3540, 3400; =CH: 3020, 2990; C=C; 1598, 1580, 1553, 1498, 1495; C=O: 1115; ring: 745, 737, 725, 700, 688.

Anal. Calcd. for $C_{24}H_{23}NO$: C, 84.42; H, 6.79; N, 4.10; active H, 2. Found: C, 84.20; H, 6.99; N, 4.26; active H, 2.01.

C. Dehydration to XIII.—Ethyl chloroformate[8] (5 ml.) was added during 5 min. to an ice-cooled and stirred solution of α-diphenylmethyl-α,2-dimethylindole-3-methanol (1.14 g., 3.35 mmoles) in 14 ml. of pyridine. The thick suspension was kept in ice for 1 hr. and then allowed to stand at room temperature for 7 hr. The resulting solution was treated with ice (5 g.) and water (10 ml.) and extracted with ether (3 × 50 ml.). The extracts were washed with water, saturated salt solution, dried through sodium sulfate and evaporated to give 1.40 g. of a yellow oil. It was purified by evaporative distillation at 120–160° (0.01 mm.) to give a yellow solid melting at 132–137°. Sublimation at 120–150° (0.01 mm.) afforded a mixture of products which was purified by crystallization from ether; small prisms (0.10 g.), m.p. 199.5–200.5°. This product proved identical with an

authentic sample of 2-methyl-3-acetylindole[14] (ultraviolet and infrared spectra; C, H, N analysis and mixed melting point).

The first ethereal filtrate was diluted with 10 ml. of petroleum ether (b.p. 30–60°), evaporated to remove ether and allowed to crystallize; 0.20 g., m.p. 133–136°. One recrystallization from ether–petroleum ether afforded XIII as clusters of small rods, m.p. 138–139°, unchanged on further recrystallization. Ultraviolet spectrum showed λmax 222 (40,500); sh 260 (8400); sh 267 (9600); 274 (10,200); sh 280 (9900); sh 290 (8100). Infrared spectrum showed OH, NH: 3380, 3300; C=C: 1628, 1605, 1585, 1552, 1497; ring: 773, 755, 750, 735, 725, 710, 703.

Anal. Calcd. for $C_{24}H_{21}N$: C, 89.12; H, 6.55; N, 4.33. Found: C, 89.12; H, 6.62; N, 4.62.

Mixed melting point of XIII with the unknown XII (m.p. 166.5–167°) was 120–124°.

(14) E. Fischer, *Ann.*, **242**, 372 (1887).

Oxidative Coupling and Cross-Coupling of Acetylenic Amines and Acetylenic Carbinols[1]

G. F. HENNION AND LEONARD PRICE[2]

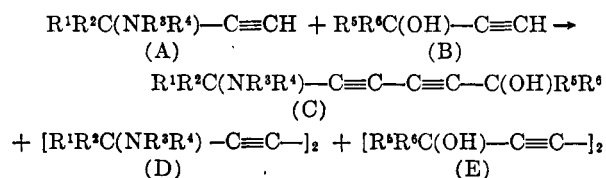*The Chemical Laboratories of the University of Notre Dame, Notre Dame, Ind.*

A number of conjugate diacetylenic 1,6-amino alcohols, $R^1R^2C(NR^3R^4)$—C≡C—C≡C—C(OH)R^5R^6, and diacetylenic 1,6-diamines, $R^1R^2C(NR^3R^4)$—C≡C—C≡C—C(NR³R⁴)R¹R², were prepared by oxidative coupling reactions. The products absorbed three moles of hydrogen rapidly (with Raney nickel in ethanol), the fourth mole slowly. Hydrogenolysis, particularly of the carbon-nitrogen bond, occurred extensively where steric hindrance was severe.

Methods have now been described for the preparation of a remarkably varied assortment of acetylenic amines of the type $R^1R^2C(NR^3R^4)$-C≡CH (A). The long list of such compounds ranges from the simplest example, propargylamine[3,4] (all R's = H), through many fully alkylated homologs[5] (all R's = alkyl), including all intermediate states of substitution.[4–7] Thus one may have these compounds with primary, secondary, or tertiary nitrogen on primary, secondary, or tertiary carbon. The corresponding acetylenic carbinols, $R^5R^6C(OH)$-C≡CH (B), are well known in many primary, secondary, and tertiary modifications (R's = H and/or alkyl).

