74. *Acetylene Reactions. Part VII. Acetylenic Amino-alcohols from Benzophenones.*

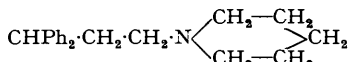
By H. P. W. Huggill and J. D. Rose.

Compounds of the type $CPh_2(OH)\cdot C{:}C\cdot CHR\cdot NR'_2$ and their semi- and completely hydrogenated analogues have been prepared for test as spasmolytics. Two methods have been used: (*a*) when R = CH_3, by interaction of 3-alkylamino- and 3-dialkylamino-but-1-ynes with benzophenones; and (*b*), when R = H, from diphenylethynylcarbinol or its acetate, formaldehyde, and a secondary amine. Some reactions of these compounds, particularly their hydrogenation, addition of hydrogen chloride, and Meyer–Schuster rearrangement with sulphuric acid, are described.

As part of a general programme of work on spasmolytic substances, unsaturated derivatives of diphenylcarbinol were required containing a basic substituent in the unsaturated side chain. Substances of type (I) and their ethylenic analogues, which have some structural similarity to "Trasentin" (II) (Meier and Salow, *Klin. Wochenschr.*, 1936, **15**, 1403, 1405), "Aspasin" (III) (B.I.O.S. Final Report No. 116, p. 57), and the 3-dialkylamino-1 : 1-diphenylpropanols (IV) (Roche Products Ltd., B.P. 615,136), seemed to be most readily accessible.

$CPh_2(OH)\cdot C{:}C\cdot CHR\cdot NR'_2$
(I.)

$CHPh_2\cdot CO\cdot O\cdot CH_2\cdot CH_2\cdot NEt_2$
(II.)


(III.)

$CPh_2(OH)\cdot CH_2\cdot CH_2\cdot NR_2$
(IV.)

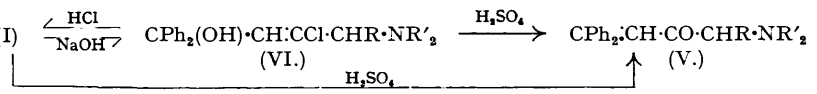
Two routes were used for the preparation of these compounds. The first was based on the availability of the 3-alkylamino- and 3-dialkylamino-but-1-ynes (Part I of this series, *J.*, 1949, 780) which condensed readily with benzophenone in the presence of alkali to give the required acetylenic amino-alcohols. This reaction was not completely general, and failed with 4 : 4′-bisdimethylaminobenzophenone (Michler's ketone).

The second route involved the Mannich reaction of diphenylethynylcarbinol (from benzophenone and acetylene), formaldehyde, and the secondary amine. In this reaction it was found advantageous to acetylate the carbinol before carrying out the Mannich condensation, as otherwise very low yields were obtained. It is noteworthy that during the Mannich condensation the acetyl group was lost and the resulting amino-acetylenic alcohols could not subsequently be reacetylated. This failure is not unexpected, since not only is the hydroxyl group tertiary, but the molecule contains in addition a strongly basic group and is too unstable to acid reagents to permit very drastic acetylation conditions.

The loss of the acetyl group during the Mannich reaction is more surprising. Judged by the difference in reactivity between the carbinol and its acetate in this reaction, it would appear that deacetylation does not precede the Mannich reaction, and the use of morpholine hydrochloride in place of the free base did not prevent deacetylation. The higher yield obtained from the acetate than from the carbinol is in accord with the findings of Jones, Marszak, and Bader (*J.*, 1947, 1578).

The acetylenic amino-alcohols underwent catalytic reduction to either the ethylenic or the saturated analogues, although there was considerable variation in the ease of reduction beyond the ethylenic stage. Those alcohols derived from the 3-dialkylamino- and 3-alkylamino-but-1-ynes (I; R = Me) tended to split off the amino-group in the second stage of the reduction, and attempted saturation of 4-morpholino-1 : 1-diphenylpent-2-yn-1-ol caused complete disruption of the molecule. Amines of the type (I; R = H) were easier to reduce and the reduction products were stable.

