

167. Acetylene Reactions. Part II. Oxidation,* Hydration, and Mannich Reactions with 3-Aminobut-1-yne.

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Air oxidation of 3-alkyl- and -dialkyl-aminobut-1-yne in presence of a copper catalyst gives high yields of 2:7-alkyl- and -dialkyl-amino-octa-3:5-diynes, which are catalytically hydrogenated to alkylated 2:7-diamino-octanes. Hydration of 3-diethylaminobut-1-yne with mercury salts gives 3-diethylaminobutan-2-one, and interaction of 3-diethylamino- and 3-morpholino-but-1-yne with formaldehyde and secondary amines affords acetylenic diamines.

RECENTLY published information from German sources on the reaction products of amines and acetylene (Rose, "Products formed by Interaction of Acetylene and Amines"; B.I.O.S. Final Report No. 359, Item No. 22, H.M.S.O. 1946; cf. Part I, preceding paper) have made the 3-mono- and -di-alkylaminobut-1-yne readily available substances offering a fruitful field for research. This paper records some reactions which have been effected with this class of compound.

The hydration of 3-dialkylaminobut-1-yne with mineral acids in the presence of mercury salts has been reported briefly as giving the corresponding amino-ketones (II) (I.G., B.P. 510,876), and this has been confirmed in the case of 3-diethylaminobut-1-yne (I; R = R' = Et), 3-diethylaminobutan-2-one (II; R = R' = Et) being obtained

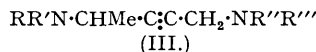
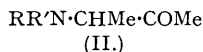
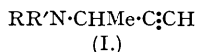
Mannich-type reactions have been described with some monosubstituted acetylenes

* Patent application pending.

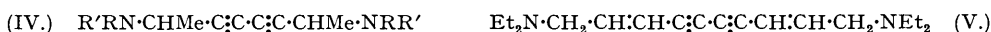
(Mannich and Chang, *Ber.*, 1933, **66**, 418; Jones, Marszak, and Bader, *J.*, 1947, 1578), and, in the presence of a copper catalyst with acetylene (I.G., B.P. 510,904), vinylacetylene (Coffmann, *J. Amer. Chem. Soc.*, 1935, **57**, 1978; U.S.P. 2,136,177), but-3-yn-2-ol (Rose, "Preparation of 5-Diethylaminopentan-2-ol by the Reppe Process," B.I.O.S. Final Report No. 353, Item No. 22, H.M.S.O.) and diacetylene (Microfilm of F.D 3781/45, p. 000686).

3-Diethylaminobut-1-yne (I; R = R' = Et) reacted readily with paraformaldehyde and diethylamine or piperidine giving the acetylenic *diamines* (III; R = R' = R'' = R''' = Et, and R = R' = Et, R''R''' = C₅H₁₀) in 70 and 55% yields respectively; catalytic hydrogenation of these afforded the corresponding saturated 1 : 4-*diaminopentanes*.

The only product which could be isolated from diethylaminobutyne (I; R = R' = Et), paraformaldehyde, and morpholine was dimorpholinomethane, but 3-morpholinobut-1-yne, with paraformaldehyde and diethylamine gave the required 4-*morpholino-1-diethylaminopent-2-yne* (III; RR' = C₄H₈O, R'' = R''' = Et).



The aerial oxidation in the presence of cuprous salts of compounds containing the ethynyl group, -C≡CH, to give diacetylenes, -C≡C-C≡C-, has previously been studied with the acetylenic hydrocarbons (Zal'kind and Fundyler, *Ber.*, 1936, **69**, 128; *J. Gen. Chem. Russia*, 1939, **9**, 1725) and acetylenic alcohols (Zal'kind *et al.*, *ibid.*, 1937, **31**, 4283; 1939, **9**, 971, 1725; Bowden, Heilbron, Jones, and Sargent, *J.*, 1947, 1579), and that this method can be used as a highly efficient industrial process has been demonstrated by the I.G. in the oxidation of propargyl alcohol to hexa-2 : 4-diyne-1 : 6-diol (Rose, "Propargyl Alcohol; Dehydration and Oxidation to Hexadiynediol," B.I.O.S. Final Report No. 357, Item No. 22, H.M.S.O.). This reaction has now been applied to the aminobutyne (I), and it was found that oxidation was most conveniently effected by using an aqueous solution of the amine hydrochloride in the presence of only a catalytic amount of cuprous chloride. Under these conditions, a homogeneous solution was obtained, and the deposition of cuprous oxide with loss of catalyst, observed when the free