Since a few preliminary experiments[8] indicated that acetylenic amines (A) undergo oxidative cross-coupling with acetylenic carbinols (B), we

have studied the reaction in greater detail to provide a sterically varied group of new conjugate diacetylenic 1,6-amino alcohols (C) and related compounds for physiological screening.[9]

$$R^1R^2C(NR^3R^4)\text{—C≡CH} + R^5R^6C(OH)\text{—C≡CH} \rightarrow$$
$$(A) \qquad\qquad\qquad (B)$$
$$R^1R^2C(NR^3R^4)\text{—C≡C—C≡C—C(OH)}R^5R^6$$
$$(C)$$
$$+ [R^1R^2C(NR^3R^4)\text{—C≡C—}]_2 + [R^5R^6C(OH)\text{—C≡C—}]_2$$
$$(D) \qquad\qquad\qquad (E)$$

The oxidative coupling[10] and cross-coupling[11] of terminal acetylenes has long been known. The more recent discovery of many polyacetylenes among natural products has revived interest in these reactions, now often used in the synthesis of such substances.[12,13]

The oxidative coupling procedure described by Zalkind[14,15] was selected for our purpose. Use of

(1) Paper No. 77 on substituted acetylenes; previous paper, G. F. Hennion and P. E. Butler, *J. Org. Chem.*, **26**, 3341 (1961).

(2) Eli Lilly Co. Fellow, 1959–61. Abstracted from the Ph.D. dissertation of L. P.

(3) C. Paal and C. Hermann, *Ber.*, **22**, 3076 (1889).

(4) A. Marszak-Fleury, *Ann. chim.* (Paris) (13), **3**, 656 (1958).

(5) (a) G. F. Hennion and K. W. Nelson, *J. Am. Chem. Soc.*, **79**, 2142 (1957); (b) G. F. Hennion and R. S. Hanzel, *J. Am. Chem. Soc.*, **82**, 4908 (1960).

(6) J. D. Rose and B. C. L. Weedon, *J. Chem. Soc.*, 782 (1949).

(7) G. F. Hennion and E. G. Teach, *J. Am. Chem. Soc.*, **75**, 1653 (1953).

(8) G. F. Hennion and A. C. Perrino, *J. Org. Chem.*, **26**, 1073 (1961).

(9) Samples were submitted for this purpose to the Lilly Research Laboratories, Indianapolis, Ind.

(10) C. Glaser, *Ber.*, **2**, 422 (1869).

(11) A. Baeyer and L. Landsberg, *Ber.*, **15**, 50, 57 (1882).

(12) J. D. Bu'Lock, *Quart. Revs.*, **10**, 371 (1956).

(13) N. A. Sorensen, *Proc. Chem. Soc.*, 98 (1961).

(14) Y. S. Zalkind and F. B. Funduiler, *Ber.*, **69B**, 128 (1936).

(15) Y. S. Zalkind and M. A. Aizikovich, *J. Gen. Chem.* (U.S.S.R.) **7**, 227 (1937); *Chem. Abstr.*, **31**, 4283 (1937).

TABLE I

DIACETYLENIC 1,6-AMINO ALCOHOLS, $R^1R^2C(NR^3R^4)-C\equiv C-C\equiv C-C(OH)R^5R^6$

