Polymethylarsonodimethylsiloxane (VI).—Ten g. of bis-(dimethylchlorosilyl)-methylarsonate was dissolved in 100 ml. of carbon tetrachloride and added gradually from a separatory funnel through a tube reaching into 100 ml. of CCl_4 agitated with 300 ml. of water, at about 40–50°, during 25–35 minutes. After cooling to room temperature and subsequent washing with water to remove hydrochloric acid found during hydrolysis, the CCl_4 (bottom) layer was drawn off, dried over anhydrous Na_2SO_4 and the solvent removed under atmospheric and reduced pressure. Three and six-tenths g. of VI, a translucent, rubbery material was obtained.

Anal. Calcd. for $C_{25}H_{75}O_{14}Si_{12}As$: Si, 33.3; As, 7.4; C, 29.7; H, 7.4. Found: Si, 33.6; As, 7.7; C, 29.8; H, 8.1.

Polymethylarsonomethylsiloxane (VII).—One hundred and nine g. of bis-(methyldichlorosilyl)-methylarsonate was leached with boiling water for about 1 hr., washed thoroughly with water of room temperature, filtered off and dried. Forty-five g. of VII, a fine white powder, was obtained.

Anal. Calcd. for $C_{13}H_{39}O_{20}Si_{12}As$: Si, 36.3; As, 8.1; C, 15.5; H, 3.9. Found: Si, 37.1; As, 7.5; C, 15.8; H, 4.6.

The above VI and VII thus appear to be copolymers of the previously given formula where X is about 12.

The aromatic chlorosilylarsonates were found to be soluble in bromobenzene which is a suitable solvent for this type of controlled hydrolysis.[3] Essentially, the same method of hydrolysis was performed as described before. So far only impure polymers have been obtained as the result of this hydrolysis. The infrared data were obtained by means of a Perkin-Elmer Double Beam Recording Infrared Spectrophotometer, Model 21. Data on infrared absorption maxima, characteristic for regular siloxane compounds, were available from the literature.[4] Unpublished data on infrared absorption maxima, characteristic for organoarsenic compounds, were available from known or novel organic arsenicals, such as methylarsonic acid, arsenomethane As-1,2-disulfide[5] and others. Compound I was examined as liquid film in capillary thickness, whereas compound VII had to be used as 2% solution in chloroform. Polydimethylsiloxane, General Electric Co.—SF-96 (300), was used as a standard reference.

INFRARED ABSORPTION CHARACTERISTICS[6]

Compound	Microns	Intensity	Assignment
Bis-(dimethylchlorosilyl) methylarsonate	3.40	Strong	C–H stretching (for $Si-CH_3$)
	5.10	Strong	
	5.50	Strong	
	6.20	Weak	As=O (As → O)
	6.75	Strong	As–C
	7.10	Strong	C–H bending
	7.95	Strong	$Si-CH_3$ rocking
	9.5	Strong, broad	Si–O stretching
	10.8	Strong, broad	
	11.6	Strong, broad	Si–C stretching
Polymethylarsonodimethylsiloxane	3.40	Strong	C–H stretching (for $Si-CH_3$)
	5.10	Weak	
	6.20	Strong	As=O (As → O)
	6.75	Weak	As–C
	7.15	Strong	C–H bending
	7.95	Strong	$Si-CH_3$ rocking
	9.50	Strong, broad	Si–O stretching
	11.65	Strong, broad	Si–C stretching
Polydimethylsiloxane	3.40	Strong	C–H stretching (for $Si-CH_3$)
	7.10	Medium	C–H bending
	7.95	Strong	$Si-CH_3$ rocking
	9.50	Strong, broad	Si–O stretching
	11.60	Medium	Si–C stretching
	12.50	Strong, broad	

Acknowledgments.—The authors wish to express their appreciation to Dr. P. A. van der Meulen and M. F. Borek of Rutgers University Chemistry Department for the infrared data and to Messrs. W. E. Bell and K. C. Braun for their assistance in the Experimental part reported in this paper.

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[3] C. E. Welsh and N. G. Holdstock, U. S. Patent 2,661,348 (1953); *C. A.*, **48**, 3063 (1954).

[4] N. Wright and M. J. Hunter, THIS JOURNAL, **69**, 803 (1947).

