers containing carbocyclic rings along the backbone of the polymer chain.[11] The method of cyclopolymerization has, in fact, been recently employed in this laboratory to prepare polymers with recurring dithiolcarbonate[12,13] and

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