base is employed, was avoided. In this manner the diacetylenic *diamines* (IV; R = R' = Et; RR' = C₄H₈O; R = Prⁱ, R' = H; R = Bu, R' = H) were prepared from the corresponding aminobutyne (I) in yields of 66—95%. A similar oxidation of 1-diethylaminopent-2-en-4-yne gave 1 : 10-*bisdiethylaminodeca-2 : 8-diene-4 : 6-diyne* (V) in 65% yield.

The light-absorption properties of the diacetylenic diamines (see table) are in good agreement with those of the corresponding diacetylenic glycols.

Compound.	$\lambda_{\text{max.}}$ A.	$\epsilon_{\text{max.}}$	Compound.	$\lambda_{\text{max.}}$ A.	$\epsilon_{\text{max.}}$
(Et ₂ N·CHMe·C≡C) ₂	2420 2550	1,200 720	(CH ₃ ·CH[OH]·C≡C) ₂ (1) ...	2300 2370	1,930 1,860
(O<[CH ₂ ·CH ₂] ₂ >N·CHMe·C≡C) ₂ †	2420 * 2505 * 2570 *	875 450 365	(Me ₂ C·[OH]·C≡C) ₂ (1)	2290 2410 2560	310 300 180
(Pr ⁱ NH·CHMe·C≡C) ₂ , H ₂ O	2420 2570	630 330	(HO·CH ₂ ·CH·CH·C≡C) ₂ (2)	2300 2370 2470 2620 2765 2930 3120	38,000 39,000 30,000 12,000 20,000 30,000 23,000
(Bu ^t NH·CHMe·C≡C) ₂	2470 * 2560 *	1,550 1,000			
(Et ₂ N·CH ₂ ·CH·CH·C≡C) ₂	2290 2390 2490 2640 2790 2960 3150	26,000 24,500 19,000 9,500 15,000 24,500 22,000			

* Indicates an inflexion.

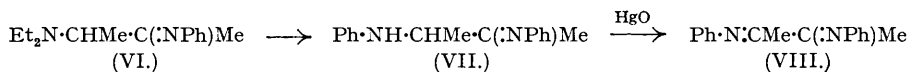
† In methanol.

(1) Bowden, Heilbron, Jones, and Sargent (*loc. cit.*).

(2) Heilbron, Jones, and Sondheimer (*J.*, 1947, 1586).

It has been shown (Loritsch and Vogt, *J. Amer. Chem. Soc.*, 1939, **61**, 1462) that aniline reacts with monoalkylacetylenes, with a boron trifluoride-mercuric oxide catalyst, to give the

anil of the corresponding methyl alkyl ketone. Treatment of 3-diethylaminobut-1-yne (I; R = R' = Et) with aniline under similar conditions gave diacetyl dianil (VIII).



The reaction probably depended on the intermediate formation of (VI) and (VII), the latter then being oxidised by mercuric oxide (the formation of mercury during the reaction was observed).

EXPERIMENTAL.

Analyses are by Mr. E. S. Morton. All m. p.s are uncorrected.

Light-absorption measurements were carried out in ethanol except where stated otherwise.