[5] R. M. Kary, U. S. Patent 2,646,440 (1953).

(6) Material supplementary to this article has been deposited as Document number 5076 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

PLAINFIELD, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Kinetics of the Hydrolysis of Acetylenic Chlorides and Their Reactions with Primary and Secondary Aliphatic Amines[1]

BY G. F. HENNION AND KENNETH W. NELSON[2]

RECEIVED NOVEMBER 30, 1956

Acetylenic chlorides of the type RR′C(Cl)—C≡CH undergo very slow solvolysis in 80% ethanol at 25°. The rate is accelerated by addition of sodium hydroxide, and the reactions then commonly follow second-order kinetics. Primary and secondary aliphatic amines are smoothly alkylated by these halides. The mechanisms of these reactions are discussed.

Discussion

It was reported in a previous paper[3] in this series that 3-chloro-3-methyl-1-butyne undergoes extremely slow solvolysis in 80% ethanol at 25° (k_1 = 7.4 × 10^{-4} hr.$^{-1}$). This was attributed to lack of steric strain, despite the tertiary structure, and the inductive (electron-withdrawing) effect of the ethynyl group. Burawoy and Spinner[4] have verified these findings (k_1 said to be 8.48 × 10^{-4} hr.$^{-1}$) in a recent study of the behavior of alkylethynyldimethylcarbinyl chlorides. It is interesting to note from the latter work that when the ethynyl hydrogen atom is replaced by an alkyl group, the rate of solvolysis is increased by a factor of 1000. In the presence of dissolved alkali, 3-chloro-3-methyl-1-butyne reacts by second-order

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[1] Paper LXIV on substituted acetylenes; previous paper, *J. Org. Chem.*, **21**, 1142 (1956).

[2] Miles Laboratories Fellow, 1954–1955; Reilly Fellow, 1955–1956. Abstracted from the Ph.D. Dissertation of K. W. N., 1956.

[3] G. F. Hennion and D. E. Maloney, THIS JOURNAL, **73**, 4735 (1951).

[4] A. Burawoy and E. Spinner, *J. Chem. Soc.*, 3752 (1954).

kinetics.[3,4] The product of this reaction is the unexpected 3-ethoxy-3-methyl-1-butyne.[3] To account for this product as well as the second-order rate observed for the reaction, the following mechanism was proposed.[3]

$$R_2C(Cl)C{\equiv}CH \xrightarrow{+OH^{\ominus}} R_2C(Cl)C{\equiv}C^{\ominus} \xrightarrow{-Cl^{\ominus}}$$

$$(R_2\overset{\oplus}{C}C{\equiv}C^{\ominus} \longleftrightarrow R_2C{=}C{=}C:) \xrightarrow{C_2H_5OH} R_2C(OC_2H_5){-}C{\equiv}CH$$

This mechanism was supported by later work in this Laboratory[5] as well as by the findings of Burawoy and Spinner[4] who demonstrated that second-order kinetics are *not* observed when the ethynyl hydrogen is replaced by alkyl.

The present study was undertaken to provide further evidence for the mechanism cited above. The rates of the reactions of the acetylenic chlorides listed in Tables I and II have now been measured. All undergo extremely slow solvolysis in 80% ethanol at 25° (Table I). In two cases, namely, 1-ethynylcyclohexyl chloride and 3-chloro-1-hexyne, the rate was too slow to measure. Reinvestigation of the solvolysis of 3-chloro-3-methyl-1-butyne gave a rate constant of 9.0 × 10^{-4} hr.$^{-1}$ in agreement with the previously published values.[3,4] This rate is 1/61 of that for *t*-amyl chloride, the saturated analog, under the same conditions.[6] Likewise, the ratio of the rate of solvolysis of 3-chloro-3-methyl-1-pentyne to that of 3-chloro-3-methylpentane is 1/69, and the ratio of the rate for 3-chloro-3-ethyl-1-pentyne to that of 3-chloro-3-ethylpentane is 1/62. The unique stabilizing influence of the ethynyl group is thus clearly demonstrated. When sodium hydroxide was added, other conditions remaining the same, the reactions were faster and usually followed clean second-order kinetics (Table II). In the case of 3-chloro-3-methyl-1-butyne, the rate constant was 1.29 l./mole hr. in excellent agreement with the earlier value[3] (1.2–1.4 l./mole hr.) but in only fair agreement with the Burawoy and Spinner measurement[4] (2.56 l./mole hr.). In two cases, namely, 3-chloro-1-hexyne and 3-chloro-3-phenyl-1-propyne, both secondary halides, clean second-order kinetics could not be obtained.

