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Allenic and Acetylenic Amines from Vinylacetylene

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Aqueous dimethylamine has been found to add to vinylacetylene to give N,N-dimethyl-2,3-butadienylamine which rearranges to N,N-dimethyl-2-butynylamine in the presence of excess dimethylamine or sodium methoxide. The structures of these amines have been established and other N-substituted-2,3-butadienylamines also have been prepared by reaction of vinylacetylene with aqueous methylamine, diethylamine, morpholine and *n*-butylamine.

Vinylacetylene, the simplest example of a conjugated enyne system, is known to give three different types of products by 1,4-addition. Where HA is the addendum, the product can be any one of the adducts. Presumably I, the primary adduct

$$\underset{\text{I}}{CH_2{=}C{=}CH{-}CH_2A} \qquad \underset{\text{II}}{CH_2{=}CA{-}CH{=}CH_2}$$

$$\underset{\text{III}}{CH_3{-}C{\equiv}C{-}CH_2{-}A}$$

is the precursor of both II and III, but this has been demonstrated only in the case of II. For example, addition of hydrogen chloride to vinylacetylene gives 1-chloro-2,3-butadiene (I, A = Cl), which in the presence of cuprous chloride rearranges to 2-chloro-1,3-butadiene (II, A = Cl).[1] Acetylenic adducts of type III (A = OR) have been obtained through the sodium alkoxide-catalyzed addition of alcohols to vinylacetylene,[2] but the allenic precursor (I, A = OR) has never been isolated in this reaction. However, it was presumed that the acetylenic ether resulted from rearrangement of the allenic ether since rearrangements of allenes to acetylenes are well known.[3]

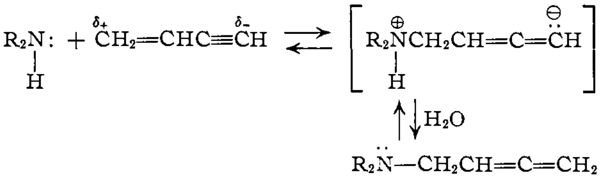
It has now been found that aqueous primary or secondary aliphatic amines will add to vinylacetylene to give either 2,3-butadienylamines (IV) or 2-butynylamines (V). This furnishes additional evidence that the primary allenic adduct is an intermediate in the formation of an acetylenic product from vinylacetylene.

$$CH_2{=}CH{-}C{\equiv}CH \xrightarrow{R_2NH} \underset{\text{IV}}{R_2N{-}CH_2{-}CH{=}C{=}CH_2} \xrightarrow{\text{base}} \underset{\text{V}}{R_2N{-}CH_2{-}C{\equiv}C{-}CH_3}$$

When molar equivalents of vinylacetylene and aqueous 25% dimethylamine were heated at 100° under autogenous pressure, N,N-dimethyl-2,3-butadienylamine was obtained. However, when an excess of dimethylamine was used or when the 2,3-butadienylamine was heated with sodium methoxide, the 2-butynylamine was formed. Other 2,3-butadienylamines have been prepared by reaction of vinylacetylene with aqueous diethylamine, morpholine, methylamine and *n*-butylamine. In the case of methylamine, N-methyl-bis-(2,3-butadienyl)-amine also was obtained. Under similar conditions diamylamine and N-methylaniline failed to add and ammonium hydroxide caused polymerization of the vinylacetylene. In these addition reactions water is a necessary constituent, for under anhydrous conditions only very low yields of impure product were obtained.