Compound	R^1	R^2	R^3	R^4	R^5	R^6	Mole Formula	Yield, %	M.P.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
I	H—	H—	—CH₂(CH₂)₃CH₂—		H—	H—	C₁₀H₁₃NO	25					
II	H—	H—	—C₂H₅—	C₂H₅—	H—	H—	C₁₀H₁₅NO	30					
III	CH₃—	CH₃—	H—	H—	CH₃—	CH₃—	C₁₀H₁₆NO	16	113–114.5	72.69	72.86	9.15	9.15
IV	H—	H—	—CH₂(CH₂)₃CH₂—		H—	H—	C₁₀H₁₆NO	6					
V	CH₃—	CH₃—	CH₃—	CH₃—	CH₃—	CH₃—	C₁₁H₁₈NO	19	124–125	73.70	73.70	9.56	9.51
VI	H—	H—	CH₃—	CH₃—	H—	CH₃—	C₁₁H₁₇NO	8					
VII	CH₃—	CH₃—	CH₃—	H—	—CH₂(CH₂)₃CH₂—		C₁₃H₁₉NO	34	115–117	76.05	75.97	9.33	9.28
VIII	CH₃—	CH₃—	CH₃—	CH₃—	—CH₂(CH₂)₃CH₂—		C₁₃H₁₉NO	65	132–135	76.66	76.84	9.65	9.51
IX	H—	H—	H—	i-C₃H₇—	H—	i-C₃H₇—	C₁₄H₂₁NO	24	84–85.5	76.66	76.27	9.65	9.45
X	H—	H—	—CH₂(CH₂)₃CH₂—		—CH₂(CH₂)₃CH₂—		C₁₄H₂₁NO	47	103–105	77.88	77.97	9.15	8.69
XI	H—	H—	—CH₂(CH₂)₃CH₂—		—CH₂(CH₂)₃CH₂—		C₁₅H₂₁NO₂	15	88–90	72.84	73.08	8.56	8.64
XII	H—	H—	—C₂H₄OC₂H₄—		—CH₂(CH₂)₃CH₂—		C₁₅H₂₃NO	45	84–86	77.20	76.99	9.94	9.80
XIII	CH₃—	CH₃—	C₂H₅—	C₂H₅—	H—	CH₃—	C₁₅H₂₃NO	41	139–142	77.20	77.14	9.94	10.18
XIV	CH₃—	CH₃—	CH₃—	CH₃—	—CH₂(CH₂)₃CH₂—		C₁₅H₂₅NO	31	76–78	76.54	76.55	10.71	10.71
XV	H—	H—	H—	i-C₄H₉—	—CH₂(CH₂)₃CH₂—		C₁₆H₂₅NO	35	105–106.5	78.32	78.87	9.45	9.70
XVI	CH₃—	CH₃—	—CH₂(CH₂)₃CH₂—		—CH₂(CH₂)₃CH₂—		C₁₇H₂₅NO	40	155–157	78.72	78.65	9.72	9.78
XVII	CH₃—	CH₃—	—CH₂(CH₂)₂CH₂—	i-C₄H₉—	—CH₂(CH₂)₃CH₂—		C₁₇H₂₇NO	69	123–125	78.12	78.22	10.41	10.38
XVIII	CH₃—	CH₃—	CH₃—	CH₃—	CH₃—	n-C₆H₁₃—	C₁₇H₂₉NO	20	74–76	77.51	77.80	11.10	11.04

the amine (A) and the carbinol (B) in a 1 to 5 mole ratio gave a crude product rich in amino alcohol (C) and glycol (E) and containing only minimum amounts of the symmetrical diamine (D). When C and E were independently high-melting (above 100° or so) and not water-soluble, the amino alcohol (C) was readily extracted from the crude solid product with dilute hydrochloric acid. Subsequently C was easily recovered and purified by a simple crystallization. Amines (A) and carbinols (B) having tertiary carbon atoms usually gave the best yields and the most stable products. Products having primary carbon atoms (R^1, R^2, R^5, and/or R^6 = H) often proved sensitive to light and air; they darkened or the crystals developed colored spots as previously noted for other polyacetylenic compounds.[16,17] This difficulty was largely overcome, however, by conversion of the amino compounds (C and D) to their hydrochlorides which proved to be much more stable. When the products (C, D, and/or E) were low-melting and/or appreciably water-soluble, separation and purification proved troublesome. In some instances (e.g., compounds I and XVIII, Table I) the crude amino alcohol could be purified only by chromatography. The diamines (D), amino alcohols (C) and glycols (E) eluted in that order from alumina. Isolation and purification procedures are amply illustrated in the Experimental, and the amino alcohols (C) and their hydrochlorides are described in Tables I and II, respectively. Notably low yields generally reflect difficulties in purification.

The symmetrical oxidative coupling of the acetylenic amines (A) to the conjugated diacetylenic 1,6-diamines (D) proceeded normally.[8,18] The products and their dihydrochlorides are described in Tables IV and V.

Anticipating future interest in the saturated analogs of the diacetylenic amino alcohols (C), the hydrogenation (with Raney nickel in ethanol) of these compounds was studied. As previously noted for other diacetylenes,[19,20] three moles of hydrogen were absorbed rapidly and the last mole very slowly. In cases where secondary or particularly tertiary nitrogen was attached to tertiary carbon, hydrogenation led to complex mixtures due to incomplete reaction and to extensive hydrogenolysis of the carbon-nitrogen bonds. These difficulties seemed to occur in proportion to the degree of steric hindrance about the two triple bonds. Hydrogenation products were isolated and purified as the hydrochloride salts; those obtained without difficulty are described in Table III.

(16) J. B. Armitage, C. L. Cook, N. Entwistle, E. R. H. Jones, and M. C. Whiting, J. Chem. Soc., 1998 (1952).