TABLE I

THE SOLVOLYSIS OF ETHYNYLCARBINYL CHLORIDES, RR'C(Cl)C≡CH, IN 80% ETHANOL AT 25°

RR'C(Cl)C≡CH R	R'	Initial concn., mole/l.	$k_1 \times 10^4$ hr.$^{-1}$ Exptl.	Mean
CH_3	CH_3	0.08336	9.02	
		.1430	8.98	9.00
CH_3	C_2H_5	.07764	12.4	
		.1049	12.3	12.4
C_2H_5	C_2H_5	.06834	16.1	
		.08623	16.1	16.1
CH_3	*i*-C_4H_9	.07002	35.5	
		.07002	34.8	35.2
$-CH_2(CH_2)_3CH_2-$[a]			[c]	
C_6H_5	H	.09684	1670	
		.1267	1680	
		.09752	1690	1680
n-C_3H_7	H		[c]	
t-Amyl chloride		.06213	530	530[b]

[a] 1-Ethynylcyclohexyl chloride. [b] Literature value, 550 × 10^{-4} hr.$^{-1}$ (ref. 6). [c] Too slow to measure.

TABLE II

THE REACTIONS OF ETHYNYLCARBINYL CHLORIDES WITH SODIUM HYDROXIDE IN 80% ETHANOL AT 25°

RR'C(Cl)C≡CH R	R'	c_0 RCl, mole/l.	c_0 NaOH, mole/l.	k_2, l./mole. hr. Exptl.	Mean
CH_3	CH_3	0.1800	0.08968	1.26	
		.09000	.08968	1.30	
		.09000	.08968	1.29	
		.09000	.1789	1.25	
		.09000	.1804	1.26	1.27
CH_3	C_2H_5	.1433	.07104	1.13	
		.1433	.07180	1.13	
		.07168	.07180	1.16	
		.07168	.07164	1.17	
		.07168	.1440	1.12	1.14
C_2H_5	C_2H_5	.1428	.07116	1.08	
		.07141	.07141	1.04	
		.07141	.07141	1.07	1.06
$-CH_2(CH_2)_3CH_2-$		.1875	.09143	0.240	
		.09375	.09375	.234	
		.09375	.1789	.218	
		.09375	.1793	.218	0.227
CH_3	*i*-C_4H_9	.08229	.08241	2.67	
		.08229	.08220	2.64	2.66
C_6H_5	H	No clean second-order reaction			
n-C_3H_7	H	No clean second-order reaction			

While these data are in complete agreement with the mechanism cited above, additional evidence for this mechanism was sought and was found in the reactions of the acetylenic chlorides with primary and with secondary amines. It is well known that tertiary aliphatic halides are not suitable for the alkylation of amines since such halides are too sensitive to HX elimination. It has been stated[7] without qualification that "amines of tertiary alkyl groups are not obtainable from the halide." The mechanism pictured above suggests *a priori* that amines which are strong bases and good nucleophilic reagents should be alkylated by acetylenic halides. This has now been found to be true and the simple reaction

$$RR'C(Cl){-}C{\equiv}CH + 2R_2NH \longrightarrow RR'C(NR_2){-}C{\equiv}CH + R_2NH{\cdot}HCl$$

gives good yields of products in a variety of applications (Table III).

The reaction of 3-chloro-3-ethyl-1-pentyne with aqueous ammonia was tried in an attempt to prepare 3-amino-3-ethyl-1-pentyne. The reaction was carried out at 100° in an autoclave. Approximately 30% of the starting material suffered HCl elimination to produce 3-ethyl-3-pentene-1-yne, the remainder being hydrolyzed to the corresponding carbinol, 3-ethyl-1-pentyne-3-ol. It appears therefore that aqueous ammonia is not sufficiently basic, even though less steric hindrance is involved in comparison with the amines used, to initiate the mechanism necessary for amine formation.

