

potassium carbonate, 13.8 g. (0.1 mole), were mixed and allowed to stand at room temperature for 5 hr., 70° for 6 hr. and at 100° for 10 hr. The mixture was cooled, poured into water, and extracted with ether. The ether was dried with anhydrous magnesium sulfate, filtered, and evaporated to leave a viscous, nonvolatile orange liquid.

(b) In a 1-l. three-neck flask fitted with dropping funnel, Trubore stirrer, and condenser were placed 100 ml. of dry dimethyl sulfoxide and 4.8 g. (0.2 mole) of sodium hydride. Then benzyl chloride, 25.2 g. (0.2 mole), and 4-hydroxybutanone-2, 17.6 g. (0.2 mole), in 100 ml. of dry ether were added over 10 min. with external cooling. The mixture was stirred 22 hr. at room temperature and then poured into 600 ml. of water containing 10 ml. of concentrated hydrochloric

acid. Extraction and treatment as above gave only orange viscous oil.

(c) A reaction similar to (b), but in ether instead of dimethyl sulfoxide, turned to a viscous, rubbery mass within 20 min. After standing overnight the mixture became less rubbery and the stirrer could be moved. No volatile product could be isolated.

Acknowledgment.—The author is grateful to Professor C. S. Marvel for a postdoctoral research associateship and for constant encouragement and stimulation throughout the course of this work.

Acetylenic Amines. IV

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Received March 12, 1962

A method of preparing 1,1-diaryl- and 1-aryl-1-alkylpropargylamines is reported. This consists of preparing from the acetylenic alcohol, the 1,3-dichloropropylene derivatives, followed by treatment of this compound with the appropriate amine; this 3-chloroallylamine was then dehydrohalogenated to give the desired acetylenic amine.

Tertiary acetylenic chlorides, $RR^1C(Cl)C\equiv CH$ are known only where R and R^1 are aliphatic groups.^{1,2}

Thus, the Hennion synthesis³⁻⁵ of acetylenic amines [$RR^1C(NHR)^2C\equiv CH$] has been limited to products in which R and R^1 are aliphatic groups. The reaction of the aromatic acetylenic carbinols (R and/or $R^1 = C_6H_5$, etc.) with hydrochloric acid, thionyl chloride, etc., has been claimed to produce chloroallenes² or dimers⁶ thereof.

Treatment of the chloroallene with a primary or secondary amine gives the conjugated Schiff's base rather than the α -acetylenic amines. Isolation of compounds of the Schiff's base type has been accomplished⁵ when the crude aliphatic chloroacetylenes were treated with lithium *t*-butylamide.

In the present study it was found that in a large-scale preparation of 3-ethylamino-3-methyl-1-butyne from the crude chloroacetylene, a considerable amount of high-boiling basic material was present. From this fraction there was isolated a material which appeared to be an ethylenic amine with one chlorine atom in the molecule. This compound was assigned the structure (IIa. $R^2 = C_2H_5$) from its elemental analyses; the structure was confirmed with infrared and n.m.r. spectra. It has been

reported⁷ that, when 3-methylbutyn-3-ol was treated with hydrochloric acid, among the products obtained was a dichloro-3-methylbutene. Of the two possible structures, Ia and IV, the authors favored structure Ia. This dichlorobutene (Ia) could react with the amine to give the product IIa.

If this be the case, it should be possible also in the aromatic series to add an additional mole of hydrogen chloride to the chloroallene to give the dichloride Ib.

The treatment of an ether solution of 3,3-diphenyl-1-propyn-3-ol with dry hydrogen chloride at room temperature gave a yellow solution from which the chloroallene could be isolated. Treatment of the product, at this point, with *t*-butylamine gave only the conjugated Schiff's base, the structure of which was confirmed by reduction to *N*-(*t*-butyl)-3,3-diphenylpropylamine. However, addition of more hydrogen chloride at 5-6° caused a color change to green, and the crude dichloropropene Ib could be isolated readily from this mixture. Treatment of Ib with ethylamine gave IIB, which was easily isolated by vacuum distillation of the basic fraction. Dehydrohalogenation of IIB with sodamide in liquid ammonia then gave the desired acetylene IIIB.