The structure of the product from dimethylamine and vinylacetylene has been established as N,N-dimethyl-2,3-butadienylamine by independent synthesis from 1-chloro-2,3-butadiene and dimethylamine[4] and by hydrogenation to N,N-dimethyl-*n*-butylamine. Evidence for a terminal allene group was furnished by infrared and Raman spectra. The structure of the rearrangement product of N,N-dimethyl-2,3-butadienylamine was shown to be N,N-dimethyl-2-butynylamine by independent synthesis from 2,3-dibromopropene according to the literature procedure for N,N-diethyl-2-butynylamine.[5]

The addition of amines to vinylacetylenes is apparently a special type of Michael condensation.[6] The base-catalyzed rearrangement of allenes and acetylenes has been postulated by Jacobs, Akawie and Cooper[7] to proceed *via* carbanion intermediates and not by addition and elimination of alcohol.



$$\begin{array}{c} \underset{\displaystyle H}{\overset{}{R_2N\!:}} + \overset{\delta+}{C}H_2{=}CHC{\equiv}\overset{\delta-}{C}H \rightleftharpoons \left[\underset{\displaystyle H}{R_2\overset{\oplus}{N}}CH_2CH{=}C{=}\overset{\ominus}{\ddot{C}}H \right] \\ \uparrow\downarrow H_2O \\ R_2\ddot{N}{-}CH_2CH{=}C{=}CH_2 \end{array}$$

These workers also demonstrated that 1-pentyne, 2-pentyne and 1,2-pentadiene in alcoholic potassium hydroxide are each converted to an equilibrium mixture containing 1.3% 1-pentyne, 3.5% 1,2-pentadiene and 95.2% 2-pentyne. Presumably a 2,3-butadienylamine rearranges to a 2-butynylamine *via* the route

$$\left[\begin{array}{c} CH_2{=}C{=}\overset{\ominus}{\ddot{C}}{-}CH_2{-}NR_2 \\ \updownarrow \\ \overset{\ominus}{C}H_3{-}C{\equiv}C{-}CH_2{-}NR_2 \end{array}\right] \begin{array}{l} \rightleftharpoons CH_3{-}C{\equiv}C{-}CH_2NR_2 \\ \\ \rightleftharpoons CH_2{=}C{=}CH{-}CH_2NR_2 \end{array}$$

Experimental

N,N-Dimethyl-2,3-butadienylamine from Vinylacetylene.[8] —Aqueous 25% dimethylamine (540 g., 3 moles) was

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[1] W. H. Carothers, G. J. Berchet and A. M. Collins, THIS JOURNAL, **56**, 1169 (1934).

[2] R. A. Jacobson, H. B. Dykstra and W. H. Carothers, *ibid.*, **56**, 1169 (1934).

[3] A. Favorskii, *J. Russ. Phys. Chem. Soc.*, **19**, 414 (1887); *Chem. Zentr.*, **58**, 1539 (1887).

[4] W. H. Carothers and G. J. Berchet, U. S. Patent 2,136,177 (Nov. 8, 1938).

[5] R. F. Parcell and C. B. Pollard, THIS JOURNAL, **72**, 2385 (1950).

[6] E. R. Alexander, "Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 149–152.

[7] T. L. Jacobs, R. Akawie and R. G. Cooper, THIS JOURNAL, **73**, 1273 (1951).

[8] V. A. Engelhardt, U. S. Patent 2,647,147 (July 28, 1953).

charged into a stainless steel, pressure resistant, liter reactor which had been flushed with nitrogen, evacuated and cooled in a Dry Ice–acetone-bath. The still partially evacuated reactor was connected to a cylindrical pressure vessel, with valves at both ends, containing vinylacetylene (156 g., 3 moles) which was then pressured into the reactor under nitrogen at 200 lb./sq. in. pressure. The reactor was then sealed and heated at 100° for 10 hours. After the reactor had been allowed to cool to room temperature, it was bled to the atmosphere and opened. The product was saturated with potassium carbonate and then extracted with ether. The solution was first dried over potassium hydroxide and then over magnesium sulfate. After distillation of ether the residual oil was distilled to give 164 g. (56% yield) of a clear, pale yellow liquid, b.p. 58–60° (155 mm.), b.p. 106–107° (atm.), n^{25}D 1.4477.

Anal. Calcd. for $C_6H_{11}N$: C, 74.17; H, 11.41; N, 14.42; neut. equiv., 97.2; quant. hydrogenation, g. H_2/g., 0.0415. Found: C, 74.52; H, 11.45; N, 13.98; neut. equiv., 99.6; quant. hydrogenation, g. H_2/g., 0.0423.