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(5) G. F. Hennion and E. G. Teach, THIS JOURNAL, **75**, 1653 (1953).

(6) H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949).

(7) F. C. Whitmore, "Organic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1937, p. 76.

Further work is in progress, particularly to determine the limitations of alkylation reactions with acetylenic halides.

Experimental

Acetylenic Carbinols.—Generous samples of 3-methyl-1-butyne-3-ol, 3-methyl-1-pentyne-3-ol, 3-ethyl-1-pentyne-3-ol, 3,5-dimethyl-1-hexyne-3-ol and 1-ethynyl-cyclohexanol were obtained from Air Reduction Chemical Co. and from Reilly Tar and Chemical Co. 1-Hexyne-3-ol was prepared by the reaction of freshly distilled butyraldehyde and sodium acetylide in anhydrous liquid ammonia as previously described.[8] Likewise, 3-phenyl-1-propyne-3-ol was prepared by the reaction of freshly distilled benzaldehyde with sodium acetylide in anhydrous liquid ammonia.

All fractional distillations, except as noted, were carried out with a 40 × 1.2 cm. column fitted with a total reflux, partial take-off distilling head, hereafter referred to as column A. All boiling points and melting points are uncorrected.

Preparation of 3-Chloro-3-methyl-1-butyne.—This compound was prepared by the reaction of 1300 ml. (15 moles) of cold concentrated hydrochloric acid (0°) containing three moles of anhydrous calcium chloride with three moles of 3-methyl-1-butyne-3-ol as described earlier.[9] The crude chloride was distilled from potassium carbonate through column A; yield, 138 g. (45%), b.p. 33–36° (175 mm.). Triple distilled material, b.p. 75.5–75.6°, $n^{25}\mathrm{D}$ 1.4145, was used for kinetic studies.

Preparation of 3-Chloro-3-methyl-1-pentyne and 3-Chloro-3-ethyl-1-pentyne.—These compounds were prepared by the reaction of 3-methyl-1-pentyne-3-ol and 3-ethyl-1-pentyne-3-ol with five times the theoretical amount of cold concentrated hydrochloric acid as described previously.[5] Crude 3-chloro-3-methyl-1-pentyne was obtained in 53% yield, b.p. 51–54° (120 mm.). Triple distilled material, b.p. 51.9–52.2° (115 mm.), $n^{25}\mathrm{D}$ 1.4307, was used for kinetic studies. Crude 3-chloro-3-ethyl-1-pentyne was obtained in 62% yield, b.p. 70–75° (100 mm.). Triple distilled material, b.p. 71.9–72.2° (101 mm.), $n^{25}\mathrm{D}$ 1.4396, was used for kinetic studies.

Preparation of 3-Chloro-1-hexyne.—This compound was prepared by the reaction of 1 mole (100 g.) of 1-hexyne-3-ol with 1.1 moles (130 g.) of thionyl chloride, using 5 g. of pyridine as a catalyst.[8] Fifty-one grams (43% yield) of crude product, b.p. 61–65° (100 mm.), was obtained in this manner. Triple distilled material, b.p. 63.1–63.4° (97 mm.), $n^{25}\mathrm{D}$ 1.4366, was used for the kinetic work.

Preparation of 3-Chloro-3-phenyl-1-propyne.—This compound was prepared by the reaction of 1.14 moles (150 g.) of 3-phenyl-1-propyne-3-ol with 1.25 moles (150 g.) of thionyl chloride using five grams of pyridine as a catalyst; yield 70 g. (41%), b.p. 100–104° (18 mm.). Triple distilled material, b.p. 45.8–46.0° (1.0 mm.), $n^{25}\mathrm{D}$ 1.5478, was used for kinetic studies.

Preparation of 1-Ethynylcyclohexyl Chloride.—Approximately 0.2 mole of freshly prepared cuprous chloride (CuCl) was dissolved in 430 ml. (5 moles) of cold concentrated hydrochloric acid contained in a 2-l. separatory funnel. One hundred and twenty-four grams (1 mole) of freshly distilled 1-ethynylcyclohexanol was then added. After 1 hr. of intermittent shaking, the lower layer was separated and discarded. The upper layer was washed twice with 200-ml. portions of concentrated hydrochloric acid to remove most of the adhering cuprous chloride and then shaken with anhydrous potassium carbonate. After this preliminary neutralization, the reaction mixture was dried overnight over a fresh layer of anhydrous potassium carbonate. Distillation through column A gave 100 g. (70% yield) of crude 1-ethynylcyclohexyl chloride, b.p. 56–58° (10 mm.). Triple distilled material, b.p. 55.0° (13 mm.), $n^{25}\mathrm{D}$ 1.4795, was used for kinetic studies.

