166. *Acetylene Reactions. Part I. Aminobutynes from Acetylene and Primary or Secondary Amines.*

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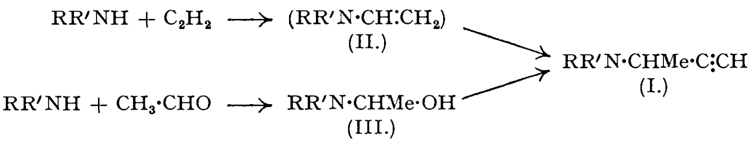
The formation of 3-mono- and -di-alkylaminobut-1-ynes from amines and acetylene under pressure in the presence of a copper catalyst is described. Some by-products of this reaction are characterised, and the experimental technique of using acetylene safely in pressure reactions is outlined.

A number of different types of reaction between acetylenes and amines has been recorded. Thus, acetylene and aromatic amines have been condensed with a variety of catalysts, *e.g.*, alumina (Chichibabin, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 703), nickel (Majima, Unno, and Ono, *Ber.*, 1922, **55**, 3854), zinc chloride (I.G., B.P. 451,794), and salts of mercury, copper, or silver (Kozlov *et al.*, *J. Gen. Chem. Russia*, 1936, **6**, 250, 1089, 1341, 1897; 1937, **7**, 54, 832, 1082; Kryuk, *ibid.*, 1940, **10**, 1507). Aromatic amines have been added to monosubstituted acetylenes in the presence of boron trifluoride and mercuric oxide (Loritsch and Vogt, *J. Amer. Chem. Soc.*, 1939, **61**, 1462).

A different type of reaction between acetylene and either primary or secondary amines, resulting in the formation of mono- and di-substituted aminobutynes (I), has been described using a copper acetylide catalyst (I.G., B.P. 510,457; General Aniline and Film Co., U.S.P. 2,268,129; Reppe, Hecht, and Gassenmeier, U.S.P. 2,342,493; J. D. Rose, B.I.O.S. Final Report No. 359, Item No. 22, " Products formed from acetylene and amines," H.M.S.O. 1946).



The publication of the German information (Rose, *loc. cit.*) of the formation of aminobutynes stimulated interest in these compounds, and their reactions were studied. They will be reported later in this series; the present communication deals largely with the formation of the aminobutynes, and confirms and amplifies the information from German sources which has already been published.

The structure of 3-diethylaminobut-1-yne (I; R = R′ = Et) was confirmed by obtaining an identical substance from acetylene and the condensation product (III) of diethylamine and acetaldehyde (B.I.O.S. Final Report No. 266, Item No. 22). That the intermediate in the formation of (I) is the vinylamine (II), and not vinylacetylene, is indicated by the fact that vinylacetylene reacts with amines, under the conditions employed, to give 2-aminobutadienes (I.G., D.R.P. 731,559).

All experiments, except those with diethylamine and aniline, were conducted in tetrahydrofuran as solvent. The secondary amines dimethylamine, diethylamine, and morpholine reacted readily to give aminobutynes in 63, 65, and 80% yields, respectively.

The reactions of the primary aliphatic amines were more complicated, and the optimum conditions for alkylaminobutyne formation were not established. The formation of higher condensation products was particularly noticeable with *iso*propylamine, though good yields of the required butynes were obtained with *n*-butyl- (65%), *cyclo*hexyl- (70%), and benzyl-amines (30%). The only identifiable product (40%) from hexamethylene diamine was 3-6′-*amino-hexylaminobut*-1-*yne* (I; R = $H_2N\cdot[CH_2]_6\cdot$, R′ = H) formed by reaction of only one of the amino-groups.

Aniline only reacted satisfactorily with acetylene to give (I; R = Ph; R′ = H) under conditions that were somewhat different from those employed in the previous examples. The aniline, in alcohol solution, was partly converted into its acetate, and then treated, in the presence of a pre-formed copper acetylide on filtercel catalyst, with a nitrogen–acetylene mixture. In this manner a 41% conversion of aniline was obtained, giving a 25% yield of 3-anilinobut-1-yne.