With sulphuric acid the 4-dialkylamino-1 : 1-diphenylpent-2-yn-1-ols underwent the Meyer–Schuster rearrangement to 4-dialkyamino-1 : 1-diphenylpent-1-en-3-ones (V), but with hydrochloric acid simple adducts (VI) of the acetylenic amines with HCl were obtained which on treatment with alkali regenerated the original amine and with sulphuric acid gave the αβ-unsaturated ketones.



The fact that (I) is regenerated by alkali treatment of (VI) disposes of the possibility that the hydrogen chloride adducts might be those of the αβ-unsaturated ketone (V), and the conversion of (VI) into (V) by dilute sulphuric acid considerably strengthens the probability that the orientation of the adduct is as shown. The addition of hydrogen chloride to acetylenic amines does not appear to have been recorded previously, although there are a few examples of its addition to acetylenic carbinols (see Johnson, "The Chemistry of the Acetylenic Compounds," Vol. I, p. 101, Arnold, 1946); in most of these cases dehydration to a vinylacetylene was possible and may have preceded addition. Where simple addition occurred, the position of the halogen was not determined.

Experimental.

The 3-alkylamino- and 3-dialkylamino-but-1-ynes used in this work were prepared by the methods of Part I of this series (*loc. cit.*).

4-Dimethylamino-1 : 1-diphenylpent-2-yn-1-ol.—A solution of benzophenone (175 g.) and 3-diethylaminobut-1-yne (105 g.) in ether (200 c.c.) was added during one hour to a stirred suspension of powdered potassium hydroxide (180 g.) in dry ether (700 c.c.) at 15—20°. After 16 hours' stirring, water (1 l.) was added, and the mixture filtered, giving 97 g. of crude amine (32% based on the dimethylaminobutyne). The ethereal layer from the filtrate was shaken with 1·5N-hydrochloric acid (1 l.) which gave, after filtration, 80 g. (24%) of the base hydrochloride. From the filtrates 49 g. of benzophenone and 36 g. of unchanged 3-dimethylaminobut-1-yne were recovered. When crystallised from methyl alcohol, *4-dimethylamino-1 : 1-diphenylpent-2-yn-1-ol* formed white plates, m. p. 144—146° (Found: C, 82·1; H, 7·2; N, 5·3. $C_{19}H_{21}ON$ requires C, 81·7; H, 7·5; N, 5·0%). The *methiodide* formed white plates (from methyl alcohol), m. p. 223° (decomp.; bath pre-heated to 205°) (Found: C, 57·0; H, 5·8; N, 3·3. $C_{20}H_{24}ONI$ requires C, 57·0; H, 5·7; N, 3·3%). The *hydrochloride*, white needles from aqueous alcohol, had m. p. 189° (decomp.; bath pre-heated to 180°) (Found: C, 66·8; 66·8; H, 6·8; 7·3; N, 4·25. $C_{19}H_{21}ON,HCl,1{\cdot}5H_2O$ requires C, 66·6; H, 7·3; N, 4·1%). Attempts to form the acetate with acetyl chloride in pyridine were unsuccessful.

4-*Morpholino*-1 : 1-*diphenylpent*-2-*yn*-1-*ol*.—3-Morpholinobut-1-yne (21 g.) and benzophenone (27·2 g.) were brought into reaction with potassium hydroxide powder (27 g.) in ether (120 c.c.) as described above for the dimethylamino-analogue. The *amino-alcohol* (17 g., 35%) was obtained as white plates, m. p. 142—144°, from methyl alcohol (Found: C, 78·6; H, 7·1; N, 4·55. $C_{21}H_{23}O_2N$ requires C, 78·5; H, 7·1; N, 4·35%). The *methiodide* formed white needles, m. p. 202—203° (decomp.), from methyl alcohol (Found: C, 56·6; H, 5·8; N, 3·0. $C_{22}H_{26}O_2NI$ requires C, 57·0; H, 5·6; N, 3·0%). The *hydrochloride* formed white plates, m. p. 186° (decomp.; bath preheated to 175°), from methyl alcohol (Found: C, 67·2; H, 6·9; N, 3·6. $C_{21}H_{23}O_2N,HCl,H_2O$ requires C, 67·2; H, 6·9; N, 3·7%). No acetyl derivative could be prepared.

