[CONTRIBUTION FROM THE ORGANIC CHEMISTRY LABORATORIES OF THE UNIVERSITY OF FLORIDA]

Tertiary Acetylenic Amines. I

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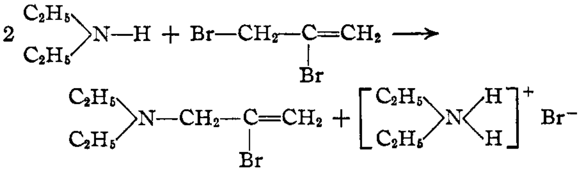
A series of tertiary acetylenic amines has been prepared in connection with a research project being conducted on the synthesis of unsaturated, aliphatic amines. 1-Dialkylamino-propyne-2 compounds have been prepared previously by the reaction of the appropriate secondary amine, formaldehyde and acetylene, using pressure and a catalyst.[2] 1-Phenyl-3-dialkylamino-propyne-1 compounds have been prepared by the reaction of phenylacetylene, formaldehyde and a dialkylamine.[3] The 1-diethylamino-heptyne-2 reported in this paper has been prepared in a similar manner.[4] Aside from these sources, no reports of other amines of this type have been located in the literature.

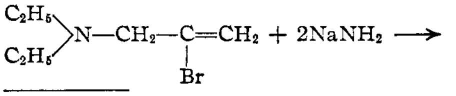
It has been shown by several investigators, among them Bourguel,[5] that sodamide can be used to introduce a triple bond into a molecule by dehydrohalogenation. Previously, this has been applied only to the synthesis of acetylenic hydrocarbons. This paper describes a method of extending the application of this reaction to the synthesis of acetylenic amines. Usually, high-boiling hydrocarbons such as mineral oil have been used as solvents for the reaction, but the use of liquid ammonia as a solvent has been reported.[6] In the synthesis of acetylenic amines, liquid ammonia was found to be a much better solvent, resulting in both better yields and purer products. However, mineral oil, xylene and toluene were used with some success.

As a basis for this series, a halogenated alkenamine was prepared by the reaction

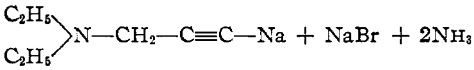


$$2\ \genfrac{}{}{0pt}{}{C_2H_5}{C_2H_5}\!>\!N{-}H + Br{-}CH_2{-}\underset{Br}{C}{=}CH_2 \longrightarrow \genfrac{}{}{0pt}{}{C_2H_5}{C_2H_5}\!>\!N{-}CH_2{-}\underset{Br}{C}{=}CH_2 + \left[\genfrac{}{}{0pt}{}{C_2H_5}{C_2H_5}\!>\!N\!<\!\genfrac{}{}{0pt}{}{H}{H}\right]^+ Br^-$$

This halogenated amine reacted with sodamide to introduce the triple bond, using liquid ammonia as a solvent



$$\genfrac{}{}{0pt}{}{C_2H_5}{C_2H_5}\!>\!N{-}CH_2{-}\underset{Br}{C}{=}CH_2 + 2NaNH_2 \longrightarrow$$



$$\genfrac{}{}{0pt}{}{C_2H_5}{C_2H_5}\!>\!N{-}CH_2{-}C{\equiv}C{-}Na + NaBr + 2NH_3$$

The sodium acetylide which was formed by the above reaction was decomposed with water to yield the free 1-diethylamino-propyne-2.

As in the preparation of higher homologs of acetylene by reaction of alkyl halides with sodium acetylide, using liquid ammonia as a solvent,[7,8,9] the sodium acetylide of 1-diethylamino-propyne-2 was coupled with various *n*-alkyl halides to prepare the higher homologs in the series. In this manner, the 1-diethylamino derivatives of butyne-2, pentyne-2, hexyne-2, heptyne-2 and octyne-2 were prepared. 1-Diethylamino-hex-5-en-2-yne was prepared by coupling allyl bromide to the sodium acetylide of 1-diethylamino-propyne-2, using xylene as a solvent, since the reaction could not be carried out in liquid ammonia. Analogously, it has been reported that allyl bromide could not be coupled to sodium acetylide in liquid ammonia to give the expected product.[8]

In the preparation of the higher homologs of this series, it was found that the isolation of the free 1-diethylamino-propyne-2 may be eliminated, if desired, by adding the alkyl halide directly into the liquid ammonia solution of the sodium acetylide of 1-diethylamino-propyne-2 before decomposing it with water, thereby completing the reaction in one direct process.