The infrared spectra were sufficient to assign the structures of the acetylenic amines, and these assignments were confirmed by the n.m.r. spectra. However, the structure of the intermediate chloro compounds II was not as readily established. In attempting to confirm the assignment of the chlo-

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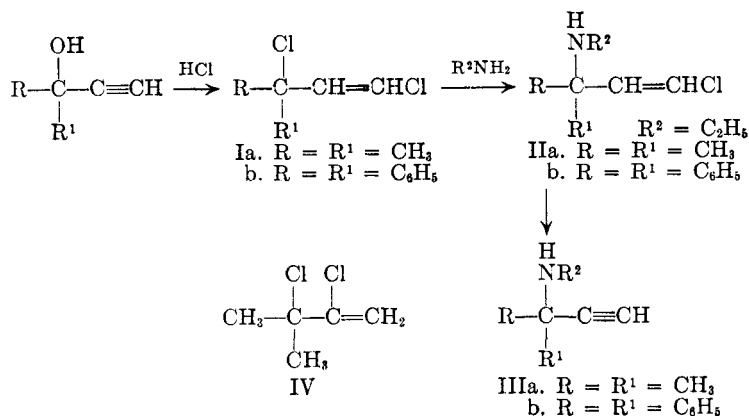
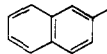



TABLE I

Ar	R	R ¹	B.p. ^a		M.p., °C.	Empirical formula	Calcd.	Found
			°C.	Mm.				
C ₆ H ₅	CH ₃	H	70-72	4	217-219	C ₁₀ H ₁₂ ClN	C, 66.11 H, 6.66	C, 66.45 H, 6.83
C ₆ H ₅	CH ₃	C ₂ H ₅	77-80	4	195-196	C ₁₂ H ₁₆ ClN	C, 68.72 H, 7.69	C, 68.55 H, 7.55
C ₆ H ₅	CH ₃	CH ₂ CH=CH ₂	88	4	177-179	C ₁₃ H ₁₆ ClN	C, 70.42 H, 7.27	C, 70.63 H, 7.47
C ₆ H ₅	CH ₃	CH ₃ (CH ₂) ₃	62-64	0.03	144-146	C ₁₄ H ₂₀ ClN	C, 70.72 H, 8.48	C, 70.72 H, 8.60
C ₆ H ₅	CH ₃	(CH ₃) ₃ C	86-88	4	190-191	C ₁₄ H ₂₀ ClN	C, 70.72 H, 8.48	C, 70.57 H, 8.51
C ₆ H ₅	CH ₃	Cyclohexyl	85-86	0.1	203-205	C ₁₆ H ₂₂ ClN	C, 72.84 H, 8.41	C, 72.67 H, 8.26
<i>p</i> -CH ₃ C ₆ H ₄	CH ₃	C ₆ H ₅ CH ₂	140-150	.2	189-191	C ₁₅ H ₁₈ ClN	C, 75.64 H, 7.05	C, 75.82 H, 6.97
<i>p</i> -ClC ₆ H ₄	CH ₃	C ₂ H ₅	63-64	.03	152-154	C ₁₂ H ₁₄ ClN ^a	C, 69.39 H, 6.79	C, 69.31 H, 6.81
	CH ₃	C ₂ H ₅	110-125	.1	205-207	C ₁₆ H ₁₈ ClN	C, 73.97 H, 6.98	C, 74.23 H, 7.05
C ₆ H ₅	C ₆ H ₅	H	72-74 ^b	—	203-205	C ₁₅ H ₁₄ ClN	C, 73.91 H, 5.79	C, 73.72 H, 5.91
C ₆ H ₅	C ₆ H ₅	C ₂ H ₅	115-120	.05	155-157	C ₁₇ H ₁₈ ClN	C, 75.12 H, 6.68	C, 75.06 H, 6.87
C ₆ H ₅		C ₂ H ₅	110-112	.04	132-134	C ₁₅ H ₁₆ ClNS	C, 64.85 H, 5.81	C, 65.12 H, 5.65

^a Free base. ^b Melting point.

rine on the terminal carbon atoms by means of the n.m.r. spectra it was found that the free base of II (R = CH₃, R¹ = *p*-ClC₆H₄, R² = C₂H₅) showed a *single* peak at $\tau = 3.87$ which indicated that the protons had the same chemical shift and therefore suggested that they might be on the same carbon atom. However, the hydrochloride showed a typical AB system with a splitting constant of 13 c.p.s. and with chemical shifts⁸ of $\tau = 3.69$ and $\tau = 3.33$. Since the spin-spin coupling constants

listed⁹ for 1,1-hydrogens are 0-3.5 c.p.s., for *cis* 1,2-hydrogens, 6-14 c.p.s., and for *trans* 1,2-hydrogens, 11-18 c.p.s., the data from the hydrochloride clearly shows a 1,2-hydrogen system but makes the assignment of *cis* or *trans* questionable.