(17) F. Bohlmann, Angew. Chem., 65, 385 (1953).

(18) J. D. Rose and B. C. L. Weedon, J. Chem. Soc., 782 (1949).

(19) Y. S. Zalkind and L. F. Chelpanova, J. Gen. Chem. (U.S.S.R.), 21, 1173 (1951); Chem. Abstr., 46, 1969 (1952).

(20) L. Audier, Ann. chim. (Paris) (13), 2, 113 (1957).

TABLE II

DIACETYLENIC 1,6-AMINO ALCOHOL HYDROCHLORIDES

Compound[a]	Mole Formula	M.P.	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found
I	$C_{10}H_{14}ClNO$	139–140[b]	60.15	60.31	7.07	7.24	7.02	6.79
II	$C_{10}H_{16}ClNO$	116–118	59.55	59.83	8.00	8.01	6.95	7.00
III	$C_{10}H_{16}ClNO$	227[b]	59.55	59.46	8.00	8.07	6.95	6.87
IV	$C_{11}H_{16}ClNO$	154–156	61.82	62.07	7.55	7.75	6.55	6.77
V	$C_{11}H_{18}ClNO$	212–213[b]	61.24	60.51	8.41	8.23	6.49	6.88
VI	$C_{13}H_{20}ClNO$	186–188	64.58	64.67	8.34	8.58	5.79	5.73
IX	$C_{15}H_{24}INO^{c}$	108–110.5	49.87	49.93	6.69	6.70	3.88	3.61
X	$C_{15}H_{22}ClNO$	138–140	67.27	67.48	8.28	8.49	5.23	5.17
XI	$C_{15}H_{22}ClNO_2$	195–197[b]	63.48	63.66	7.82	7.76	4.94	4.84
XII	$C_{15}H_{24}ClNO$	150–152	66.77	67.30	8.97	8.97	5.19	4.99
XIII	$C_{15}H_{24}ClNO$	247–248[b]	66.77	66.83	8.97	9.10	5.19	5.19
XIV	$C_{15}H_{26}ClNO$	159–161	66.52	66.44	9.30	9.59	5.17	4.95
XV	$C_{16}H_{24}ClNO$	166–168[b]	68.19	68.39	8.58	8.59	4.97	4.97
XVI	$C_{17}H_{26}ClNO$	217–218[b]	69.01	69.04	8.86	9.02	4.73	4.48
XVIII	$C_{17}H_{30}ClNO$	188–190	68.08	68.15	10.08	9.97	4.67	4.82

[a] Numbers correspond to compounds identified in Table I.   [b] Melts with decomposition.   [c] Methiodide.

TABLE III

SATURATED 1,6-AMINO ALCOHOL HYDROCHLORIDES, $R^1R^2C(NR^3R^4)$—$(CH_2)_4$—$C(OH)R^5R^6 \cdot HCl$

Compound[a]	Origin[b]	Mole Formula	Yield, %	M.P.	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found
XIX	III	$C_{10}H_{24}ClNO$	42	185–186	57.26	56.98	11.53	11.25	6.68	6.50
XX	VII	$C_{13}H_{28}ClNO$	51	156–157	62.50	62.39	11.30	11.04	5.61	5.48
XXI	VIII	$C_{14}H_{30}ClNO$	64	119–121	63.67	63.83	11.46	11.25	5.31	5.01
XXII	X	$C_{15}H_{30}ClNO$	26	128–130	65.31	65.37	10.96	10.71	5.08	4.92
XXIII	XV	$C_{16}H_{32}ClNO$	40	144–146	66.29	66.44	11.13	11.01	4.83	4.94

[a] From hydrogenation of compounds listed under Origin.   [b] Numbers correspond to compounds identified in Table I.