3-Diethylaminobutan-2-one.—Mercuric sulphate (0.2 g.) was added to a solution of 3-diethylaminobut-1-yne (5 g.) in sulphuric acid (*d* 1.84; 12 c.c.) and water (3 c.c.). The mixture was heated on the steam-bath for 1 hour, cooled, and poured on ice. Excess of sodium hydroxide solution (40% w/v) was added to the solution, and the precipitated oil extracted with ether. Evaporation of the ethereal solution and distillation of the residue gave 3-diethylaminobutan-2-one (4.5 g.), b. p. 56–58°/10 mm., n_D^{20} 1.4303 (Found: C, 67.0; H, 11.65; N, 9.7. Calc. for $\text{C}_8\text{H}_{17}\text{ON}$: C, 67.1; H, 11.8; N, 9.8%) (I.G., B.P. 510,876, give b. p. 168°). An aqueous alcoholic solution of the amino-ketone and semicarbazide acetate was left overnight. The *semicarbazone* was precipitated on addition of excess of alkali; it crystallised from alcohol in needles, m. p. 189.5–190.5° (Found: C, 54.25; H, 9.8; N, 27.8. $\text{C}_9\text{H}_{20}\text{ON}_3$ requires C, 54.0; H, 10.05; N, 28.0%).

1:4-Bisdiethylaminopent-2-yne (III; R = R' = R'' = Et).—A mixture of 3-diethylaminobut-1-yne (12.5 g.), diethylamine (8 g.), paraformaldehyde (4 g.), and dioxan (20 c.c.) was heated on the steam-bath for 13 hours, cooled, and diluted with water (400 c.c.). The product was extracted with ether, the ethereal solution evaporated, and the residue distilled, giving 1:4-bisdiethylaminopent-2-yne (15.3 g.), b. p. 104–106°/8 mm., n_D^{18} 1.4598 (Found: C, 74.4; H, 12.15. $\text{C}_{13}\text{H}_{26}\text{N}_2$ requires C, 74.2; H, 12.45%). The *dihydrochloride*, m. p. 205–206°, crystallised from alcohol-ether (Found: C, 55.25; H, 9.75; N, 9.6. $\text{C}_{13}\text{H}_{26}\text{N}_2\cdot 2\text{HCl}$ requires C, 55.1; H, 9.95; N, 9.9%). The *dipicrate*, m. p. 167–168.5°, crystallised in prisms from 2-ethoxyethyl alcohol (Found: C, 44.95; H, 4.75; N, 16.35. $\text{C}_{13}\text{H}_{26}\text{N}_2\cdot 2\text{C}_6\text{H}_5\text{O}_7\text{N}_3$ requires C, 44.9; H, 4.8; N, 16.75%). The *dimethiodide*, m. p. 168°, was prepared in acetone solution and purified from alcohol-ether (Found: C, 36.45; H, 6.65; N, 5.55. $\text{C}_{15}\text{H}_{32}\text{N}_2\text{I}_2$ requires C, 36.45; H, 6.55; N, 5.65%).

1:4-Bisdiethylaminopentane.—A solution of 1:4-bisdiethylaminopent-2-yne (4 g.) in methanol (50 c.c.) was shaken with hydrogen and Raney nickel until absorption was complete. After filtration, acidification, and evaporation of the solution, excess of sodium hydroxide (20%) was added to the residue, and the product isolated with ether. Distillation gave 1:4-bisdiethylaminopentane (2 g.), b. p. 105°/10 mm., n_D^{15} 1.4446 (Found: C, 73.2; H, 13.95; N, 13.2. $\text{C}_{13}\text{H}_{30}\text{N}_2$ requires C, 72.85; H, 14.1; N, 13.05%). The *dipicrate*, m. p. 192–194°, crystallised in needles from 2-ethoxyethyl alcohol (Found: C, 44.65; H, 5.4; N, 16.65. $\text{C}_{13}\text{H}_{30}\text{N}_2\cdot 2\text{C}_6\text{H}_5\text{O}_7\text{N}_3$ requires C, 44.6; H, 5.05; N, 16.9%).