A methiodide, m.p. 193–194°, was prepared. *Anal.* Calcd. for $C_7H_{14}IN$: C, 35.16; H, 5.90; N, 5.86; I, 53.08. Found: C, 35.38; H, 6.06; N, 5.55; I, 52.93.

Comparison of the infrared and Raman spectra of N,N-dimethyl-2,3-butadienylamine with those of 1-chloro-2,3-butadiene and 1,2-butadiene showed the presence of a terminal allene group, the absence of conjugated olefinic groups and only trace amounts of terminal and internal acetylene groups. Absorption at 5.10 and 11.88 μ indicated a terminal allene group, and bands at 11.0, 10.1 and 6.0 μ for a $CH_2{=}CH-$ group were absent. The Raman spectra showed only a slight band for C≡C at 2103 cm.$^{-1}$ and no bands for terminal and internal olefinic structures.

N,N-Dimethyl-2,3-butadienylamine (25.9 g., 0.27 mole) in 75 ml. of absolute alcohol with 1 g. of 5% Pd/C catalyst was hydrogenated under a pressure of 500–1500 lb./sq. in. at room temperature for one hour. The solution was filtered from catalyst, acidified with 25 ml. of hydrochloric acid and concentrated under reduced pressure. The residue was made alkaline with aqueous 20% sodium hydroxide, saturated with potassium carbonate and extracted with ether. After drying over sodium hydroxide pellets and removal of ether, distillation of the residue gave 15.4 g. of N,N-dimethyl-*n*-butylamine, b.p. 90° (atm.), n^{25}D 1.3954. The picrate (m.p. 97–98°) and infrared spectrum of this compound were identical with those of an authentic sample of N,N-dimethyl-*n*-butylamine.

When the reaction of dimethylamine with vinylacetylene was repeated under anhydrous conditions only a 1.8% yield of the butadienylamine was obtained.

N,N-Dimethyl-2,3-butadienylamine from 1-Chloro-2,3-butadiene.—1-Chloro-2,3-butadiene (88.6 g., 1 mole) was added dropwise with stirring to a solution of dimethylamine (100 g., 2.2 moles) in dry benzene (400 ml.) in a 1-l. three-necked flask equipped with a stirrer and a Dry Ice reflux condenser. After stirring for 5 hours the solution was allowed to stand at room temperature for 5 days and then was briefly heated to reflux. The mixture was extracted with three 100-ml. portions of 12% sulfuric acid. The acidic extracts were made alkaline with 40% sodium hydroxide, saturated with sodium carbonate and extracted with ether. The ether solution was dried over potassium hydroxide pellets. After distillation of ether, N,N-dimethyl-2,3-butadienylamine (32.7 g.), b.p. 57.5–58.5° (150 mm.), n^{25}D 1.4479, was obtained. The picrate of this amine melted at 123.5–124.5° and there was no depression in melting point on admixture with the picrate (m.p. 122–123°) from the amine derived from vinylacetylene and dimethylamine. The infrared spectra of the two amines were identical.

N,N-Dimethyl-2,3-butadienylamine also was obtained in 12% yield by heating 1-chloro-2,3-butadiene (1 mole) with aqueous 33% dimethylamine (2 moles) for 10 hours at 100°.

N,N-Dimethyl-2-butynylamine from Vinylacetylene and Excess Dimethylamine.—Vinylacetylene (104 g., 2 moles) and aqueous 25% dimethylamine (720 g., 4 moles) were heated at 100° for 20 hours and the product was isolated in the same manner as described for N,N-dimethyl-2,3-butadienylamine. Distillation of the product gave a clear, colorless liquid mixture (78.8 g.) boiling at 107–113° under atmospheric pressure. On refractionation through a Podbielniak column under atmospheric pressure, the product was separated into a lower boiling fraction of N,N-dimethyl-2,3-butadienylamine (17 g., b.p. 107–109°) and a higher boiling fraction of N,N-dimethyl-2-butynylamine (39 g., b.p. 116.5–117°). The infrared spectrum of a heart cut of the higher boiling fraction, b.p. 117°, n^{25}D 1.4339, showed no band at 5.1 μ for an allenic structure and no bands for terminal acetylenic, conjugated or allenic systems. However, the Raman spectrum indicated an internal acetylenic structure by bands in the 2200 wave number region.