TABLE IV

DIACETYLENIC 1,6-DIAMINES, $R^1R^2C(NR^3R^4)$—C≡C—C≡C—$C(NR^3R^4)R^1R^2$

Compound	R^1	R^2	R^3	R_4	Mole Formula	Yield, %	M.P.	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
XXIV	CH_3—	CH_3—	H—	H—	$C_{10}H_{16}N_2$	34	53.5–55				
XXV	CH_3—	CH_3—	H—	CH_3—	$C_{12}H_{20}N_2$	35	82–83.5	74.94	74.57	10.48	10.20
XXVI	H—	H—	—$CH_2(CH_2)_2CH_2$—		$C_{14}H_{20}N_2$	75	51–53	77.73	78.12	9.32	9.46
XXVII	H—	H—	—$C_2H_4OC_2H_4$—		$C_{14}H_{20}N_2O_2$	26	107–108	67.71	67.88	8.12	8.16
XXVIII	H—	H—	C_2H_5—	C_2H_5—	$C_{14}H_{24}N_2$	14	[a]				
XXIX	H—	H—	—$CH_2(CH_2)_3CH_2$—		$C_{16}H_{24}N_2$	47	60–62	78.63	78.56	9.90	10.14
XXX	CH_3—	CH_3—	—$C_2H_4OC_2H_4$—		$C_{18}H_{28}N_2O_2$	73	208–210[b]	71.01	71.24	9.27	9.37
XXXI	CH_3—	CH_3—	H—	t-C_4H_9—	$C_{18}H_{32}N_2$	77	77–83	78.20	78.81	11.67	11.22

[a] Recovered by distillation; b.p. 120° at 1.3 mm., n^{25}D 1.4990.   [b] Melts with decomposition.

TABLE V

DIACETYLENIC 1,6-DIAMINE DIHYDROCHLORIDES

Compound[a]	Mole Formula	M.P.[b]	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found
XXIV	$C_{10}H_{18}Cl_2N_2$	272	50.64	50.86	7.65	7.67	11.81	11.69
XXVI	$C_{14}H_{24}Cl_2O^{c}$	170	54.71	54.91	7.87	8.11	9.12	8.94
XXVII	$C_{14}H_{22}Cl_2N_2O_2$	219	52.34	52.48	6.90	6.93	8.72	8.65
XXVIII	$C_{14}H_{26}Cl_2N_2$	210–220	57.33	57.47	8.94	8.99	9.55	9.44
XXIX	$C_{16}H_{26}Cl_2N_2$	200	60.56	60.89	8.26	8.47	8.83	8.77
XXXI	$C_{18}H_{34}Cl_2N_2$	215–217	61.88	61.70	9.81	9.92	8.02	8.05

[a] Numbers correspond to compounds identified in Table IV.   [b] All melt with decomposition.   [c] Monohydrate of dihydrochloride.

Experimental

Materials.—1-Dimethylamino-2-propyne and the corresponding diethylamino, piperidino, and morpholino compounds were provided by the Dow Chemical Co., through the courtesy of Dr. E. J. Watson. 1-Pyrrolidino-2-propyne was prepared as described by Biel and DiPierro.[21] Other acetylenic amines were available from earlier studies or were prepared essentially as reported.[5-8] Propargyl alcohol was provided by General Aniline and Film Corp., and the other acetylenic alcohols by Air Reduction Chemical Co.

1-(1'-Hydroxycyclohexyl)-5-dimethylamino-5-methyl-1,3-hexadiyne (XIII).—A solution consisting of 5.55 g. (0.05 mole) of 3-dimethylamino-3-methyl-1-butyne,[8] 31 g. (0.25 mole) of 1-ethynylcyclohexanol, 30 ml. of methanol, 27 ml. of 2 N hydrochloric acid, 57 ml. of water, 7.5 g. ammonium chloride, and 12 g. of cuprous chloride was pre-

(21) J. H. Biel and F. DiPierro, *J. Am. Chem. Soc.*, **80**, 4609 (1958).

pared in a 500-ml. wide-mouth bottle provided with a rubber stopper having a gas inlet tube. The solution was shaken mechanically under a slight positive pressure of oxygen for a period of 4 hr. Solid appeared after 1 hr. of shaking and the mixture gradually became very pasty. The mixture was cooled (ice bath) and made alkaline with 50 ml. of cold concd. ammonium hydroxide. The solids were collected by suction filtration and washed thoroughly with cold dilute ammonium hydroxide and finally with cold water. The filter cake was extracted twice with 75-ml. portions of 2 N hydrochloric acid. The acid-insoluble residue was washed with water and dried, yielding 23.2 g. of crude 1,4-bis(1'-hydroxycyclohexyl)butadiyne, m.p. 171–173.5° (lit.,[15] m.p. 173–174°). The combined acid extract was cooled, made alkaline with 50 ml. of cold concd. ammonium hydroxide and allowed to stand for 2 hr. The precipitate was collected and dried. Two crystallizations from ethanol–water gave 4.78 g. (41% yield) of white crystals, m.p. 139–143°.

