had a peak at 2150 Å. with an intensity of absorption of E = 1.34 at a dilution of 1×10^{-5} in cyclohexane.

A 31-g. portion of N-cyclohexyl-2-butenylidenimine was reduced in a Parr hydrogenation apparatus at 50 p.s.i.g. at room temperature in ethanol with platinum as catalyst. The mass and infrared spectra of the crude reduction product were compared to the corresponding spectrum of an authentic sample of N,N-diethylcyclohexylamine. No diethylcyclohexylamine,[3] b.p. 98° (31 mm.), n^{20}D 1.4532, was obtained. The phenylthiourea derivative, m.p. 102–103°, was prepared and its melting point was not depressed when mixed with an authentic sample of the phenylthiourea derivative of N-*n*-butylcyclohexylamine (see below).

Bicyclohexyl was used as a chaser in the distillation. A small amount of an unknown amine distilled at the end of the bicyclohexyl cuts. Its thiourea derivative, m.p. 107–109°, was prepared.

Anal. C, 68.6; H, 8.8; N, 8.5.

A portion of a reaction product, prepared as before from cyclohexylamine and acetylene over cadmium and zinc acetates at 140°, was flash distilled, and all material which distilled below 78° (0.3 mm.) was hydrogenated over platinum in ethanol as solvent. n-Heptane and cetane were added before distillation to facilitate a separation of products. By ultraviolet analysis, 0.14 ml. (1.6 mmoles) of benzene was found to be present in the cuts boiling below 45° (8 mm.). A portion of the highest boiling material taken overhead, b.p. 73–99° (0.7 mm.), crystallized. The crystals, m.p. 105–106°, were shown by infrared analysis to be an amide and were positively identified as N-cyclohexylacetamide by a mixed m.p. with an authentic sample. The yield, 2.6 g., corresponded to 50% of theory based upon the moles of acetate catalyst used.

N-*n*-Butylcyclohexylamine was prepared by a modification of the procedure described by Campbell, *et al.*,[6] for its preparation from butyraldehyde and cyclohexylamine. The modified procedure employed *n*-butylamine and cyclohexanone. The phenylthiourea derivative, m.p.103–104°, was prepared from a portion of the amine, b.p. 113° (29 mm.), n^{20}D 1.4530 (lit.[6] b.p. 87–90° [12 mm.], n^{20}D 1.4533).

Anal. Calcd. for $C_{17}H_{26}N_2S$: C, 70.3; H, 8.97. Found: C, 70.2; H, 8.8.

N-*n*-Hexylcyclohexylamine was also prepared by the procedure referred to above; cyclohexanone and *n*-hexylamine were used in this case.

Anal. Calcd. for $C_{12}H_{25}N$: C, 78.7; H, 13.6. Found: C, 78.7; H, 13.6.

The phenylthiourea derivative, m.p. 91–91.5°, was prepared from a fractionally distilled portion of the amine, b.p. 66° (0.6 mm.), n^{20}D 1.4560.

Anal. Calcd. for $C_{19}H_{30}N_2S$: C, 71.7; H, 9.52. Found: C, 71.6; H, 9.3.

Acknowledgment.—The authors are indebted to H. W. Rollmann for interpretation of mass spectral data, and to R. S. Silas and M. E. Smith for analyses of infrared spectra.

(6) K. N. Campbell, A. H. Sommers and B. K. Campbell, THIS JOURNAL, **66**, 82–84 (1944).

[CONTRIBUTION FROM RESEARCH DIVISION, PHILLIPS PETROLEUM CO., BARTLESVILLE, OKLA.]

N,N-Dialkyl-1,1-dimethyl-2-butynylamines by the Reaction of Propyne with Secondary Aliphatic Amines

BY C. W. KRUSE AND R. F. KLEINSCHMIDT

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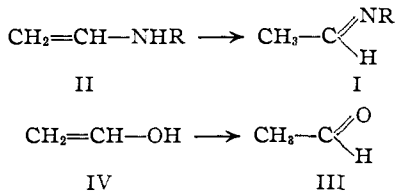
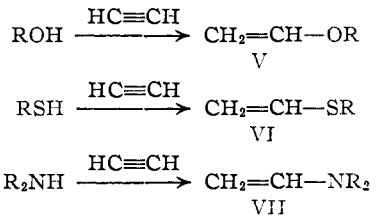
Propyne was allowed to react in a 2:1 molar ratio with secondary aliphatic amines in the presence of cadmium and zinc acetates to produce N,N-dialkyl-1,1-dimethyl-2-butynylamines (XI) in excellent yields. The structure was proved by an independent synthesis. 2-Methyl-1-penten-3-yne was obtained by pyrolysis of the amine oxide of XI. The normal hydrogenation of the triple bond was accompanied by hydrogenolysis of the tertiary carbon–nitrogen bond when ethanol was used as a solvent. Mesityl oxide was obtained by acid hydrolysis of XI.