Anal. Calcd. for $C_6H_{11}N$: N, 14.42; neut. equiv., 97.2; g. H_2/g., 0.0415. Found: N, 13.86; neut. equiv., 97.0; g. H_2/g., 0.0428.

N,N-Dimethyl-2-butynylamine from Rearrangement of N,N-Dimethyl-2,3-butadienylamine.—A solution of N,N-dimethyl-2,3-butadienylamine (50 g., 0.51 mole) and sodium methoxide (27.8 g., 0.51 mole) in 97 ml. of absolute methanol was charged into an evacuated, cooled reactor which was then pressured to 200 lb./sq. in. with nitrogen and heated at 105° for 8 hours. The solution was acidified with hydrochloric acid, and methanol was removed under reduced pressure. The residue was cooled, made alkaline with aqueous 20% sodium hydroxide, and extracted with ether. After drying over magnesium sulfate, the ether was removed by distillation. Distillation of the residual oil under nitrogen at atmospheric pressure gave 37.7 g. (75% yield) of rearranged amine, b.p. 114–115.5° (atm. pressure), n^{25}D 1.4330. The absence of a terminal acetylenic group was shown by the failure of this compound to react with potassium mercuric iodide reagent. A sample was redistilled in a micro Podbielniak column and a heart cut submitted for analysis.

Anal. Calcd. for $C_6H_{11}N$: C, 74.17; H, 11.41; neut. equiv., 97.2; g. H_2/g., 0.0415. Found: C, 74.22; H, 11.57; neut. equiv., 98; g. H_2/g., 0.0422.

A methiodide, m.p. 164–165° after recrystallization from alcohol, was prepared by addition of methyl iodide to an alcohol solution of the amine. Mixture of this methiodide with that of N,N-dimethyl-2-butynylamine, obtained from the reaction of vinylacetylene with excess dimethylamine, caused no depression in melting point. The infrared spectrum of this amine and that obtained from the reaction of vinylacetylene with excess dimethylamine were identical.

Anal. Calcd. for $C_7H_{14}NI$: C, 35.16; H, 5.90; I, 53.08. Found: C, 35.13; H, 5.99; I, 52.49.

N,N-Dimethyl-2-butynylamine.—An authentic sample of N,N-dimethyl-2-butynylamine was prepared from 2,3-dibromopropene by using dimethylamine in place of diethylamine in the procedure of Parcell and Pollard[5] for N,N-diethyl-2-butynylamine. The dimethylamino compound (n^{25}D 1.4337) boiled at 115.5–116° under atmospheric pressure. The methiodide (m.p. 164–165°) and the infrared spectrum of this compound were identical with those of the samples of N,N-dimethyl-2-butynylamine prepared by the previously described methods.

N-Methyl-2,3-butadienylamine.—Aqueous 40% methylamine (232 g., 3 moles) and vinylacetylene (156 g., 3 moles) were charged into a liter reactor, heated at 100° for 10 hours, and then worked up in the same manner as described for N,N-dimethyl-2,3-butadienylamine. The product consisted of N-methyl-2,3-butadienylamine, obtained as a clear, colorless liquid (30.8 g.), b.p. 59–59.5° (141 mm.), and 100 g. of tar. This amine was redistilled under atmospheric pressure and the heart cut, b.p. 105–106°, n^{25}D 1.4616, was submitted for analysis.