Preparation of 3-Chloro-3,5-dimethyl-1-hexyne.—One hundred and twenty-six grams (1 mole) of 3,5-dimethyl-1-hexyne-3-ol and 5 ml. of concentrated hydrochloric acid were placed in a 500-ml. three-neck round-bottom flask fitted with a stirrer, gas inlet tube and thermometer. Dry hydrogen chloride gas was passed into the carbinol at a rate of approximately 4 to 5 bubbles per second. The reaction mixture was periodically cooled with running water to maintain the temperature at 20–25°. After 52 g. of hydrogen chloride had been absorbed, the addition of the gas was terminated. The reaction mixture was placed in a separatory funnel and the small water layer was removed. After two washings with 200 ml. of water, the organic layer was dried overnight with anhydrous potassium carbonate. Distillation through column A gave 55 g. (38%) of chloride, b.p. 56–63° (39 mm.). The first fractions from this distillation were found to contain a considerable amount of an unidentified impurity containing a conjugated double bond system as indicated by the infrared spectrum. Five distillations were required to give a product which was suitable for kinetic studies; b.p. 56.7–57.0° (39 mm.), $n^{25}\mathrm{D}$ 1.4370.

Preparation of Solutions for Kinetic Studies.—The ethanol (80%) was prepared by mixing four volumes of absolute ethanol and one volume of freshly boiled distilled water. The densities of two batches prepared in this manner were found to be 0.8495 and 0.8498 at 25.0°. A carbonate-free solution of sodium hydroxide in 80% ethanol was prepared by dissolving approximately 17 g. of crushed sodium hydroxide pellets in 100 ml. of 80% ethanol. Filtration of this solution through a sintered glass funnel and dilution with one liter of 80% ethanol gave an approximately $0.4N$ sodium hydroxide solution. Standardization of the above solution as well as that of aqueous hydrochloric acid and aqueous sodium hydroxide were performed with potassium acid phthalate and sodium carbonate using as an indicator a mixture consisting of two parts of 0.1% methyl red solution and three parts of 0.1% brom cresol green solution, both in absolute ethanol.[10]

General Kinetic Procedures, First-order Rate Constants.—A sample of halide (*ca.* 1–2 g.) was weighed in a thin-walled glass ampoule and sealed. The ampoule was crushed under solvent previously adjusted to 25.0°. The solution was rapidly transferred to a 100-ml. volumetric flask, diluted to the mark with more solvent, mixed and returned to the constant temperature bath. Periodically, approximately every 24 hr., 10-ml. aliquots were removed by a pipet, quenched in 50 ml. of absolute methanol and titrated immediately with standard sodium hydroxide using the forementioned indicator. A total of six to eight aliquots were taken from each reaction, following the first 30–60% reaction. The first-order rate constants were calculated from the integrated rate expression.

Second-order Rate Constants.—A sample of halide (*ca.* 4–5 g.) was weighed in a 50-ml. volumetric flask. The flask was then filled to the mark with 80% ethanol, the temperature of which was previously adjusted to 25°; 5- or 10-ml. aliquots of this solution were placed in 100-ml. flasks. A predetermined amount of standard sodium hydroxide in 80% ethanol (delivered from a buret) was added to the 100-ml. flasks, and the flasks were filled to the mark with 80% ethanol, shaken and returned to the constant temperature bath. Periodically, approximately every hour, 10-ml. aliquots were removed and quenched in 5 or 10 ml. of standard acid dissolved in absolute methanol. Each aliquot was then back-titrated with standard base. A total of six to eight aliquots were taken from each reaction covering the first 30–70% reaction. The second-order rate constants were calculated from the appropriate integrated rate expressions.