Recent studies in our laboratories[1] have shown that N-alkylethylidenimines (I), not N-vinylamines (II), are produced by the cadmium acetate–zinc acetate-catalyzed reaction of acetylene with primary amines. An analogous reaction is observed when acetylene reacts with water in the presence of mercuric ion; acetaldehyde (III), not vinyl alcohol (IV), is obtained. It is reasonable, but not necessary, to assume that vinyl derivatives II and IV are intermediate products, and that tautomerization favors the imino form in the nitrogen system as it does the keto form in the oxygen compounds.



Tautomerization is possible, however, only when there is a hydrogen atom attached to the hetero atom. Vinyl ethers (V) and vinyl sulfides (VI) can be prepared readily from alcohols or mercaptans by Reppe's vinylation techniques.[2] By analogy, one would expect to obtain N-vinyldialkylamines (VII) in the same manner.



Reppe reported that although secondary amines absorbed acetylene in the presence of basic compounds (sodium or potassium hydroxides) or in the presence of cadmium salts and zinc salts, in most cases only unidentified, resin-like products were formed.[2] Although conditions were not found for a simple vinylation of secondary amines with acetylene, cuprous acetylide catalyzed a reaction in a 2:1 molar ratio to produce N,N-dialkyl-1-methyl-2-propynylamines (VIII) in 50 to 67% theoretical yields.[3]

(1) C. W. Kruse and R. F. Kleinschmidt, THIS JOURNAL, **83**, 213 (1961).

(2) W. Reppe and co-workers, *Liebig's Ann. Chem.*, **601**, 81 (1956).

$$R_2NH + HC{\equiv}CH \xrightarrow{Cu_2Cl_2} [R_2NCH{=}CH_2] \text{ (VII)} \xrightarrow{HC{\equiv}CH} CH_3CHC{\equiv}CH \quad (NR_2 = \text{VIII})$$

It appeared reasonable to assume that the initial reaction of acetylene with a secondary amine was the same in the presence of either the acetates or cuprous chloride, but that the acetates promoted further reactions at the terminal acetylenic group of VIII giving rise to non-distillable resins. The acetate catalyst was then used for reactions of propyne with secondary amines, because the products corresponding to VIII would not contain an acetylenic hydrogen atom capable of further reaction.

A colorless oil, b.p. 67.5° (60 mm.), was produced by a reaction of propyne with dimethylamine at 120° in the presence of a mixture of cadmium and zinc acetates. An elemental analysis corresponded to $C_6H_9N(CH_3)_2$ and the presence of an internal triple bond was confirmed by infrared spectral data. The yield, based upon the amount of amine charged, was 71.5%, and no non-distillable material was formed. The same amine was obtained when cuprous chloride was used as the catalyst in a yield of 40%. A non-distillable residue amounting to 22% by weight of the reactants was formed.

Diethylamine was also treated with propyne in the presence of cadmium and zinc acetates. An amine, b.p. 60° (9 mm.), whose elemental analysis corresponded to $C_6H_9N(C_2H_5)_2$, was obtained in 80% yield.

As shown in the equations below, an amine can add to the triple bond of propyne in two ways. It was assumed that the second acetylenic molecule became attached to IX or X at the carbon atom bearing the nitrogen to produce either XI or XII. Neither of these structures had been reported in the literature.

$$R_2NH + CH_3C{\equiv}CH$$

$$[CH_3C(=CH_2)NR_2] \text{ (IX)} \xrightarrow{CH_3C{\equiv}CH} CH_3CC(CH_3){\equiv}CCH_3 \quad (NR_2)$$

XIa, R = CH_3–
b, R = C_2H_5–

$$[CH_3CH{=}CHNR_2] \text{ (X)} \xrightarrow{CH_3C{\equiv}CH} CH_3CH_2CHC{\equiv}CCH_3 \quad (NR_2)$$

XII

The strongest peaks in the mass spectra of the N,N-dimethyl- and N,N-diethylacetylenic amines were 15 mass units lower than their respective molecular weights. This was indicative of the cleavage of a CH_3– group. It was unlikely that this CH_3– group was the one attached to the acetylenic carbon; a comparison of the mass spectra of several methylacetylenes with the spectra of the acetylenic amines in question showed that the tendency to undergo loss of CH_3– was much greater for the acetylenic amines than for any of the methylacetylenes. A study of the mass spectra of several tertiary amines with branched chains showed a strong tendency for cleavage to occur between the carbon atoms alpha–beta to the nitrogen atom. These considerations and the fact that the spectra of the new acetylenic amines also showed mass peaks corresponding to the loss of $CH_3C{\equiv}C$—groups favored structure XI.