Anal. Calcd. for C_5H_9N: N, 16.85; neut. equiv., 83.1; g. H_2/g. 0.0485. Found: N, 16.55; neut. equiv., 84.7; g. H_2/g., 0.0495. The infrared spectrum of this amine exhibited bands at 5.1 and 11.8 μ for a terminal allenic structure and a band at 13.4 μ for a secondary amino nitrogen.

N-Methyl-N-(2,3-butadienyl)-N′-phenylthiourea.—A phenylthiourea, prepared from phenyl isothiocyanate,[9] was obtained as colorless crystals, m.p. 62.0–63.5°, after recrystallization from alcohol–water.

Anal. Calcd. for $C_{12}H_{14}N_2S$: C, 66.02; H, 6.46. Found: C, 66.06; H, 6.66.

N-Methyl-bis-(2,3-butadienyl)-amine.—Vinylacetylene (686 g., 13.2 moles) and aqueous 25% methylamine (1.49

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[9] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 179.

kg., 12 moles) were charged into a cooled, evacuated 2-gallon autoclave equipped with a stirrer. The autoclave was pressured to 200 lb./sq. in. with nitrogen and heated at 100° for 15 hours. The reaction mixture was treated as described previously and distillation of the product gave 80.9 g. of N-methyl-2,3-butadienylamine, b.p. 105–107.5° (atm. pressure), and 186 g. of N-methyl-bis-(2,3-butadienyl)-amine as a clear, colorless liquid, b.p. 70–71° (15 mm.), $n^{25}\mathrm{D}$ 1.4988. The infrared spectrum showed strong absorption bands at 5.1 and 11.9 μ for an allenic structure and was similar to that of N,N-dimethyl-2,3-butadienylamine.

Anal. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36; neut. equiv., 135; g. H_2/g., 0.060. Found: C, 80.22; H, 9.95; N, 10.08; neut. equiv., 135; g. H_2/g., 0.064.

N,N-Diethyl-2,3-butadienylamine.—A mixture of diethylamine (141 g., 1.93 moles), water (260 ml.) and vinylacetylene (100 g., 1.92 moles) was charged into a liter reactor, heated at 100° for 15 hours, and then worked up in the same manner as described for the dimethylamine reaction. Distillation of the product gave 57.5 g. of forerun, mostly diethylamine, 29 g. of the diethylamino adduct, b.p. 91–92° (147 mm.), $n^{25}\mathrm{D}$ 1.4505, and 29 g. of tar. The infrared spectrum of N,N-diethyl-2,3-butadienylamine showed bands at 5.1 and 11.9 μ, characteristic of a terminal allenic structure.

Anal. Calcd. for $C_8H_{15}N$: C, 76.73; H, 12.08; N, 11.19; g. H_2/g., 0.0322; neut. equiv. 125. Found: C, 76.66; H, 12.15; N, 10.81; g. H_2/g., 0.0371; neut. equiv., 127.

A methiodide, m.p. 109–110° after recrystallization from acetone, was prepared.

N-(2,3-Butadienyl)-morpholine.—In the same manner as described previously for the reaction with dimethylamine, a mixture of vinylacetylene (100 g., 1.92 moles), morpholine (168 g., 1.93 moles) and 260 ml. of water were charged into a liter reactor and heated at 100° for 10 hours. After preliminary purification the product was distilled to give 72 g. of adduct as a clear, colorless liquid, b.p. 70.5–71.5° (9 mm.), $n^{25}\mathrm{D}$ 1.4917. The infrared spectrum of this substituted morpholine had bands at 5.1 and 11.8 μ for a terminal allenic structure.

Anal. Calcd. for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.06; neut. equiv., 139; g. H_2/g., 0.029. Found: C, 69.05; H, 9.51; N, 10.04; neut. equiv., 141; g. H_2/g., 0.030.

The methiodide of this amine melted at 105–107° after recrystallization from absolute alcohol.

When the reaction of vinylacetylene with morpholine was repeated in the absence of water, the yield was only 1.9% and the product was impure.