The aminobutynes readily gave both silver and copper salts. The presence of an ethynyl group, –C⋮CH, was also demonstrated by a determination of active hydrogen (Zerewitinoff).

On reduction, 3-diethylaminobut-1-yne gave 2-diethylaminobutane which was identified by comparison with a specimen synthesised by an unequivocal route.

The product from a large-scale preparation of 3-diethylaminobut-1-yne contained small amounts of higher boiling amines, $C_{11}H_{19}N$ and $C_{14}H_{28}N_2$ (*i.e.*, $2Et_2NH + 3C_2H_2$). Both these substances gave silver salts and were characterised by means of solid derivatives. The structures of these bases have not as yet been elucidated, but (IV) is tentatively suggested for the diamine $C_{14}H_{28}N_2$.

(IV.) $CH_3{\cdot}CH(NEt_2){\cdot}CH_2{\cdot}CH(NEt_2){\cdot}C{\vdots}CH$

EXPERIMENTAL.

Apparatus.—Two autoclaves were employed: (*a*) an 8-l. mild steel rocking autoclave fitted with 5 vertical mild steel baffles, and (*b*) a 1·2-l. stainless steel (Baskerville and Lindsay) autoclave fitted with an electromagnetically operated stirrer. The progress of a reaction was followed by the decrease in the acetylene pressure which was not allowed to fall below *ca.* 150 lb./sq. in. Safety precautions included the installation of the acetylene cylinder outside the building, the insertion of a non-return bunsen type valve between the cylinder and the autoclave, and enclosure of the autoclave by blast-proof walls. All operations during a run were carried out by remote control.

3-*Diethylaminobut*-1-*yne* (I; $R = R^1 = Et$).—Diethylamine (2100 g.) and cuprous chloride (213 g.) were charged into the 8-l. autoclave, and the air displaced by flushing 3—4 times with nitrogen. The pressure in the autoclave was raised to 50 lb./sq. in. with nitrogen and then to about 200 lb./sq. in. with acetylene. Rocking and heating of the autoclave was begun, and the absorption of acetylene, initially very rapid, allowed to proceed at 80—100°. After 39 hours the rate of absorption had greatly diminished and the reaction was terminated. The product was filtered and distilled rapidly, and the distillate fractionated, giving the following (*a*) 3-diethylaminobut-1-yne (2250 g.), b. p. 123—126°, m. p. 10° (Rose, *loc. cit.*, gives b. p. 128°, m. p. 10°) (Found: N, 11·3. Calc. for $C_8H_{15}N$: N, 11·2%). The *methiodide* (deliquescent), crystallised from methanol–ether, had m. p. 108—109·5° (Found: C, 40·35; H, 6·95; N, 5·25. $C_9H_{18}NI$ requires C, 40·45; H, 6·8; N, 5·25%). The *hydrochloride*, m. p. 178—179·5°, crystallised from methanol–ether (Found: C, 59·15; H, 9·75; N, 8·25. $C_8H_{16}NCl$ requires C, 59·45; H, 9·95; N, 8·65%). (*b*) An *amine* (14 g.), b. p. 64°/25 mm., 32—34°/0·06 mm., $n_{\mathrm{D}}^{14^\circ}$ 1·4600 (Found: C, 79·5; H, 11·2; N, 8·35. $C_{11}H_{19}N$ requires C, 79·9; H, 11·55; N, 8·5%). The *methiodide*, m. p. 113—114°, formed prisms from acetone–ether (Found: N, 4·25; $C_{12}H_{22}NI$ requires N, 4·55%). (*c*) A *diamine* (*ca.* 12 g.), b. p. 56°/0·1 mm., $n_{\mathrm{D}}^{21^\circ}$ 1·4729 (after purification *via* the hydrochloride) (Found: N, 12·4. $C_{14}H_{28}N_2$ requires N, 12·5%); a Zerewitinoff determination gave 0·9 active H per molecule. The *dimethiodide*, b. p. 200—205°, crystallised in prisms from alcohol (Found: C, 37·6; H, 6·7; N, 5·25. $C_{16}H_{34}N_2I_2$ requires C, 37·8; H, 6·7; N, 5·5%). The *dihydrochloride*, m. p. 260° (decomp.), formed prisms from alcohol (Found: C, 56·5; H, 9·7; N, 9·45. $C_{14}H_{30}N_2Cl_2$ requires C, 56·5; H, 10·1; N, 9·45%). The *dipicrate*, m. p. 213° (decomp.), formed prisms from acetone (Found: C, 45·65; H, 4·8; N, 16·75. $C_{14}H_{28}N_2,2C_6H_3O_7N_3$ requires C, 45·7; H, 5·0; N, 16·4%). On hydrogenation in methanol (Raney nickel catalyst), the diamine absorbed 2 molar proportions of hydrogen, giving a basic product, b. p. 64—65°/0·25 mm., $n_{\mathrm{D}}^{21^\circ}$ 1·4560, which was characterised as the *dimethiodide*, m. p. 193—196° (decomp.) (Found: C, 37·3; H, 7·15; N, 5·3. $C_{16}H_{35}N_2I_2$ requires C, 37·7; H, 6·9; N, 5·5%). (*d*) An amine (10 g.), b. p. 86—88°/0·09 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·4785 (after purification *via* the hydrochloride) (Found: C, 77·8; H, 10·9; N, 11·3%).