The hydrochloride was prepared from 2 g. (8.6 mmoles) dissolved in 150 ml. of absolute ether by precipitation with cold etheral hydrogen chloride soltion. Crystallization from ethyl acetate–absolute ethanol gave 2 g. (88% yield), m.p. 244–245° dec.

2-t-Butylamino-2,8-dimethyl-3,5-nonadiyne-7-ol (XIV).—The procedure described above was used with a solution of 6.95 g. (0.05 mole) of 3-t-butylamino-3-methyl-1-butyne,[5b] 24.5 g. (0.25 mole) of 4-methyl-1-pentyne-3-ol, 60 ml. of ethanol, 30 ml. of 2 N hydrochloric acid, 75 ml. of water, 24 g. of ammonium chloride, and 14.8 g. of cuprous chloride. After shaking under oxygen for 5 hr., the mixture separated into an upper (yellow) oily layer and a lower (green) aqueous layer. The lower layer was extracted with two 75-ml. portions of ether; the ether extracts were added to the original upper oily layer. The combined ether solution was then extracted with three 25-ml. portions of 2 N hydrochloric acid and the acid extracts were added to the original aqueous layer. The green aqueous solution was then cooled and made alkaline with 100 ml. of cold concd. ammonium hydroxide. The desired product separated and was recovered as an oil which solidified on standing. Crystallization from ethanol plus petroleum ether (b.p. 30–60°) gave 3.6 g. (31% yield), m.p. 75–76.5°.

The hydrochloride was prepared from 2 g. of the amino alcohol; yield, 0.9 g., m.p. 159–161°.

6-Pyrrolidino-2,4-hexadiyne-1-ol hydrochloride (I).—A 500-ml. wide-mouth bottle was charged with a solution prepared from 14.8 g. of cuprous chloride, 8 g. of ammonium chloride, 27 ml. of 2 N hydrochloric acid and 75 ml. of water. A solution of 5.45 g. (0.05 mole) of 1-pyrrolidino-2-propyne[21] and 28 g. (0.5 mole) of propargyl alcohol in 75 ml. of water was then added and the mixture was shaken under oxygen for 7 hr. The mixture was then extracted three times with 100-ml. portions of ether. The ether extracts were combined, washed with dilute ammonium hydroxide, and dried over anhydrous potassium carbonate. Evaporation of the ether gave 13.6 g. of crude 2,4-hexadiyne-1,6-diol, m.p. 108–111°. The original aqueous layer was cooled and made alkaline with 50 ml. of cold concd. ammonium hydroxide. The amber colored oil which separated was removed and the blue aqueous layer was extracted with two 50-ml. portions of ether. The ether extracts were combined, washed with dilute ammonia and added to the amber colored oil. This ethereal solution was dried over anhydrous potassium carbonate and the ether evaporated, leaving about 10 g. of soft, brown solid. This material was stirred with 100 ml. of 10% ether–90% benzene solvent. The solution was decanted (0.7 g. insoluble) and chromatographed on 250 g. of alumina (Alcoa F-20) first wetted with 10% ether–90% benzene. The column was eluted with 300 ml. of 10% ether–90% benzene, 200 ml. of 30% ether–70% benzene, 200 ml. of 40% ether–60% benzene 200 ml. of 60% ether–40% benzene, 200 ml. of 80% ether–20% benzene, 200 ml. of ether, 200 ml. of 20% methanol–

80% ether and finally with 100 ml. of methanol. The eluate was collected in 50-ml. portions (32 fractions).

Fractions 8–12 yielded 0.16 g. of 1,6-bispyrrolidino-2,4-hexadiyne (XXVI), m.p. 52–54°. Fractions 26–32 gave 0.85 g. of 2,4-hexadiyne-1,6-diol, m.p. 102–106°. Fractions 14–25 gave colorless oils which darkened on standing. The oils were taken up in anhydrous ether, treated with charcoal and the etheral solution filtered. The pale yellow filtrate was treated immediately with cold etheral hydrogen chloride until no more solid precipitated. The solid was collected and dried; yield 4 g., m.p. 132–133° dec. Two crystallizations from absolute ethanol–ethyl acetate gave 2.7 g. of cubical crystals, m.p. 139–141° dec.