This new synthesis appears to be relatively general and makes possible the preparation of a wide variety of α -acetylenic amines containing aromatic groups. The yields of the chloroallylamines range from 10-35%, and the yields of the acetylenic amines from the chloroallylamines were from 50-70%.

These new α -acetylenic amines undergo the typical reactions^{1,2} of the aliphatic α -acetylenic amines such as semihydrogenation and hydration.

(8) This was calculated by use of the equation⁸ $(1-3) = (2-4) = \sqrt{(\delta_B - \delta_A)^2 + J_{AB}^2}$.

(9) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959.

Experimental

As a general rule, the dichloro compounds were not isolated. The crude product from the treatment with hydrogen chloride was concentrated at reduced pressure and treated with the amine. It was usually found advantageous to partially purify the aminochloropropene by distillation and then purify the acetylenic amine. The 3-phenyl-1-butyne-3-ol was generously supplied by the Air Reduction Chemical Co. Melting points are uncorrected and were taken in an open capillary tube.

N-Ethyl-1,1-diphenylpropargylamine.—Dry hydrogen chloride was bubbled into a mixture of 36.5 g. of 3,3-diphenyl-1-propyne-3-ol in 500 ml. of ether at room temperature for 1 hr. The mixture was then cooled to 0° and the addition of hydrogen chloride continued for 3 hr. The mixture was concentrated at reduced pressure. The residue was dissolved in ether, the ether solution was dried over magnesium sulfate, filtered, and concentrated at reduced pressure. The greenish residual oil was kept at a pressure of 6 mm. for 30 min.

Anal. Calcd. for $C_{15}H_{12}Cl_2$: Cl, 26.84. Found: Cl, 26.30. (Very few of these crude dichlorides had publishable analyses.)

A mixture of crude 1,3-dichloro-3,3-diphenyl-1-propene and an excess of ethylamine was kept at 20–22° for 3 days. The excess ethylamine was evaporated, and the residue was taken up in ether; the ether solution was washed with dilute hydrochloric acid and then with concentrated hydrochloric acid. The acid layers were combined and made basic with sodium hydroxide; the mixture was then extracted with ether, and the ether layer was dried over magnesium sulfate. The ether was removed at reduced pressure and the residue distilled. Material boiling at 135–150°/0.1 mm. was collected and used in the next experiment.¹⁰

An ethereal solution of 5 g. of 3-chloro-N-ethyl-1,1-diphenylallylamine was added dropwise to a solution of sodamide (from 3 g. of sodium) in 500 ml. of liquid ammonia. The resulting mixture was stirred for 1 hr., after which it was diluted with 300 ml. of ether. The mixture was stirred as it was allowed to come to room temperature. The mixture was washed with 100 ml. of water and dried over magnesium sulfate. It was then concentrated at reduced pressure and the residue distilled; b.p. 100–104°/0.01 mm.

Anal. Calcd. for $C_{17}H_{17}N$: C, 86.77; H, 7.28. Found: C, 86.55; H, 7.43.

The hydrochloride was recrystallized from methyl ethyl ketone and melted at 155–157°.

Anal. Calcd. for $C_{17}H_{18}NCl$: C, 75.12; H, 6.68. Found: C, 75.06; H, 6.87.

N-*t*-Butyl-3,3-diphenylacrylaldimine Hydrochloride.—Dry hydrogen chloride was bubbled into a mixture of 36.5 g. of 3,3-diphenyl-1-propyne-3-ol in 500 ml. of ether (acetic acid can also be used) at room temperature for 1 hr., by this time the mixture had turned yellow. The ether was distilled at reduced pressure, and the residue was added to a mixture containing 75 g. of *t*-butylamine, 25 g. of water, 1 g. of cuprous chloride, and 1 g. of copper-bronze powder.