2-*Diethylaminobutane.*—3-Diethylaminobut-1-yne (5 g.) in methanol (50 c.c.), was shaken, in the presence of Raney nickel, with hydrogen at 100 atm. pressure until no further absorption occurred. The product was filtered and acidified with concentrated hydrochloric acid, and the solvent evaporated. Excess of sodium hydroxide solution (20% w/v) was added to the residue, and the precipitated oil isolated by means of ether, giving 2-*diethylaminobutane* (3 g.), b. p. 130—131°/766 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4165 (Found: N, 11·05. $C_8H_{19}N$ requires N, 10·8%). The *picrate*, m. p. 116—117°, crystallised as needles from aqueous methanol (Found: N, 15·9. $C_{14}H_{22}O_7N_4$ requires N, 15·65%); its m. p. was undepressed on admixture with a specimen prepared by a method analogous to that of Leithe (*Ber.*, 1930, **63**, 800) for (+)-2-diethylaminobutane (b. p. 131°; picrate, m. p. 117°).

3-*Morpholinobut*-1-*yne* (I; $RR' = O{<}[CH_2{\cdot}CH_2]_2{>}$).—Morpholine (200 g.), tetrahydrofuran (250 c.c.), and cuprous chloride (20 g.) were treated at 85° (in the 1·2-l. autoclave) with acetylene–nitrogen, as described above, giving 3-*morpholinobut*-1-*yne* (255 g.), b. p. 76—78°/17 mm., m. p. 5·5°, $n_{\mathrm{D}}^{22^\circ}$ 1·4715 (Found: C, 69·35; H, 9·0; N, 10·35. $C_8H_{13}ON$ requires C, 69·05; H, 9·4; N, 10·05%. Zerewitinoff determination gave 1 active H per molecule). The *hydrochloride*, m. p. 157—158°, crystallised as needles from acetone (Found: N, 8·1. $C_8H_{14}ONCl$ requires N, 8·0%). The *methiodide* crystallised in prisms from alcohol, m. p. 183·5—184·5° (Found: C, 38·7; H, 5·45; N, 5·3. $C_9H_{16}ONI$ requires C, 38·45; H, 5·75; N, 5·0%).