An unanticipated hydrogenolysis reaction provided additional evidence for structure XI. 2-Methylpentane and 4-methyl-2-pentene were indicated by gas chromatography to be present in the products of the hydrogenation of the N,N-diethyl compound at room temperature in ethanol over platinum.

These indications were confirmed by an unequivocal synthesis of N,N,1,1-tetramethyl-2-butynylamine (XIa) and by conversion of XIa to methylisopropenylacetylene *via* pyrolysis of the amine oxide. N,N,1,1-Tetramethyl-2-propynylamine (XV) was prepared from 2-methyl-3-butyn-2-ol (XIII) by a method described in the literature.[4] The acetylenic hydrogen was then replaced by methylation of the sodium salt with methyl iodide in liquid ammonia. The authentic sample had the same physical properties as the acetylenic amine prepared in one step from propyne and dimethylamine, and infrared spectral comparisons showed the two to be identical. The amine oxide of XIa was prepared and pyrolyzed by the procedure of Cope.[5] The pyrolysis product was shown to contain methylisopropenylacetylene (XVI) by comparison of its infrared spectrum and its gas chromatogram with those of an authentic sample prepared from isopropenylacetylene.

$$CH_3CC(CH_3)(OH){\equiv}CH \text{ (XIII)} \xrightarrow[CaCl_2]{HCl} CH_3CC(CH_3)(Cl){\equiv}CH \text{ (XIV)} \xrightarrow[(CH_3)_2NH]{\text{aqueous}} CH_3CC(CH_3)[N(CH_3)_2]{\equiv}CH \text{ (XV)}$$

$$\text{XV} \xrightarrow[CH_3I]{NaNH_2,\ \text{liq. } NH_3} CH_3CC(CH_3)[N(CH_3)_2]{\equiv}CCH_3 \text{ (XIa)}$$

$$(CH_3)_2NH + 2CH_3C{\equiv}CH \xrightarrow[Zn(OAc)_2]{Cd(OAc)_2} \text{XIa}$$

$$\text{XIa} \xrightarrow{H_2O_2} \text{Amine oxide} \xrightarrow{\Delta} CH_2{=}CC(CH_3){\equiv}C{-}CH_3 \text{ (XVI)}$$

$$CH_2{=}CC(CH_3){\equiv}CH \xrightarrow[CH_3I]{NaNH_2,\ \text{liq. } NH_3} \text{XVI}$$

In a preliminary experiment, propyne was treated with di-*n*-butylamine in the presence of cadmium and zinc acetates until the amount of propyne consumed approximated 1:1 molar ratio. The crude reaction product could be hydrogenated only after

(3) W. Reppe and co-workers, *Liebig's Ann. Chem.*, **596**, 1 (1955); C. Gardner, V. Kerrigan, J. D. Rose and B. C. L. Weedon, *J. Chem. Soc.*, 780 (1949).

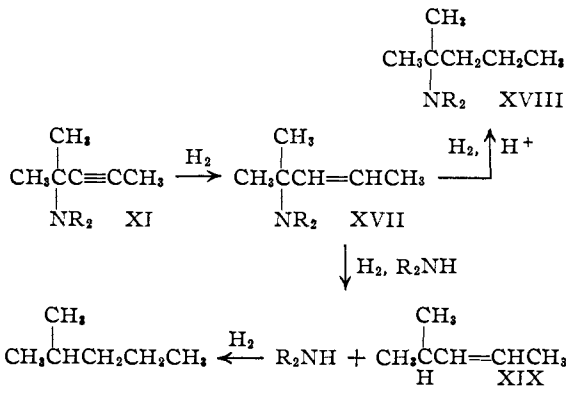
(4) G. F. Hennion, J. J. Sheehan and D. E. Maloney, THIS JOURNAL, **72**, 3542 (1950); G. F. Hennion and K. W. Nelson, *ibid.*, **79**, 2142 (1957).

(5) A. C. Cope, R. A. Pike and C. F. Spencer, *ibid.*, **75**, 3212 (1953).

precipitation of the cadmium and zinc salts as hydroxides. The reduced material was distilled; only a small amount of material boiling higher than di-*n*-butylamine was obtained. A satisfactory explanation was not forthcoming until it became evident from other experiments that, under the conditions employed, propyne reacts with secondary amines in a 2:1 molar ratio even with excess amine present and that the presence of excess secondary amine during the hydrogenation of the product XI favors hydrogenolysis to yield the original secondary amine and C_6-hydrocarbons.