The physical constants and percentage yields of the members of this series may be found in Table I.

Experimental

Sodamide.—The sodamide used throughout these reactions was prepared by the method of Vaughn, Vogt and Nieuwland.[6]

1-Diethylamino-2-bromopropene-2.—One thousand grams (5 moles) of 2,3-dibromopropene-1 and a solution of 730 g. (10 moles) of diethylamine in 3 liters of ether were placed in the refrigerator in separate containers. When both were chilled to 10°, the 2,3-dibromopropene-1 was added in 50-ml. portions at one-hour intervals, with swirling, to the ethereal solution of diethylamine, allowing the containers to remain in the refrigerator between additions. After the addition of the first portion of 2,3-dibromopropene-1, there was formed a white precipitate of diethylamine hydrobromide which became continuously heavier throughout the course of the additions. When the addition was complete, the reaction mass was removed from the refrigerator and allowed to come to room temperature by standing overnight. The diethylamine hydrobromide was then filtered off. The ether was removed from the filtrate by evaporation on a steam-bath, some further precipitation of diethylamine hydrobromide occurring meanwhile. When the ether was completely removed, the residue was filtered again, and the filtrate was

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[1] This paper is abstracted from a portion of a dissertation submitted by R. F. Parcell to the Graduate Council of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy, February, 1950.

[2] I. G. Farbenindustrie A.-G., British Patent 510,904, August 10, 1939; French Patent 839,875, April 13, 1939.

[3] C. Mannich and Fu Tsong Chang, *Ber.*, **66B**, 418–420 (1933).

[4] Jones, Marszak and Bader, *J. Chem. Soc.*, 1578–1579 (1947).

[5] Bourguel, *Compt. rend.*, **177**, 688 and 823 (1923); *Ann. chim.*, [10] **3**, 231 (1925).

[6] Vaughn, Vogt and Nieuwland, This Journal, **56**, 2120–2122 (1934).

[7] Lebeau and Picon, *Compt. rend.*, **156**, 1077 (1913).

[8] Henne and Greenlee, This Journal, **67**, 484–485 (1945).

[9] Vaughn, Vogt, Hennion and Nieuwland, *J. Org. Chem.*, **2**, 1 (1937).

TABLE I

PHYSICAL CONSTANTS AND PERCENTAGE YIELDS OF SEVEN TERTIARY ACETYLENIC AMINES

Compound	B. p.,[a] °C.	Yield, %	$n^{25}\mathrm{D}$	d^{25}_4	Molar refraction Found	Molar refraction Calcd.	Nitrogen, % Found	Nitrogen, % Calcd.
1-Diethylamino-propyne-2[f]	119.5–120.1	82.5[b]	1.4296	0.8042	36.10	36.46	12.29	12.66
1-Diethylamino-butyne-2	152.5–153	73.5[c]	1.4413	.8075	40.97	41.08	11.19	11.25
1-Diethylamino-pentyne-2	168.4–169.9	59[c]	1.4402	.8029	45.72	45.70	10.11	10.06
1-Diethylamino-hexyne-2	187.4–188.4	72.5[c]	1.4431	.8058	50.44	50.33	9.02	9.18
1-Diethylamino-hex-5-en-2-yne	52–53 (11 mm.)	33[b,d,e]	1.4452	.8085	49.92	49.85	9.20	9.26
1-Diethylamino-heptyne-2[f]	84–85 (10 mm.)	60[c] 55[b,d]	1.4450	.8071	55.16	54.94	8.31	8.37
1-Diethylamino-octyne-2	100/10 mm.	66[c]	1.4466	.8097	59.78	59.55	7.69	7.73

[a] Boiling point °C., corrected; atmospheric pressure unless otherwise indicated. [b] Based upon 1-diethylamino-2-bromopropene-2. [c] Based upon 1-diethylamino-propyne-2. [d] Straight through reaction, without isolating intermediate 1-diethylamino-propyne-2. [e] Xylene used as a solvent. [f] Previously prepared.[2,4]

distilled through a Vigreux column under reduced pressure. The fraction boiling from 93–96° (cor.) under 73 mm. (b. p. 54° under 10 mm.) was collected. The yield was 820 g., which corresponded to 85% of the theoretical amount, based upon the 2,3-dibromopropene-1 used.