3-*Dimethylaminobut*-1-*yne* (I; $R = R' = Me$).—Dimethylamine (250 g.), tetrahydrofuran (200 c.c.), and cuprous chloride (25 g.) were treated at 85° with acetylene–nitrogen. Distillation of the product gave much recovered dimethylamine and 3-dimethylaminobut-1-yne (124 g.), b. p. 92—95° (Rose, *loc. cit.*, gives b. p. 96°). The *methiodide* formed needles from methyl alcohol, m. p. 214—216° (decomp.) (Found: C, 35·6; H, 5·9. $C_7H_{14}NI$ requires C, 35·15; H, 5·9%).

3-iso*Propylaminobut*-1-*yne* (I; $R = Pr^i, R' = H$).—*iso*Propylamine (200 g.), tetrahydrofuran (200 c.c.), and cuprous chloride (20 g.) were treated at 113° with acetylene–nitrogen, giving 3-iso*propylaminobut*-1-*yne* (110 g.), b. p. 108—112°, m. p. 28—29° (Found: equiv., 111·8. $C_7H_{13}N$ requires equiv., 111·2). The α-*naphthylurea*, m. p. 111—113°, formed needles from aqueous methanol or light petroleum (b. p. 80—100°) (Found: C, 76·7; H, 7·4; N, 10·3. $C_{18}H_{20}ON_2$ requires C, 77·1, H, 7·2; N, 10·0%). The *hydrochloride*, crystallised from alcohol–ether, had m. p. 198—200° (decomp.) (Found: C, 56·6; H, 9·45. $C_7H_{14}NCl$ requires C, 56·95; H, 9·55%). The *urethane*, formed from the amine and ethyl chloroformate, was a pleasant-smelling liquid, b. p. 90—92°/13 mm., $n_{\mathrm{D}}^{22^\circ}$ 1·4420, which readily gave a silver salt with Tollens's reagent (Found: N, 7·6. $C_{10}H_{17}N$ requires N, 7·65%).

3-n-*Butylaminobut*-1-*yne* (I; $R = Bu, R' = H$).—*n*-Butylamine (103 g.), tetrahydrofuran (225 c.c.), and cuprous chloride (10 g.) were treated at 106° with acetylene–nitrogen, giving 3-*n*-butylaminobut-1-yne (115 g.), b. p. 76—79°/65 mm., $n_D^{17°}$ 1·4388 (Found : N, 11·3. Calc. for $C_8H_{15}N$: N, 11·2%) (Rose, *loc. cit.*, gives b. p. 148°). The *hydrochloride* had m. p. 122—123° (Found : C, 59·35, H, 9·6. $C_8H_{16}NCl$ requires C, 59·45, H, 9·95%). The *α-naphthylurea*, m. p. 90—91°, crystallised as needles from aqueous methanol (Found : C, 77·25; H, 7·5; N, 9·7. $C_{19}H_{22}ON_2$ requires C, 77·5; H, 7·55; N, 9·5%). The 2 : 4-*dinitrophenylurea* (cf. McVeigh and Rose, *J.*, 1945, 621) formed plates from light petroleum, m. p. 117° (Found : C, 53·6; H, 5·1; N, 17·0. $C_{15}H_{18}O_5N_4$ requires C, 53·9; H, 5·4; N, 16·8%).