In addition to 2-methylpentane, 4-methyl-2-pentene (XIX) was one of the C_6-hydrocarbons shown to be present in the products of the hydrogenation of XIa in ethanol as solvent. This same hydrogenation also produced a mixture of two C_8-amines believed to be N,N,1,1-tetramethyl-2-butenylamine (XVII, R = CH_3–) and N,N,1,1-tetramethylbutylamine (XVIII, R = CH_3–). Their parent peaks (mass spectrography) were 127 and 129 mass units and an infrared spectrum of the mixture indicated the presence of a double bond. The fact that all carbon–carbon double bonds were not reduced suggested that some component, possibly the secondary amine produced by the hydrogenolysis, was inhibiting the reduction of these bonds. Diethylamine was added to an ethanol solution of XIb before a micro-hydrogenation, and the rate was found to be slower than in ethanol alone (see Fig. 1). When the micro-hydrogenation was carried out in glacial acetic acid, the rate was very fast. The molar ratio of hydrogen to acetylenic amine was nearer to two, indicating less cleavage (see Fig. 1). This indication of less cleavage in acetic acid was substantiated by a reduction of a large quantity of XIa. The mass spectrogram indicated that the main product had a parent peak at 129 mass units, corresponding to the saturated C_8-amine (XVIII).

The reactions shown in the accompanying equations are now believed to occur during the hydrogenation of N,N-dialkyl-1,1-dimethyl-2-butynylamines, and the fate of XVII, whether to XVIII or to XIX, is influenced by the absence or presence of secondary amines. The effect of amines can be explained by assuming that the rate of reduction of carbon–carbon double bonds is retarded by secondary amines, but that the rate of hydrogenolysis of the allylamine structure XVII is independent of or at least not greatly lowered by secondary amines.



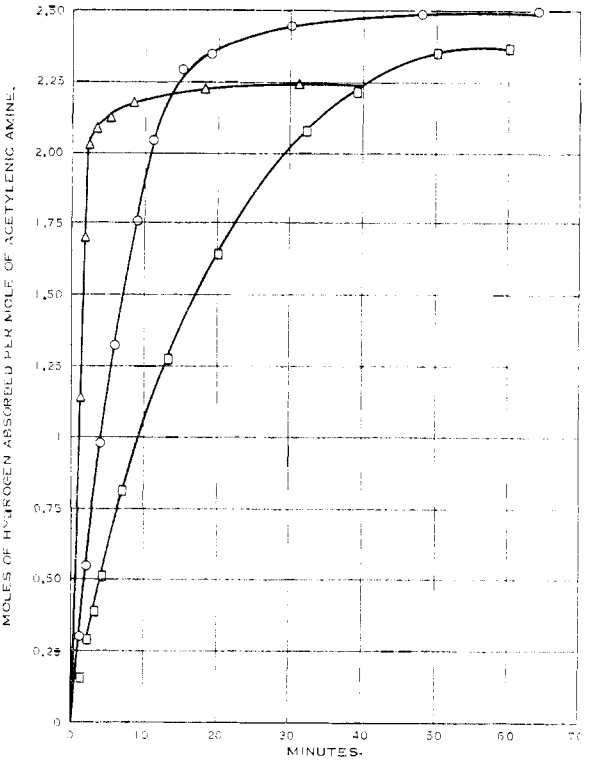


Fig. 1.—Hydrogenation of N,N-diethyl-1,1-dimethyl 2-butynylamine: △, in acetic acid; ○, in ethanol; □, in ethanol and diethylamine.

Mesityl oxide was isolated when N,N,1,1-tetramethyl-2-butynylamine (XIa) was treated with sulfuric acid either in the presence or absence of mercuric ion. The reaction may have proceeded *via* the elimination of dimethylamine from an intermediate ketoamine formed by hydration. Other plausible courses for the reaction include an SN1 mechanism *via* the resonance-stabilized propargyl-allenyl carbonium ion or a concerted SN2′ reaction involving nucleophilic attack with rupture of the C–N bond.[6]

In the present investigation an authentic sample of methylisopropenylacetylene was prepared by methylation of commercially available isopropenylacetylene. The physical properties, b.p. 82° (747 mm.), $n^{20}D$ 1.4498, did not correspond to those reported in the literature,[7] but the infrared spectrum confirmed the structure by indicating the presence of an internal triple bond, a double bond and a terminal methylene group.

Experimental[8]

Instrumentation.—A one-liter, stainless steel, Magne Dash autoclave (rated at 500 p.s.i. working pressure) manufactured by Autoclave Engineers, Inc., and equipped with suitable pressure gages and blowout disks was used.

Infrared spectra were obtained from a Perkin–Elmer model 21 double beam recording spectrophotometer equipped with sodium chloride optics.

Mass spectra were obtained from a Consolidated Electrodynamics mass spectrometer type 21-103B.

Catalyst Preparation.—The cadmium–zinc acetate catalyst was prepared as described previously.[1] The cuprous

(6) Y. R. Bhatia, P. D. Landor and S. R. Landor, *J. Chem. Soc.*, 24 (1959).

(7) C. D. Hurd and F. L. Cohen, THIS JOURNAL, **53**, 1068 (1931).