1-Piperidino-4-diethylaminopent-2-yne (III; R = R' = Et, R''R''' = C_5H_{10}).—3-Diethylaminobut-1-yne (12.5 g.), piperidine (8.5 g.), paraformaldehyde (4 g.), and dioxan (20 c.c.) were heated on the steam-bath for 13 hours, and the product isolated as usual. Distillation gave 1-piperidino-4-diethylaminopent-2-yne (11.5 g.), b. p. 132–136°/9 mm., n_D^{19} 1.4810 (Found: C, 75.75; H, 11.5. $\text{C}_{14}\text{H}_{26}\text{N}_2$ requires C, 75.6; H, 11.8%). The *dihydrochloride*, crystallised from alcohol-ether, had m. p. 200–202° (decomp.) (Found: C, 56.55; H, 9.35; N, 9.85. $\text{C}_{14}\text{H}_{26}\text{N}_2\cdot 2\text{HCl}$ requires C, 56.95; H, 9.55; N, 9.5%). The *dipicrate*, m. p. 190–191° (decomp.), crystallised in needles from acetone (Found: C, 46.1; H, 4.6. $\text{C}_{14}\text{H}_{26}\text{N}_2\cdot 2\text{C}_6\text{H}_5\text{O}_7\text{N}_3$ requires C, 45.85; H, 4.75%). The *dimethiodide*, m. p. 198–201° (decomp.), was crystallised from alcohol-ether (Found: C, 37.6; H, 6.0; N, 5.5. $\text{C}_{16}\text{H}_{32}\text{N}_2\text{I}_2$ requires C, 37.95; H, 6.35; N, 5.55%).

1-Piperidino-4-diethylaminopentane.—A solution of 1-piperidino-4-diethylaminopent-2-yne (2.25 g.) in methanol was shaken with hydrogen and Raney nickel until absorption was complete. Isolation of the product gave 1-piperidino-4-diethylaminopentane (1.3 g.), b. p. 130–134°/12 mm., n_D^{17} 1.4644 (Found: N, 12.1. $\text{C}_{14}\text{H}_{30}\text{N}_2$ requires N, 12.35%). The *dipicrate*, m. p. 177–178°, crystallised as needles from aqueous acetone (Found: C, 45.6; H, 5.25; N, 16.5. $\text{C}_{14}\text{H}_{30}\text{N}_2\cdot 2\text{C}_6\text{H}_5\text{O}_7\text{N}_3$ requires C, 45.35; H, 5.25; N, 16.3%).

4-Morpholino-1-diethylaminopent-2-yne (III; RR' = $\text{C}_4\text{H}_8\text{O}$, R'' = R''' = Et).—A mixture of 3-morpholinobut-1-yne (13.9 g.), diethylamine (8 g.), paraformaldehyde (4 g.), and dioxan (20 c.c.) was heated on the steam-bath for 15 hours. Isolation of the product gave 4-morpholino-1-diethylaminopent-2-yne (18.5 g.), b. p. 86–90°/0.1 mm., n_D^{22} 1.4800 (Found: N, 12.45. $\text{C}_{13}\text{H}_{24}\text{ON}_2$ requires N, 12.5%). The *dipicrate*, m. p. 204–206°, formed needles from glycol monomethyl ether (Found: C, 44.3; H, 4.45; N, 16.35. $\text{C}_{13}\text{H}_{24}\text{ON}_2\cdot 2\text{C}_6\text{H}_5\text{O}_7\text{N}_3$ requires C, 44.0; H, 4.45; N, 16.45%).

2:7-Bisdiethylamino-octa-3:5-diyne (IV; R = R' = Et).—A solution of 3-diethylaminobut-1-yne (75 g.) in dilute hydrochloric acid (2N; 310 c.c.) was added to a mixture of cuprous chloride (15 g.), ammonium chloride (45 g.), and water (53 c.c.). The resulting solution was warmed to 50–55° and stirred vigorously, and air was bubbled through it until green salts began to be deposited (9 hours). The mixture was cooled and filtered, and excess of concentrated ammonia solution added to the filtrate. The precipitated oil was extracted with ether, the ethereal solution evaporated, and the residue distilled, giving 2:7-bisdiethylamino-octa-3:5-diyne (68 g.), b. p. 130–134°/0.2 mm., n_D^{18} 1.4958 (Found: C, 77.35; H, 11.2; N, 11.25. $\text{C}_{16}\text{H}_{28}\text{N}_2$ requires C, 77.3; H, 11.35; N, 11.3%). The *dipicrate*, m. p. 230°

(decomp.) (bath preheated to 190°), crystallised as leaflets from 2-ethoxyethyl alcohol (Found : C, 47·8; H, 4·85; N, 16·3. $C_{16}H_{28}N_2 \cdot 2C_6H_5O_7N_3$ requires C, 47·6; H, 4·85; N, 15·9%).