3-cyclo*Hexylaminobut*-1-*yne* (I; R = C_6H_{11}, R′ = H).—*cyclo*Hexylamine (200 g.), tetrahydrofuran (200 c.c.), and cuprous chloride (20 g.) were treated at 106° with acetylene–nitrogen, giving recovered *cyclo*hexylamine (50 g.) and 3-*cyclo*hexylaminobut-1-yne (155 g.), b. p. 82—85°/17 mm., m. p. 43° (Rose, *loc. cit.*, gives b. p. 60°/5 mm., m. p. 44°). The *α-naphthylurea*, m. p. 132—133°, formed prisms from methanol (Found : C, 78·45; H, 7·7; N, 8·8. $C_{21}H_{24}ON_2$ requires C, 78·7; H, 7·5; N, 8·75%). The *hydrochloride*, m. p. 181°, crystallised in needles from ether–alcohol (Found : C, 63·6; H, 9·25; N, 7·55; Cl, 19·1. $C_{10}H_{18}NCl$ requires C, 64·0; H, 9·6; N, 7·5; Cl, 18·9%). The *picrate* formed yellow prisms from benzene, m. p. 156° (Found : C, 50·45; H, 4·8; N, 14·8. $C_{10}H_{17}N,C_6H_3O_7N_3$ requires C, 50·45; H, 5·2; N, 14·7%).

3-*Benzylaminobut*-1-*yne* (I; R = Ph·CH_2, R′ = H).—Benzylamine (200 g.), tetrahydrofuran (200 c.c.), and cuprous chloride (20 g.) were treated at 85° with acetylene–nitrogen, giving 3-benzylaminobut-1-yne (90 g.), b. p. 110—112°/20 mm., $n_D^{14°}$ 1·5290 (Rose, *loc. cit.*, gives b. p. 98°/9 mm.). The *hydrochloride*, m. p. 210—211°, crystallised as prisms from alcohol (Found : C, 67·25; H, 6·95; N, 7·15. $C_{11}H_{14}NCl$ requires C, 67·5; H, 7·2; N, 7·15%).

3-6′-*Aminohexylaminobut*-1-*yne* (I; R = NH_2·$[CH_2]_6$, R′ = H).—Hexamethylenediamine (100 g.), tetrahydrofuran (300 c.c.), and cuprous chloride (10 g.) were treated at 113—115° with acetylene–nitrogen, giving 3-6′-*aminohexylaminobut*-1-*yne* (46 g.), b. p. 118—120°/10 mm., 80—86° (mainly 83—86°)/0·6 mm., $n_D^{20°}$ 1·4700 (Found : C, 71·1; H, 11·6; N, 16·55; equiv., 86·1. $C_{10}H_{20}N_2$ requires C, 71·35; H, 12·0; N, 16·65%, equiv., 84·2).

3-*Anilinobut*-1-*yne* (I; R = Ph, R′ = H).—Hydroxylamine hydrochloride (96 g.) was added to a solution of copper sulphate pentahydrate (39·6 g.) in water (500 c.c.) and ammonia (*d* 0·88; 102 c.c.) with stirring. " Filtercel " (12 g.) was then added, and a rapid stream of acetylene passed through the mixture for 0·5 hour. The solid was filtered off, washed with water, then with alcohol, and added as an alcohol paste to the autoclave containing aniline (110 g.), alcohol (286 g.), acetic acid (43 g.), and *β*-dinaphthol (2·4 g.; " Cuprene " inhibitor). The stirred mixture was treated with acetylene–nitrogen for 19 hours at 20° and finally for 2 hours at 60°. After filtration, the alcohol was distilled off under reduced pressure and the resulting viscous residue treated with excess (15%) of aqueous sodium hydroxide. The product was isolated in the usual way. Distillation gave recovered aniline (65 g.) and 3-anilinobut-1-yne (18 g.), b. p. 110—120°/20 mm., which solidified readily and was recrystallised from light petroleum (b. p. 40—60°), giving colourless needles, m. p. 69—71° (U.S.P. 2,342,493 gives b. p. 110—112°/15 mm., m. p. 74°) (Found : C, 82·4; H, 7·55; N, 9·9. Calc. for $C_{10}H_{11}N$: C, 82·7; H, 7·6; N, 9·65%). The *picrate* crystallised in leaflets from aqueous methanol, m. p. 192—194° (Found : C, 51·7; H, 3·65; N, 15·25. $C_{16}H_{14}O_7N_4$ requires C, 51·35; H, 3·75; N, 15·0%).

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