Preparation of 3-Dimethylamino-3-methyl-1-butyne Hydrochloride.—Ten grams of 3-chloro-3-methyl-1-butyne and 50 ml. of 40% aqueous dimethylamine were placed in a stout bottle and shaken mechanically for a period of 15 hr. The orange colored solid was collected by filtration, dissolved in 100 ml. of ether and dried over potassium hydroxide pellets. The hydrochloride of this amine was precipitated by addition of excess hydrogen chloride dissolved in absolute ether. After collection by suction filtration, this material was recrystallized from an ethyl acetate-ethanol mixture; yield 10 g. (70%) of material melting at 241–242.5° dec. A small sample of the free base was isolated and purified by sublimation, m.p. 99–102°.

Preparation of 3-Pyrrolidino-3-methyl-1-butyne.—Twenty-five grams of 3-chloro-3-methyl-1-butyne, 60 ml. of pyrrolidine and 20 ml. of water were placed in a 125-ml. erlenmeyer flask and set aside for 24 hr. The product was collected by filtration and washed with water. Recrys-

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(8) G. F. Hennion and J. J. Sheehan, THIS JOURNAL, **71**, 1964 (1949).

(9) G. F. Hennion, *et al.*, *ibid.*, **72**, 3542 (1950).

(10) H. C. Brown, *et al.*, *ibid.*, **76**, 4515 (1954).

TABLE III

ACETYLENIC AMINES FROM ACETYLENIC CHLORIDES

	$R^1R^2C(NR^3R^4)—C\equiv CH$				B.p.,					
Cmpd.	R^1	R^2	R^3	R^4	°C.	Mm.	M.p., °C.	$n^{25}D$	d^{25}	Yield, %
I[a]	CH_3	CH_3	CH_3	CH_3			99–102			70
II	CH_3	CH_3	$(CH_2)_4$				76–78			62
III	$(CH_2)_5$		$(CH_2)_4$				65–66.5			73
IV	$(CH_2)_5$		$(CH_2)_5$				94–95.5			60
V	$(CH_2)_5$		CH_3	CH_3			57–58.5			68
VI[b]	CH_3	C_2H_5	C_2H_5	H	74–79	120		1.4308		52
VII	C_3H_7	H	$(CH_2)_4$		70–72	11		1.4597	0.8693	63
VIII	C_3H_7	H	C_4H_9	H	71–72	11		1.4365	0.8043	56

[a] *Cf.* G. F. Hennion and J. M. Campbell, *J. Org. Chem.*, **21**, 792 (1956). [b] *Cf.* G. F. Hennion and E. G. Teach, THIS JOURNAL, **75**, 4298 (1953).

TABLE IV

ACETYLENIC AMINE DERIVATIVES AND ANALYTICAL DATA

				Hydrochloride			Methiodide		
		Nitrogen, %			Nitrogen, %			Nitrogen, %	
Cmpd.	Mol. formula	Calcd.	Obsd.	M.p., °C.	Calcd.	Obsd.	M.p., °C.	Calcd.	Obsd.
I	$C_7H_{13}N$[a]			241–242.5	9.49	9.69			
II	$C_9H_{15}N$[a]			232–233	8.07	8.30	181–182	5.02	5.12
III	$C_{12}H_{19}N$	7.90	8.02	235–236	6.55	6.78	155–157	4.39	4.30
IV	$C_{13}H_{21}N$	7.32	7.50	239–240	6.15	5.87	181–182	4.20	4.29
V	$C_{10}H_{17}N$[a]			222–223	7.46[b]	7.46	175	4.78	4.50
VII	$C_{10}H_{17}N$	9.26	9.37	176–177	7.46	7.59	131–133	4.78	4.64
VIII	$C_{10}H_{19}N$	9.14	9.35	166	7.38	7.21			

[a] Too volatile for analysis. [b] Calcd. for $C_{10}H_{18}NCl$: C, 63.98; H, 9.67. Found: C, 63.88; H, 9.73.

tallization from a water–ethanol mixture gave 21 g. (62%) of material melting at 76–78°.

Preparation of 1-Pyrrolidino-1-ethynylcyclohexane.—Ten grams of 1-ethynylcyclohexyl chloride, 20 ml. of pyrrolidine and 10 ml. of water were placed in a 50 ml. erlenmeyer flask and set aside for 24 hr. The solid material was collected by filtration, washed with water and recrystallized from an ethanol–water mixture; yield 8 g. (73%) of material melting at 65–66.5°.