2-Dimethylamino-2,7-dimethyl-3,5-tridecadiyne-7-ol (XVIII) was obtained very crude, m.p. 71–above 130°, in 58% yield. Attempts to purify by crystallization failed. The material (7.4 g.) was dissolved in 50 ml. of 66% benzene–33% petroleum ether (b.p. 60–70°) and chromatographed on 250 g. of alumina (Alcoa F-20) wet with 66% benzene–33% petroleum ether. The column was eluted with 100 ml. of 66% benzene–33% petroleum ether, 400 ml. of 80% benzene–20% petroleum ether, 200 ml. of benzene, 200 ml. of 10% ether–90% benzene, 300 ml. of 30% ether–70% benzene, 200 ml. of 50% ether–50% benzene and finally with 200 ml. of methanol. The eluate was collected in 25-ml. portions (40 fractions). Fractions 11–32 combined gave 2.6 g. of desired product, m.p. 74–76°.

1,6-Dipiperidino-2,4-hexadiyne (XXIX) was prepared by shaking under oxygen a solution prepared from 4.95 g. of cuprous chloride, 8 g. of ammonium chloride, 50 ml. of 2 N hydrochloric acid, 50 ml. of water, 15 ml. of ethanol, and 12.3 g. (0.1 mole) of 1-piperidino-2-propyne. After 5 hr. the reaction mixture was cooled, made alkaline by addition of 100 ml. of cold concd. ammonium hydroxide, allowed to stand for 1 hr. and then filtered. The filter cake was washed with dilute ammonia, then with cold water and dried. Crystallization from aqueous ethanol gave 5.8 g. (47% yield), m.p. 60–62°.

The dihydrochloride was precipitated from 1.1 g. dissolved in ether by addition of ethereal hydrogen chloride. Crystallization from ethyl acetate–absolute ethanol–petroleum ether (b.p. 60–70°) gave 1 g. (70% yield), m.p. 215–220° dec.

2,7-Diamino-2,7-dimethyl-3,5-octadiyne Dihydrochloride (XXIV).—The synthesis was accomplished as described in the examples above from 8.3 g. (0.1 mole) of 3-amino-3-methyl-1-butyne,[7] 15 ml. of ethanol, 15 ml. of water, 50 ml. of 2 N hydrochloric acid 2.5 g. of cuprous chloride, and 4 g. of ammonium chloride. After shaking under oxygen for 5 hr., addition of cold concd. ammonia yielded a clear, blue solution. This was extracted six times with 50-ml. portions of ether. The combined etheral extract was washed with a small amount of water and dried with anhydrous potassium carbonate. Evaporation of the ether gave 7 g. of soft solid, soluble in water, ethanol, and petroleum ether. The solid was dissolved in anhydrous ether and cold etheral hydrogen chloride was added with stirring. The precipitate (dried) weighed 6.9 g., m.p. 272–280° dec. Crystallization from ether–ethanol gave 4 g. (34% yield), m.p. 272° dec.

1-(5-Piperidinopentyl)cyclohexanol Hydrochloride (XXIII).—A solution of 4.9 g. (0.02 mole) of 1-(1-hydroxy-cyclohexyl)-5-piperidino-1,3-pentadiyne (XV) in 50 ml. of ethanol containing 1 g. of Raney nickel (wet with water) was shaken under hydrogen at 60 p.s.i.g. (Parr apparatus). The pressure dropped by 5 p.s.i.g. within 25 min. (75% of the theoretical amount of hydrogen absorbed). Further hydrogenation then proceeded very slowly and an additional 6.5 hr. was required to achieve a pressure drop of 7 p.s.i.g., corresponding to absorption of 0.08 mole of hydrogen (theoretical amount). The nickel was removed by filtration and the ethanol by distillation in vacuo. The viscous residue was shaken with 75 ml. of 2 N hydrochloric acid.

The emulsion so formed was broken by extraction with ether (discarded). The aqueous solution was made alkaline with 50 ml. of cold 20% sodium hydroxide solution. The oil so liberated was taken up in ether and the etheral solution was dried with anhydrous potassium carbonate and filtered. Ethereal hydrogen chloride was then added. The precipitate was crystallized from ethyl acetate–absolute ethanol and gave 2.3 g. (40% yield), m.p. 144–146°.

1,6-Dipyrrolidinohexane.—A solution of 5.4 g. (0.025 mole) of 1,6-dipyrrolidino-2,4-hexadiyne (XXVI) in 50 ml. of absolute ethanol containing 1 g. of Raney nickel (wet with water) was hydrogenated at an initial pressure of 60 p.s.i.g. The pressure dropped by 6.3 p.s.i.g. within 20 min. and an additional 3.5 hr. was required to complete the reaction (pressure drop of 8.4 p.s.i.g.). The nickel was removed by filtration. Distillation gave 2.7 g. of

product, b.p. 151–156° at 6.5 mm. Redistillation provided 1.7 g., b.p. 144–146° at 4.5 mm. (lit.,[22] b.p. 148–149° at 4 mm.).