(8) All melting and boiling points are uncorrected.

chloride catalyst was prepared from concentrated hydrochloric acid by pouring into large excess of water.

Chemicals.—The anhydrous dimethylamine was purchased from the Matheson Co. and the diethylamine and di-*n*-butylamine from Distillation Products Industries. Propyne (99 mole per cent.) and isopropenylacetylene were obtained from Air Reduction Chemical Co.

N,N,1,1-Tetramethyl-2-butynylamine. A. From Propyne and Dimethylamine with Cadmium and Zinc Acetates.—A mixture of 175 g. (3.9 moles) of dimethylamine, 170 g. (4.25 moles) of propyne and 8.5 g. of catalyst was heated with stirring for 17 hours at 120°. The pressure decreased from an initial value of 550 to 160 p.s.i.g. The autoclave and contents were cooled to 10°, 168 g. (4.2 moles) of propyne was added, and the temperature was again raised to 120°. The pressure reached 350 p.s.i.g. and then dropped to 75 p.s.i.g. after 22 hours. After cooling the reaction mixture to room temperature, 2.7 l. (0.1 mole) of propyne was vented to the atmosphere through a wet test meter.

The product, a clear yellow oil, was diluted with approximately 300 ml. of ether and then shaken vigorously with four 100-ml. portions of 5% sodium carbonate to precipitate the cadmium and zinc salts. The aqueous slurry which formed after each treatment was removed, and the last carbonate treatment was followed by a water wash. The ethereal solution was dried, and the ether was removed on a steam-bath leaving 449 g. of product. By rapid distillation through a Vigreux column, 348 g. of 71% theoretical yield of crude N,N,1,1-tetramethyl-2-butynylamine, b.p. 90–95° (170 mm.), was obtained. Only 4 g. of column hold-up remained. An analytical sample, b.p. 67.5° (60 mm.), $n^{20}D$ 1.4439, was obtained by fractionation of a heart cut.

Anal. Calcd. for $C_8H_{15}N$: C, 76.74; H, 12.08. Found: C, 76.90, 76.65; H, 12.05, 12.00.

The mass spectrum had a parent peak at 125 mass units. The strongest peak was at 110, corresponding to the loss of a $-CH_3$ group. Peaks at 44 and 81 mass units indicated some fragmentation at the C—N bond and peaks at 39 and 86 may have indicated the formation of $CH_3C{\equiv}C-$ and $(CH_3)_2NC(CH_3)_2-$ groups. The infrared spectrum indicated an internal triple bond by a band at 4.5 μ. The picrate had a decomposition point of 255°.

Anal. Calcd. for $C_{14}H_{18}N_4O_7$: C, 47.5; H, 5.1; N, 15.8. Found: C, 47.8; H, 5.4; N, 15.6.

B. **From Propyne and Dimethylamine with Cuprous Chloride.**—A mixture of 46 g. (1.02 moles) of dimethylamine, 82 g. (2.05 moles) of propyne and 5 g. of cuprous chloride was heated from 10 to 89° over a 30-minute period. The pressure increased from 20 to 310 p.s.i.g. At this point an exothermic reaction took place and the external heating was discontinued. The pressure rose rapidly to 530 p.s.i.g. as the temperature increased spontaneously to 130°. The pressure dropped rapidly, but the temperature remained near 130° for several minutes even though the reactor was being cooled by a stream of air. After 1 hour the temperature was 103°, and the pressure was 100 p.s.i.g. When the temperature was decreased to 17°, there was less than 5 p.s.i.g. pressure remaining in the autoclave. The catalyst was removed by filtration, and the product was distilled rapidly through a Vigreux column. The yield of N,N,1,1-tetramethyl-2-butynylamine, 78° (90 mm.), $n^{20}D$ 1.4440, was 51 g. or 40%. The amount of material which did not distil, when the pot temperature was 156° and the pressure was less than 2 mm., was 27.7 g. or 22% of the reactants charged.

C. **By Methylation of N,N,1,1-Tetramethyl-2-propynylamine.**—A solution of sodamide in 150 ml. of liquid ammonia was prepared in a 500-ml., three-necked, Morton flask from 5.75 g. (0.25 mole) of sodium by the procedure of Vaughn, *et al.*[9] A solution of 27.6 g. (0.25 mole) of N,N,1,1-tetramethyl-2-propynylamine[4] in 250 ml. of diethyl ether was added slowly followed by dropwise addition of 36 g. (0.25 mole) of methyl iodide. The mixture was stirred for an additional 30 minutes at the temperature of refluxing ammonia. The flask was warmed gently and the ammonia was allowed to escape. When the temperature of the mixture reached 20°, ice and water were added. The ethereal phase was separated and dried over potassium carbonate. By distillation, 13.7 g. or 44% theoretical yield of N,N,1,1-tetramethyl-2-butynylamine, b.p. 68° (62 mm.), $n^{20}D$ 1.4432, was obtained. This material was shown by infrared spectral comparisons and by preparation of the picrate derivative to be the same as the samples prepared from propyne.