After stirring overnight, the mixture was poured into 500 ml. of water. This mixture was extracted with ether, the ether solution was washed with water, dried, and concentrated. The N-*t*-butyl-3,3-diphenylacrylaldimine boiled at 118–122° under 0.07 mm. The hydrochloride was recrystallized from a mixture of isopropyl alcohol and methyl ethyl ketone, m.p. 235–236°.

Anal. Calcd. for $C_{19}H_{22}ClN$: C, 76.11; H, 7.40. Found: C, 76.02; H, 7.10.

N-(*t*-Butyl)-3,3-diphenylpropylamine Hydrochloride.—The Schiff's base was hydrogenated in ethanol over platinum oxide. The catalyst was filtered and the solvent removed at reduced pressure. The hydrochloride was prepared, m.p. 233–235° (recrystallized from methyl ethyl ketone-isopropyl alcohol).

Anal. Calcd. for $C_{19}H_{26}NCl$: C, 75.10; H, 8.63. Found: C, 75.36; H, 8.80.

N-(*t*-Butyl)-3,3-diphenylallylamine Hydrochloride.—The Schiff's base was hydrogenated in ethanol over Raney nickel until 1 mole of hydrogen had been absorbed. The catalyst was filtered, the alcohol was distilled at reduced pressure, and the hydrochloride was made from the residual oil. After recrystallization from methyl ethyl ketone it melted at 198–200°.

Anal. Calcd. for $C_{19}H_{24}ClN$: C, 75.60; H, 8.01. Found: C, 75.56; H, 8.09.

3-Ethylamino-3-phenyl-2-butanone.—To a well stirred suspension of 60 g. of sulfuric acid, 44 ml. of methanol, 56 ml. of water, and 4 g. of mercuric oxide there was added slowly 30 g. (0.173 mole) of N-ethyl-1-phenyl-1-methylpropargylamine; air was bubbled into the mixture during the addition and the ensuing heating period. The mixture was refluxed for 4 hr., cooled, and filtered. The solution was made basic with aqueous sodium hydroxide and extracted with ether. The ether was dried and concentrated at reduced pressure. The product (17.5 g., 53% yield) distilled at 100–102° at 4 mm. pressure.

Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96. Found: C, 75.00; H, 9.06.

N-Ethyl-2-phenyl-3-butenyl-2-amine Hydrochloride.—The acetylenic amine was hydrogenated at 40–50 p.s.i. in petroleum ether (b.p. 60–68°) over 5% palladium-on-carbon. The hydrochloride was prepared and recrystallized from an ethyl acetate-ethyl ether mixture, m.p. 129–130°.

Anal. Calcd. for $C_{13}H_{19}ClN$: C, 68.07; H, 8.57. Found: C, 67.88; H, 8.77.

N-Ethyl-2-phenyl-2-butylamine Hydrochloride.—The acetylenic amine was hydrogenated over Raney nickel in alcohol. The hydrochloride was recrystallized from ethyl acetate, m.p. 155–157°.

Anal. Calcd. for $C_{12}H_{20}ClN$: C, 67.42; H, 9.43. Found: C, 67.47; H, 9.47.

Acknowledgment.—The microanalyses were performed by Messrs. William Brown, Howard Hunter, George Maciak, and Alfred Brown. The infrared spectra were obtained by Mrs. Doris Stephens and Miss Martha Hoffmann. The authors especially wish to thank Messrs. Paul Landis and Donald Woolf, Jr., for their invaluable services in interpreting and compiling the infrared and n.m.r. data. The authors also express their sincere appreciation to Dr. George Hennion for his many helpful suggestions and much appreciated encouragement.

(10) Two compounds in this series were isolated as hydrochlorides (recrystallized from methyl ethyl ketone).

1-Chloro-N-ethyl-3-phenyl-1-butenyl-3-amine hydrochloride; m.p. 169–171°. *Anal.* Calcd. for $C_{12}H_{17}Cl_2N$: C, 58.54; H, 6.96. Found: C, 58.76; H, 7.12.

1-Chloro-N-ethyl-3-*p*-chlorophenyl-1-butenyl-3-amine hydrochloride; m.p. 175–177°. *Anal.* Calcd. for $C_{12}H_{16}Cl_2N$: C, 51.36; H, 5.75. Found: C, 51.08; H, 6.00.