The dihydrochloride had m.p. 235–238° dec. (lit.,[22] m.p. 238–239°).

(22) A. P. Phillips, *J. Am. Chem. Soc.*, **77**, 1693 (1955).

Hydridic Reducing Agent–Group VIII Metal Compound. A New Catalyst System for the Polymerization of Acetylenes and Related Compounds. I

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A new catalyst system for the polymerization of acetylenic compounds is described. The system consists of an hydridic reducing agent such as sodium borohydride, plus a salt or complex of a Group VIII metal, *i.e.*, nickel chloride. This system polymerizes acetylene itself to linear, *trans* high molecular weight polyacetylene. Monosubstituted acetylenes are polymerized largely to dimers and trimers. These reactions proceed smoothly, rapidly, and in good yield. Olefinic compounds such as ethylene, butadiene, and allene are also polymerized by these catalyst systems.

Reppe[1] has reported the catalytic preparation of a number of aromatic products from acetylene and monosubstituted acetylenes, using catalysts such as $(R_3P)_2Ni(CO)_2$. The literature contains a number of other references to the use of diphosphine nickel dicarbonyl catalysts for the aromatization of acetylenes.[2] More recently the scope of these catalysts for linear oligomerization, as well as aromatization of substituted acetylenes has been discussed.[3–5] Franzus[6] has demonstrated the aromatization of acetylene compounds by the use of Ziegler-Natta type catalysts. Natta and co-workers[7] have prepared linear high polymers of acetylene and monosubstituted acetylenes, using catalyst systems such as $Ti(OC_4H_9)_4 + Al(C_2H_5)_3$.

Chatt[8] has described the preparation of stable phosphine–platinum–acetylene complexes by the reduction of the corresponding bis(phosphine)-

platinum dichloride complexes with powerful reducing agents such as hydrazine. The present work involves the use of a cocatalyst system composed of an hydridic reducing agent, such as sodium borohydride, plus a compound of a Group VIII metal.[9] This co-catalyst system brings about the polymerization of acetylene to a linear, black product, totally unlike cuprene, and similar to the polyacetylene described by Natta and co-workers. The same cocatalyst system also brings about the polymerization of many substituted acetylenes, to dimers, trimers, tetramers, and higher polymers. Trimeric products may be (a) aromatized, *i.e.*, three acetylene groups may fuse to form a substituted benzene ring, or (b) may be linear instead. These reactions are truly catalytic, and high turnover numbers of substrate are observed. For example, in the presence of a several-fold molar excess of reducing agent, one mole of a co-catalyst such as $(Bu_3P)_2NiCl_2$ can cause the polymerization of several thousand moles of phenylacetylene in a few minutes. Olefinic compounds such as ethylene, butadiene, and allene are also polymerized by these catalyst systems.

Experimental

Chemicals.—The acetylene derivatives used were all purchased from Farchan Research Laboratories. In most

(1) W. Reppe, *Ann.*, **560**, 104 (1948).

(2) See, for example, J. Rose and F. Statham, *J. Chem. Soc.*, 69 (1950); R. Kleinschmidt, U. S. Patent 2,542,417 (1951).

(3) L. S. Meriwether, E. C. Colthup, G. W. Kennerly, and R. N. Reusch, *J. Org. Chem.*, **26**, 5155 (1961).

(4) L. S. Meriwether, E. C. Colthup, and G. W. Kennerly, *J. Org. Chem.*, **26**, 5163 (1961).

(5) E. C. Colthup and L. S. Meriwether, *J. Org. Chem.*, **26**, 5169 (1961).

(6) B. Franzus, R. J. Canterino, and R. A. Wickliffe, *J. Am. Chem. Soc.*, **81**, 1514 (1959).

(7) G. Natta, G. Mazzanti, and R. Corradini, *Atti. Accad. Nazl. Lincei, Rend. Classe Sci. Fis. Mat. Nat.* [8], **25**, 3 (1958); see also Australian Patent 219,925, July 8, 1956.

(8) J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957).

(9) For a preliminary communication, see also L. B. Luttinger, *Chem. Ind.* (London), 1135 (1960). Also M. L. H. Green, M. Nehme, and G. Wilkinson, *ibid.*, 1136 (1960).