2 : 7-Bisdiethylamino-octane.—2 : 7-Bisdiethylamino-octa-5 : 7-diyne (4·5 g.) in methanol (50 c.c.) was hydrogenated (Raney nickel), giving 2 : 7-bisdiethylamino-octane (2 g.), b. p. 83—87°/0·1 mm., n_D^{20} 1·4612 (Found : N, 11·15; equiv., 128·2. $C_{16}H_{36}N_2$ requires N, 10·9%; equiv., 128·2). The *dipicrate*, m. p. 186—190° (decomp.), crystallised from 2-ethoxyethyl alcohol as leaflets (Found : C, 47·2; H, 5·6. $C_{16}H_{36}N_2 \cdot 2C_6H_5O_7N_3$ requires C, 47·05; H, 5·9%).

2 : 7-Dimorpholino-octa-3 : 5-diyne (IV; $RR' = C_4H_8O$).—3-Morpholinobut-1-yne (25 g.) was dissolved in hydrochloric acid (2N; 85 c.c.), and the solution added to a mixture of cuprous chloride (4 g.), ammonium chloride (12 g.), and water (14 c.c.). Aerial oxidation (for 5·5 hours) and isolation as in the case of the diethylamino-analogue gave 2 : 7-dimorpholino-octa-3 : 5-diyne (22 g.), which crystallised from alcohol in prisms, m. p. 114—115° (Found : C, 69·4; H, 8·4; N, 9·9. $C_{16}H_{24}O_2N_2$ requires C, 69·55; H, 8·75; N, 10·15%). The *dipicrate*, m. p. 224—227° (decomp.), crystallised in prisms from 2-ethoxyethyl alcohol (Found : C, 45·8; H, 4·3. $C_{16}H_{24}O_2N_2 \cdot 2C_6H_5O_7N_3$ requires C, 45·75; H, 4·1%). The *dihydrochloride*, leaflets from aqueous acetone, had m. p. 242° (decomp.) (Found : N, 8·15. $C_{16}H_{24}O_2N_2 \cdot 2HCl$ requires N, 8·0%).

2 : 7-Diisopropylamino-octa-3 : 5-diyne (IV; R = Pr; R' = H).—A solution of 3-isopropylaminobut-1-yne (100 g.) in dilute hydrochloric acid (2N; 440 c.c.) was added to a mixture of cuprous chloride (20 g.), ammonium chloride (60 g.), and water (70 c.c.), and the oxidation carried out as usual. Isolation gave 2 : 7-diisopropylamino-octa-3 : 5-diyne monohydrate (105 g.), m. p. 61°, which crystallised as needles from aqueous methanol (Found : C, 70·7; H, 10·95; N, 11·95. $C_{14}H_{24}N_2 \cdot H_2O$ requires C, 70·5; H, 11·0; N, 11·75%). On standing in a desiccator this solid gives an oil, presumably the anhydrous diamine, which on exposure to the atmosphere is rapidly reconverted into the original hydrate. The *dipicrate*, m. p. 198—200° (decomp.), crystallised in prismatic needles from aqueous methanol (Found : C, 45·85; H, 4·4; N, 16·7. $C_{14}H_{24}N_2 \cdot 2C_6H_5O_7N_3$ requires C, 46·05; H, 4·45; N, 16·5%). The *dihydrochloride*, purified from alcohol-ether, had m. p. 242·5—243·5° (Found : C, 56·95; H, 8·7; N, 9·25. $C_{14}H_{24}N_2 \cdot 2HCl$ requires C, 57·35; H, 8·95; N, 9·55%).