Preparation of 1-Piperidino-1-ethynylcyclohexane.—Twenty grams of 1-ethynylcyclohexyl chloride, 40 ml. of piperidine and 20 ml. of water were placed in a 125-ml. erlenmeyer flask. After 48 hr. had elapsed, the solid material was collected by filtration, washed with water and recrystallized from aqueous acetone; yield 16 g. (60%) of material melting at 94.5–95.5°.

Preparation of 1-Dimethylamino-1-ethynylcyclohexane.—Twenty grams of 1-ethynylcyclohexyl chloride, 60 ml. of 40% aqueous dimethylamine and 55 ml. of acetone were placed in a 125-ml. erlenmeyer flask. After 24 hr., 60 ml. of volatile solvent was removed by distillation. Solidification of the desired product resulted when the two-phase residue was cooled to approximately −10°. Filtration of the solid material and subsequent recrystallization from aqueous alcohol gave 14.5 g. (68%) of material melting at 57–58.5°.

Preparation of 3-Ethylamino-3-methyl-1-pentyne.—One hundred and fifty ml. of 70% aqueous ethylamine and 40 g. of 3-chloro-3-methyl-1-pentyne were placed in a stout bottle. After 12 hr., the reaction mixture appeared in two layers. The mixture was then shaken mechanically for an additional period of 30 hr. The upper layer was separated and the bottom layer was diluted with an equal volume of water. The upper layer was again separated and added to the first. After adding 100 ml. of ether and washing twice with water, the solution was dried over potassium hydroxide pellets. Distillation gave a 25.5-g. fraction, b.p. 70–79° (120 mm.). Redistillation gave 22 g. (52%), b.p. 74–79° (120 mm.), $n^{25}D$ 1.4308.

Preparation of 3-Pyrrolidino-1-hexyne.—Thirty grams of 3-chloro-1-hexyne, 90 ml. of pyrrolidine and 30 ml. of water were refluxed for 18 hr. (inside temperature, 95°). The upper layer was separated and the bottom layer was diluted with an equal volume of water. The upper layer was again separated and combined with the first. An equal volume of ether was added and the ether solution was washed twice with water and dried overnight over potassium hydroxide pellets. Distillation gave 25 g. (63%) of material boiling at 71–72° (12 mm.), $n^{25}D$ 1.4597, d^{25} 0.8693.

Preparation of 3-*n*-Butylamino-1-hexyne.—Thirty-four grams of 3-chloro-1-hexyne, 90 ml. of *n*-butylamine and 30 ml. of water were placed in a 300-ml. round-bottom flask and heated at about 65° for 5 days.

The upper layer was separated and the bottom layer was diluted with an equal amount of water. The upper layer was again separated and combined with the first. After an equal volume of ether had been added, the solution was washed with water and dried over potassium hydroxide pellets. Distillation gave a 29.5-g. fraction, b.p. 68–72.5° (11 mm.). Redistillation gave a fraction weighing 25 g. (56%) of material, b.p. 71–72° (11 mm.), $n^{25}D$ 1.4365, d^{25} 0.8043.

As derivatives, the hydrochlorides and methiodides of most of the amines were prepared. The hydrochlorides were prepared by treating 1 g. of the amine dissolved in 25 ml. of absolute ether with excess ethereal hydrogen chloride. Purification was achieved by recrystallization from an ethyl acetate–ethanol mixture. The methiodides were prepared by treating 1 g. of the amine dissolved in 15 ml. of absolute ethyl acetate with twice the theoretical amount of methyl iodide. They were crystallized from an ethyl acetate–ethanol mixture.

The physical properties and analyses of the amines and their derivatives are shown in Tables III and IV.

Acknowledgments.—The authors are indebted to Dr. F. E. Cislak, Reilly Tar and Chemical Corp., Indianapolis, Ind., and to Dr. C. O. Herman, Air Reduction Chemical Co., New York, for generous supplies of acetylenic carbinols. Thanks are due to G. M. Maciak and Miss Gloria Beckman of the Lilly Research Laboratories, Indianapolis, for the analyses reported in Table IV.

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