2-Methyl-1-penten-3-yne.—A solution of sodamide in 300 ml. of liquid ammonia was prepared from 11.5 g. (0.5 mole) of sodium in a one-liter, three-necked flask by the procedure of Vaughn, *et al.*[9] A solution of 33 g. (0.5 mole) of freshly distilled 2-methyl-1-buten-3-yne in 50 ml. of diethyl ether was added dropwise to a stirred ammoniacal sodamide solution. The mixture was stirred for 30 minutes before adding 71 g. (0.5 mole) of methyl iodide in 50 ml. of diethyl ether over a 45-minute period. The reaction mixture was left overnight in the flask without external cooling. Most of the ammonia evaporated. About 200 ml. of ice and water was added, the phases were separated, and the aqueous phase was extracted with a little ether. The ethereal solution was dried over potassium carbonate and was distilled in a 0.5 by 11 inch column packed with Penn State packing. The yield was 17 g. or 42% of 2-methyl-1-penten-3-yne, b.p. 82° (747 mm.), $n^{20}D$ 1.4498. Gas chromatography on a 14-ft. squalane column at 100° showed only 0.5% impurities in the freshly distilled material, but when elemental analyses were carried out it was found that the carbon–hydrogen total became progressively lower. An oxygen determination showed that oxygen was being taken up by this compound. Two of the sample tubes exploded during analyses and attempts to obtain pure samples were discontinued.

The infrared spectrum was consistent with the structural features present: internal triple bond, 4.45 μ; conjugated double bond, 6.17 μ; and $R_1R_2C{=}CH_2$, 11.15 μ. The mass spectrum had a parent peak at 80 mass units.

N,N,1,1-Tetramethyl-2-butynylamine Oxide and its Pyrolysis.—The amine oxide was prepared by the procedure described by Cope, *et al.*,[5] for the preparation of other amine oxides. To a solution of 25 g. (0.2 mole) of N,N,1,1-tetramethyl-2-butynylamine in 60 ml. of methanol in a 500-ml. flask fitted with a stirrer, a thermometer and a dropping funnel was added slowly 60 g. (0.53 mole) of 30% hydrogen peroxide at 0–10°. A crystalline solid formed, but it dissolved or melted at room temperature. The reaction mixture stood at room temperature 4 days. Platinum black was prepared by the hydrogenation of 0.2 g. of platinum dioxide in methanol, and it was added to the reaction mixture. A negative peroxide test was obtained the following day with lead sulfide paper. The methanol and water were removed on a rotary evaporator at 30–40°. The residue amounted to 30 g.

One-half of the product was transferred to a 200-ml. distillation flask which was connected to a Vigreux column and three Dry Ice-cooled traps in series. The pressure was reduced to 15 mm. and the amine oxide was heated slowly to 140° with an oil-bath, yielding approximately 6 ml. of distillate. The pressure was then reduced to 3 mm. to remove the remaining volatile products. The more volatile product, which condensed in the Dry Ice-cooled traps, was diluted with ether and dried over potassium carbonate. Six grams of *n*-heptane was added as a chaser before distillation. An infrared spectrum of a cut, b.p. 75–81° (752 mm.), showed clearly the presence of 2-methyl-1-penten-3-yne. Gas chromatography also showed a peak corresponding to that of 2-methyl-1-penten-3-yne.

N,N-Diethyl-1,1-dimethyl-2-butynylamine from Propyne and Diethylamine.—A mixture of 73.0 g. (1 mole) of diethylamine, 66.0 g. (1.65 moles) of propyne and 4 g. of cadmium–zinc acetate catalyst was heated with stirring at 120° for 7 hours. The pressure decreased from an initial value of 325 to 195 p.s.i.g. The reactor was cooled to 5° and 67.1 g. (1.68 moles) of propyne was added. The temperature was raised to 120° for 15 hours at which time the pressure had dropped from 390 to 215 p.s.i.g. The temperature was raised to 130° for 1 hour and then to 140° for 1.5 hours. There was no indication of any additional reaction at the higher temperature. The reactor was cooled to 32° and propyne (29.5 g.) was removed into a trap cooled with Dry Ice. The product was a light brown, clear liquid with a small amount of red material which remained on the walls of the autoclave.