Since 1-diethylamino-2-bromopropene-2 is somewhat unstable, it should be stored in brown bottles and kept in a refrigerator, where it may remain indefinitely with only slight decomposition.

1-Diethylaminopropyne-2.—In a 3-liter, 3-necked, round-bottomed flask equipped with a mercury-sealed stirrer, a dropping funnel, and a Dry Ice–acetone reflux condenser, 90 g. (2.3 moles) of sodamide was prepared in liquid ammonia. The contents of the flask were then brought up to a total volume of 2 liters by addition of liquid ammonia. In the dropping funnel was placed 192 g. (1.0 mole) of 1-diethylamino-2-bromopropene-2, which was added dropwise into the flask over a period of one hour. Refluxing of the ammonia was continued for a period of five hours after completion of the addition. The Dry Ice–acetone reflux condenser was then replaced by a tube leading into the hood, and the ammonia was allowed to evaporate. In three to four hours, the total volume had decreased to about 500 ml., and the reaction was stopped by cautiously adding 500 ml. of ether and 500 ml. of water into the flask. Stirring was continued until the ice had melted from the flask, at which time the contents of the flask were filtered. The ether layer in the filtrate was separated, dried over solid sodium hydroxide, and heated on a steam-bath until all ether was removed. The residue from the ether layer was then fractionated, collecting the portion boiling from 119–121° (cor.). The yield was 91.5 g., corresponding to 82.5% of the theoretical amount, based upon the 1-diethylamino-2-bromopropene-2.

1-Diethylamino-butyne-2.—In a 3-liter, 3-necked, round-bottomed flask equipped as above, there was prepared a solution of 30.5 g. (0.78 mole) of sodamide in 2 liters of liquid ammonia. In the dropping funnel was placed 66.5 g. (0.6 mole) of 1-diethylamino-propyne-2, which was added dropwise into the flask over a period of one-half hour. Stirring was then continued for a period of one hour to ensure the complete formation of the acetylide. The dropping funnel was rinsed with ether and replaced on the flask. In it was placed 110 g. (0.78 mole) of methyl iodide, which was added dropwise into the flask over a period of two hours. Refluxing of the ammonia was continued for a period of three hours after completion of this addition, at which time the reflux condenser was replaced by a tube leading into the hood. In three to four hours the total volume had decreased to about 500 ml., and the reaction was stopped by the cautious addition of 500 ml. of ether and 500 ml. of water. When the ice had melted from the flask, stirring was discontinued, and the contents of the flask were filtered. The ether layer was removed from the filtrate, dried over solid sodium hydroxide, and heated on a steam-bath until all ether was removed. The residue from the ether layer was then fractionated, collecting the portion boiling from 152–152.6° (cor.). The yield was 46 g., corresponding to 73.5% of the theoretical, based upon the 1-diethylaminopropyne-2.

Other 1-Diethylamino-alkynes.—The other alkyne derivatives in this series have been prepared as described above, except that in all other cases the alkyl bromide was used, and the reaction time was increased with increasing chain length of the alkyl group added up to ten hours in the preparation of 1-diethylamino-octyne-2.

In carrying this process straight through in liquid ammonia, without isolating the intermediate 1-diethylamino-propyne-2, 2.3 moles of sodamide were used for each mole of 1-diethylamino-2-bromopropene-2; and 1.3 moles of alkyl halide were added directly into the flask after completion of the time required for introduction of the triple bond. This method increases the over-all yields from 5–10% and results in a considerable saving of time.

1-Diethylamino-hex-5-en-2-yne.—The coupling reaction of allyl bromide with the sodium acetylide of 1-diethylamino-propyne-2 was carried out using xylene as a solvent since the coupling did not proceed in liquid ammonia to yield the expected product.

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Summary

A method has been devised for introducing a triple bond into tertiary amine molecules. By this method 1-diethylamino-propyne-2 has been prepared. By coupling the sodium acetylide of this compound with various alkyl halides, a series of 1-diethylamino-alkyne-2 compounds has been prepared and their physical constants established.

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