4-*Diethylamino*-1 : 1-*diphenylpent*-2-*yn*-1-*ol*.—A solution of benzophenone (180 g.) and 3-diethylaminobut-1-yne (120 g.) in ether (250 c.c.) was added during one hour to a stirred suspension of powdered potassium hydroxide (180 g.) in dry ether (750 c.c.) at 15—20°. After 16 hours' stirring, water (1 l.) was added, and the ethereal layer separated and extracted with water (1 l.) containing concentrated hydrochloric acid (150 c.c.). The aqueous layer was made strongly alkaline with 10N-sodium hydroxide and extracted with ether. Distillation of the dried ethereal solution gave 53 g. (44%) of unchanged diethylaminobutyne and a residue (135 g.) of 4-*diethylamino*-1 : 1-*diphenylpent*-2-*yn*-1-*ol*, which after crystallisation from light petroleum (b. p. 60—80°) formed white prisms m. p. 81—82° (Found: C, 81·7; H, 7·8; N, 4·35. $C_{21}H_{25}ON$ requires C, 82·1; H, 8·1; N, 4·55%). The *methiodide* formed white needles, m. p. 183°, from water (Found: C, 58·6; H, 5·75; N, 3·0. $C_{22}H_{28}ONI$ requires C, 58·9; H, 6·24; N, 3·1%). The *hydrochloride* formed white needles, m. p. 178° (decomp.), from dioxan (Found: N, 3·9. $C_{21}H_{25}ON,HCl$ requires N, 4·0%). No acetyl derivative could be obtained.

4-*Diethylamino*-1 : 1-*di*-p-*tolylpent*-2-*yn*-1-*ol*.—Di-*p*-tolyl ketone (5 g.), 3-diethylaminobut-1-yne (5 g.), and powdered potassium hydroxide (5 g.) were caused to interact as above in ether (50 c.c.) for 48 hours to give the *amino-alcohol* (2·0 g.) as white prisms, m. p. 85°, from light petroleum (b. p. 60—80°) (Found: C, 82·1; H, 8·35; N, 3·7. $C_{23}H_{29}ON$ requires C, 82·4; H, 8·7; N, 4·2%). The *methiodide* formed white prisms (from ethyl alcohol), m. p. 183—185° (decomp.) (Found: C, 60·6; H, 6·8; N, 2·7. $C_{24}H_{32}ONI$ requires C, 60·4; H, 6·7; N, 2·9%).

4-*Diethylamino*-1-*phenyl*-1-p-*tolylpent*-2-*yn*-1-*ol*.—This was prepared from 3-diethylaminobut-1-yne (16 g.), phenyl *p*-tolyl ketone (25 g.), and powdered potassium hydroxide in the usual manner. The *amino-alcohol* formed white prisms, m. p. 66—67°, from light petroleum (b. p. 60—80°) (Found: C, 82·2; H, 8·3; N, 4·2. $C_{22}H_{27}ON$ requires C, 82·2; H, 8·4; N, 4·4%). The *methiodide* formed white prisms (from alcohol), m. p. 212—214° (decomp.; bath preheated to 205°) (Found: C, 59·1; H, 6·5. $C_{23}H_{30}ONI$ requires C, 59·5; H, 6·5%). The *hydrochloride* formed white needles, m. p. 175° (decomp., bath preheated to 165°), from water (Found: C, 72·5; H, 7·8. $C_{22}H_{27}ON,HCl,0{\cdot}5H_2O$ requires C, 72·05; H, 7·8%).

4-iso*Propylamino*-1 : 1-*diphenylpent*-2-*yn*-1-*ol*.—Similarly prepared from benzophenone (30 g.), 3-*iso*propylaminobut-1-yne (20 g.), and potassium hydroxide (30 g.), this *amino-alcohol* formed white prisms, m. p. 79—80°, from light petroleum (b. p. 60—80°) (Found: C, 82·0; H, 7·8; N, 4·95. $C_{20}H_{23}ON$ requires C, 81·9; H, 7·8; N, 4·8%). The *hydrochloride* formed white needles, m. p. 180°, from acetone (Found: N, 4·1. $C_{20}H_{23}ON,HCl$ requires N, 4·2%). The N-*acetyl* derivative, white needles from *cyclo*hexane, has m. p. 98—99° (Found: C, 78·65; H, 7·5; N, 4·65. $C_{22}H_{25}O_2N$ requires C, 78·8; H, 7·5; N, 4·2%).