The product was diluted with 200 ml. of ether. The ethereal solution was shaken with five 100-ml. portions of 5% sodium carbonate to remove the catalyst, and then was

(9) T. H. Vaughn, R. R. Vogt and J. A. Nieuwland, THIS JOURNAL, 56, 2120 (1934).

washed with water. The ethereal solution was dried over calcium sulfate, and the ether was removed at atmospheric pressure until the pot temperature reached 117°. The weight of product was 149.2 g. By distillation, 123 g. or 80% theoretical yield of N,N-diethyl-1,1-dimethyl-2-butynylamine was obtained. A portion of the same amine prepared in a similar manner in another experiment was carefully distilled to obtain an analytical sample, b.p. 60° (9 mm.), $n^{20}D$ 1.4470.

Anal. Calcd. for $C_{10}H_{19}N$: C, 78.5; H, 12.4. Found: C, 78.4; H, 12.3.

The picrate had a decomposition point of 117–118°.

Anal. Calcd. for $C_{16}H_{22}N_4O_7$: C, 50.3; H, 5.8; N, 14.7. Found: C, 50.2; H, 6.0; N, 14.6.

The mass spectrum showed a parent peak at 153, but the strongest peak was at 138 corresponding to loss of a $-CH_3$ group. The infrared spectrum indicated the presence of an internal triple bond by a band 4.45 μ.

Reaction of Di-*n*-butylamine with Propyne and Reduction of the Product.—The following method for the addition of propyne is not the preferred method, but it was used before a technique was developed for an accurate weighing of the amount of propyne charged. To a mixture of 114 g. (0.88 mole) of di-*n*-butylamine and 4 g. of cadmium–zinc acetate catalyst at 38° was added propyne as follows. Without stirring, the pressure was brought to 75 p.s.i.g. with propyne. The closed autoclave was stirred and the pressure dropped to 45 p.s.i.g. The autoclave was again pressured to 75 p.s.i.g. without stirring and the valve was closed. The temperature was raised to 120° and stirring was continued for 3 hours. The pressure reached 310 p.s.i.g. and decreased to 80 p.s.i.g. Propyne was added twice during the next 2 hours at 120° to keep the total pressure between 145 and 230 p.s.i.g. The product weighed 152 g. corresponding to absorption of 34 g. (0.85 mole) of propyne.

The lower boiling components were removed from a 58-g. portion of the effluent by subjecting it to 3–5 mm. pressure at room temperature for 7 hours in a 500-ml., round-bottom flask connected to a rotary evaporator. The 45 g. of material which remained was transferred to a Parr hydrogenator, and an attempt was made to hydrogenate the material in ethanol over Adams catalyst. No hydrogen was absorbed in 5 hours at room temperature and 3 atmospheres pressure. Platinum-on-charcoal (0.125% platinum) and 5% palladium-on-calcium carbonate were also ineffective. The catalysts were removed by filtration and the filtrate was treated with several portions of 5% sodium carbonate totaling 400 ml. to precipitate the cadmium and zinc salts. After removal of these catalyst poisons, the material was returned to the Parr hydrogenator and 0.14 mole of hydrogen was absorbed over Adams catalyst. After removal of the catalyst by filtration, the ethanol was removed by distillation at atmospheric pressure. The pressure was then reduced and 20.1 g. of di-*n*-butylamine, b.p. 49–51° (9.5 mm.), distilled. Only 2 g. of higher boiling material, 50–103° (9.7 mm.), $n^{20}D$ 1.4335, and a residue of 2 g. were obtained.

Hydrogenation of N,N-Diethyl-1,1-dimethyl-2-butynylamine. A. Identification of Diethylamine.—A 0.2982-g. (1.94 mmoles) sample of pure N,N-diethyl-1,1-dimethyl-2-butynylamine in ethanol absorbed 5.2 mmoles of hydrogen in 84 minutes at room temperature and atmospheric pressure over platinum catalyst. Another sample of the same amine, 0.2417 g. (1.58 mmoles), was added and an additional 5 mmoles of hydrogen was absorbed in 2 hours. The molar ratio of hydrogen to amine was 2.9:1. The ethanol solution of the reduction products was then heated and a few milligrams of oxalic acid was dissolved in the first 2 ml. of distillate. The oxalate derivative of diethylamine, m.p. 209–210° dec., precipitated upon addition of 5 ml. of diethyl ether. A mixed melting point with an authentic sample was not depressed.

B. Identification of 2-Methylpentane.—In another experiment a 0.6171-g. sample of pure N,N-diethyl-1,1-dimethyl-2-butynylamine in methylcyclohexane absorbed 11.1 mmoles of hydrogen in 9 hours over platinum catalyst. Gas chromatography of the solution showed that it contained 1.3 weight % 2-methylpentane which corresponded to a 54% theoretical yield.

C. Dependence of the Hydrogenation Rate and of the Quantity Absorbed Upon the Acidity of the Solution.—Samples of N,N-diethyl-1,1-dimethyl-2-butynylamine (0.061 to 0.1014 g.) were reduced in the presence of platinum catalyst in a micro-hydrogenation apparatus in (a) ethanol, (b) in ethanol and diethylamine (mole ratio of diethylamine to N,N-diethyl-1,1-dimethyl-2-butynylamine 4:1 minimum), and (c) in glacial acetic acid. The results are summarized in Fig. 1.