2 : 7-Diisopropylamino-octane.—A solution of 2 : 7-diisopropylamino-octa-3 : 5-diyne monohydrate (92 g.) in methanol (800 c.c.) was hydrogenated over Raney nickel until absorption was complete. Isolation of the product gave 2 : 7-diisopropylamino-octane (71 g.), b. p. 92—95°/0·5 mm., n_D^{20} 1·435 (Found : N, 12·2. $C_{14}H_{28}N_2$ requires N, 12·25%). The *dihydrochloride*, crystallised from alcohol-ether, had m. p. 270° (decomp.) (Found : C, 55·65; H, 11·25. $C_{14}H_{28}N_2 \cdot 2HCl$ requires C, 55·8; H, 11·35%).

2 : 7-Di-n-butylamino-octa-3 : 5-diyne (IV; R = Bu; R' = H).—A solution of 3-n-butylaminobut-1-yne (11 g.) in dilute hydrochloric acid (2N; 45 c.c.) was added to a mixture of cuprous chloride (2 g.), ammonium chloride (6 g.), and water (7 c.c.). Aerial oxidation (14 hours) at 50° and isolation of the product gave 2 : 7-di-n-butylamino-octa-3 : 5-diyne (7·2 g.), b. p. 128—132°/0·06 mm., n_D^{21} 1·4952 (Found : N, 11·4. $C_{16}H_{28}N_2$ requires N, 11·3%). The *di- α -naphthylurea*, m. p. 163—164°, crystallised in micro-needles from aqueous alcohol (Found : C, 77·7; H, 7·1; N, 9·25. $C_{38}H_{42}O_2N_4$ requires C, 77·75; H, 7·2; N, 9·55%).

1 : 10-Bisdiethylaminodeca-2 : 8-diene-4 : 6-diyne (V).—A solution of 1-diethylaminopent-2-en-4-yne (4 g.); prepared from pent-2-en-4-yn-1-ol by chlorination with thionyl chloride and then treatment of the chloride with diethylamine, cf. Jones, Lacey, and Smith, *J.*, 1946, 940) in dilute hydrochloric acid (2N, 14 c.c.) was added to a mixture of cuprous chloride (0·65 g.), ammonium chloride (1·9 g.), and water (2·25 c.c.). Aerial oxidation (5·5 hours) and isolation of the product gave bisdiethylaminodeca-2 : 8-diene-4 : 6-diyne (2·6 g.), b. p. 155—160°/0·1 mm., n_D^{25} 1·5630 (Found : C, 78·6; H, 9·8. $C_{18}H_{28}N_2$ requires C, 79·3; H, 10·3%). The *dipicrate*, m. p. 146—148°, crystallised in prisms from aqueous acetone (Found : C, 49·0; H, 4·85; N, 15·3. $C_{18}H_{28}N_2 \cdot 2C_6H_5O_7N_3$ requires C, 49·3; H, 4·7; N, 15·35%). The *dimethiodide*, needles from alcohol, had m. p. 211° (decomp.) (Found : C, 43·2; H, 6·1; N, 4·85. $C_{20}H_{34}N_2I_2$ requires C, 43·15; H, 6·15; N, 5·05%). The *dihydrochloride*, m. p. 215° (decomp.), crystallised as needles from alcohol (Found : N, 8·25. $C_{18}H_{28}N_2 \cdot 2HCl$ requires N, 8·1%). Light absorption in methanol : maxima 2380, 2490, 2775, 2970, 3160; ϵ_{max} , 28,500, 26,000, 9,500, 16,500, 27,000 and 23,000 respectively.

Diacetyl Dianil (VIII).—A mixture of aniline (45 g.), mercuric oxide (15 g.), and boron trifluoride-ether complex (6 g.) was warmed to 50°, and 3-diethylaminobut-1-yne (60 g.) added dropwise (0·5 hour) with rapid stirring. The mixture was stirred at 50° for a further 4 hours, cooled, and filtered. Distillation of the filtrate gave 3-diethylaminobut-1-yne (30 g.), aniline (15 g.), and a residue which on trituration with methanol solidified. Recrystallisation from the same solvent gave diacetyl dianil (17 g.) as yellow plates, m. p. 138° undepressed on admixture with an authentic specimen (von Pechmann, *Ber.*, 1888, 21, 1415, gives m. p. 139°) (Found : N, 12·0. Calc. for $C_{18}H_{16}N_2$: N, 11·85%).

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