N-*n*-Butyl-2,3-butadienylamine.—Vinylacetylene (100 g., 1.92 moles), *n*-butylamine (141 g., 1.93 moles) and 258 ml. of water were charged into a liter reactor, heated at 100° for 10 hours and treated as described for the dimethylamino compound. Distillation gave 68 g. of unreacted *n*-butylamine and 5.9 g. of adduct, b.p. 89–90° (33 mm.), $n^{25}\mathrm{D}$ 1.4582. The infrared spectrum showed bands at 5.1 and 11.9 μ for a terminal allenic structure and a band at 13.4 μ for a secondary amino nitrogen.

Anal. Calcd. for $C_8H_{15}N$: C, 76.74; H, 12.08; N, 11.19; neut. equiv., 125; g. H_2/g., 0.0322. Found: C, 77.03; H, 12.02; N, 11.41; neut. equiv., 127; g. H_2/g., 0.0319.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Thermal Dimerization of Allene to 1,2-Dimethylenecyclobutane[1]

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Allene dimer, 1,2-dimethylenecyclobutane (I), is obtained in *ca.* 50% yield upon passing allene over glass beads heated at 500–510°. This thermal dimer contains no 2-vinyl-1,3-butadiene, but does contain traces of 2-bromopropene, a contaminant of the allene used. I is not cleaved at 500–600° to 2-vinyl-1,3-butadiene in the presence or absence of acetic acid. Two Diels–Alder adducts of allene dimer with maleic anhydride can be obtained. The first, formed at temperatures up to 78°, is the previously described bicyclooctene 1:1 adduct of I. The second, a $\Delta^{4a,8a}$-octahydronaphthalene derivative, derives from the first on heating at 150° with maleic anhydride.

The rather interesting properties of 1,2-dimethylenecyclobutane (I) indicated in a recent study[3] encouraged us to examine a more direct route for its preparation and to study further certain of its properties.

In 1913, Lebedev reported the thermal dimerization of allene to I by heating allene in a sealed glass tube at 140–150° for 3 days.[4] The thermal dimer, obtained in low yield (*ca.* 5%), was contaminated with substantial amounts of inseparable 2-bromopropene or ether depending upon the method used for preparing allene. The assignment of structure I to the dimer was based on its oxidation to succinic acid by permanganate.

For the present study allene was prepared by debromination of 2,3-dibromo-1-propene using zinc dust and ethanol.[5] It proved to be difficult for us to remove the accessory product 2-bromopropene, and even after five careful fractional distillations through a special column designed for low boiling liquids the allene still contained traces of the bromo compound. Infrared analysis of the allene, b.p. −36 to −35°, showed that it contained no methylacetylene.

Repetition of the Lebedev experiment confirmed essentially the original observations. There was obtained about a 5% yield of a product, b.p. 55–60° and $n^{25}\mathrm{D}$ 1.4322, whose ultraviolet spectrum indicated the presence of I; absorption maxima at 238 mμ, log ϵ 3.39, and 246 mμ, log ϵ 3.47, with a shoulder at 255 mμ. Our best sample of "synthetic" I, b.p. 73–74° and $n^{20}\mathrm{D}$ 1.4721, showed the maxima 237 mμ, log ϵ 3.99, and 246 mμ, log ϵ 4.01, with a shoulder at 254 mμ.[3] Thus, the liquid product contained about 30% of I. Infrared analysis and sodium fusion tests indicated that the impurity present was probably 2-bromopropene.

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[1] The work reported here was done as part of a research program at the Baker Laboratory of Chemistry, Cornell University, sponsored by the B. F. Goodrich Co.

[2] Abstracted from part of the dissertation presented by Joseph A. Verdol in February, 1955, to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] A. T. Blomquist and J. A. Verdol, THIS JOURNAL, **77**, 1806 (1955).

[4] C. B. Lebedev, *J. Russ. Phys. Chem. Soc.*, **45**, 1357 (1913); *C. A.*, **9**, 799 (1915).

[5] C. D. Hurd, R. N. Meinert and L. U. Spence, THIS JOURNAL, **52**, 1143 (1930).