Hydrogenation of N,N,1,1-Tetramethyl-2-butynylamine. A. In Ethanol.—A 100-g. portion of crude product from a dimethylamine–propyne reaction, which had been treated with sodium carbonate to remove cadmium and zinc salts, was diluted with 75 ml. of ethanol and hydrogenated under 3 atmospheres pressure of hydrogen at room temperature over platinum. Approximately 1.2 moles of hydrogen was absorbed in 24 hours. After removal of the catalyst by filtration, the filtrate was distilled in a Vigreux column. Upon removal of the lower boiling components including the alcohol solvent, 63.4 g. of oil remained. Of this amount, 55.5 g. distilled at 130° (746 mm.) to 80° (9 mm.), and the refractive index varied from $n^{20}D$ 1.4240 to 1.4710. This material was carefully fractionated. The first cut, b.p. 33–38° (20 mm.), $n^{20}D$ 1.4120, was shown to contain a ketone by infrared spectroscopy, and it was identified as methyl isobutyl ketone by preparation of the 2,4-dinitrophenylhydrazone derivative. Mass and infrared spectrograms of a 15-g. portion of the distillate, 45–46° (20–22 mm.), $n^{20}D$ 1.4315, indicated that the hydrogenation was incomplete and that the material was probably a mixture of N,N,1,1-tetramethyl-2-butenylamine, $C_8H_{17}N$, mol.wt. 127, and N,N,1,1-tetramethylbutylamine, $C_8H_{19}N$, mol.wt. 129. The mass spectrum had peaks at 127 and 129 mass units and the infrared spectrum possessed a band characteristic of a double bond at 6.05 μ.

The lower boiling cuts, b.p. 48–83° (746 mm.), were diluted with 250 ml. of water and hydrochloride acid was added until the solution was acidic. About 2.7 g. of a colorless oil separated to the top. It was removed and dried over calcium sulfate. Gas chromatography analyses showed that four hydrocarbons with retention times in the C_6-range and a higher boiling oxygenated compound whose retention time corresponded to methyl isobutyl ketone were present. One of the C_6-peaks corresponded to 2-methylpentane. Two of the remaining peaks corresponded to 2-methyl-1- or 2-pentene and *cis*-4-methyl-2-pentene. An infrared spectral analysis of the same sample was consistent with the presence of methyl isobutyl ketone, 2 methyl-2-pentene and *trans*-4-methyl-2-pentene.

B. In Glacial Acetic Acid.—A 25-g. (0.2 mole) sample of pure N,N,1,1-tetramethyl-2-butynylamine was hydrogenated at room temperature in approximately 100 ml. of glacial acetic acid. The hydrogen absorbed at approximately 3 atmospheres pressure over a 2-hour period amounted to 0.4 mole. The acetic acid solution was poured into 150 ml. of ammonium hydroxide and ice, and the oil was extracted with ether. The ethereal solution was dried over calcium sulfate before distillation of the product. The yield of product, b.p. 134–138° (758 mm.), $n^{20}D$ 1.4210–1.4232, was 12.8 g. The mass spectrogram of a cut, b.p. 138°, $n^{20}D$ 1.4228, indicated that the principal component had a mass of 129.

Hydration of N,N,1,1-Tetramethyl-2-butynylamine.—The procedure of Rose and Wheedon[10] was employed. A mixture of 10 g. (0.08 mole) of N,N,1,1-tetramethyl-2-butynylamine and 0.4 g. of mercuric sulfate in an aqueous sulfuric acid solution prepared from 24 ml. of concentrated sulfuric acid and 6 ml. of water was heated on a steam-bath for 1 hour. The solution was poured into ice and left overnight. About 35 ml. of 30% sodium hydroxide was added. An oil layer which separated was extracted with ether. The solution was dried over magnesium sulfate and calcium sulfate before removal of the ether at atmospheric pressure. The 8.3 g. of oil remaining was distilled, and 3.8 g. of mesityl oxide was obtained, b.p. 127–133°. The 2,4-dinitrophenylhydrazone, m.p. 200–201°, was prepared and a mixed melting point with an authentic sample of mesityl oxide was not depressed.

Hydrolysis of N,N,1,1-Tetramethyl-2-butynylamine.—A 10-g. portion of N,N,1,1-tetramethyl-2-butynylamine was treated in the same manner as described above except that the mercuric sulfate was omitted. A cut, b.p. 130–134° (3.1 g.), was found to be a mixture of mesityl oxide and the unreacted amine by preparation of derivatives.

(10) J. D. Rose and B. C. L. Wheedon, *J. Chem. Soc.*, 784 (1949).