4-*Diethylamino*-1-*phenyl*-1-p-*methoxyphenylpent*-2-*yn*-1-*ol*.—*p*-Methoxybenzophenone (18 g.), 3-diethylaminobut-1-yne (12 g.), and potassium hydroxide (15 g.), when similarly interacting in ether (75 c.c.), gave an oil (11 g.) which crystallised when set aside at 0° for 7 days. After recrystallisation from light petroleum (b. p. 40—60°) the *amino-alcohol* was obtained as white prisms, m. p. 50—52° (Found: C, 78·6; H, 8·3; N, 3·9. $C_{23}H_{27}O_2N$ requires C, 78·3; H, 8·0; N, 4·2%). The *methiodide* formed white prisms, m. p. 152—153°, from acetone (Found: C, 57·1; H, 6·35; N, 2·5. $C_{23}H_{30}O_2NI$ requires C, 57·6; H, 6·3; N, 2·9%).

4-*Diethylamino*-1 : 1-*di*-p-*methoxyphenylpent*-2-*yn*-1-*ol*.—This was prepared in the usual way from *pp'*-dimethoxybenzophenone (5 g.), 3-diethylaminobut-1-yne (5 g.), and potassium hydroxide (5 g.). The *amino-alcohol* was obtained as white prisms, m. p. 100°, from light petroleum (b. p. 60—80°) (Found: C, 75·15; H, 7·7; N, 4·1. $C_{23}H_{29}O_3N$ requires C, 75·2; H, 7·9; N, 3·8%).

Diphenylethynylcarbinyl Acetate.—Diphenylethynylcarbinol (20 g.; Campbell, Campbell, and Eby, *J. Amer. Chem. Soc.*, 1938, **60**, 2882) was dissolved in dry pyridine (20 c.c.), and acetyl chloride (8 g.) added dropwise with stirring and cooling. After being kept at 40—50° for 3 hours, the mixture was poured into ice and water (200 g.), and the product extracted with ether and washed with dilute hydrochloric acid (twice) and water. The dried ($MgSO_4$) ethereal solution was distilled, giving 5 g. of an oil, b. p. 120°/1 mm., which solidified when kept for 14 days at 0° and recrystallised from *cyclo*hexane to give colourless prisms of *diphenylethynylcarbinyl acetate*, m. p. 79—80° (Found: C, 81·65; H, 5·5. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%).

4-*Morpholino*-1 : 1-*diphenylbut*-2-*yn*-1-*ol*.—(a) *From diphenylethynylcarbinyl acetate*. The acetate (30 g.), paraformaldehyde (5 g.), morpholine (12 g.), and dioxan (35 c.c.) were heated together at 100° for 16 hours. The dioxan was removed by distillation *in vacuo*, the residue dissolved in ether, and the ethereal solution washed with dilute sodium hydroxide solution and shaken with hydrochloric acid (125 c.c. of 2N.). The white solid (12 g.) which separated was collected and crystallised from water, giving 4-*morpholino*-1 : 1-*diphenylbut*-2-*yn*-1-*ol hydrochloride*, small prisms (from water), m. p. 203° (decomp.; bath preheated to 190°) (Found: C, 69·5; H, 6·0; N, 3·95. $C_{20}H_{21}O_2N,HCl$ requires C, 69·9; H, 6·4; N, 4·1%). The free *amine*, obtained by basification of a warm aqueous solution of the hydrochloride, formed colourless needles from methyl alcohol, m. p. 150—152° (Found: C, 78·4; H, 7·1; N, 4·8. $C_{20}H_{21}O_2N$ requires C, 78·2; H, 6·85; N, 4·6%). The *methiodide* formed plates, m. p. 168—170° (decomp.), from methyl alcohol (Found: C, 55·9; H, 5·45; N, 3·0. $C_{21}H_{24}O_2NI$ requires C, 56·1; H, 5·35; N, 3·1%). The acetyl derivative could not be prepared.

(b) *From diphenylethynylcarbinol*. The carbinol (21 g.), paraformaldehyde (4 g.), morpholine (10 g.), and dioxan (30 c.c.) were heated at 100° for 16 hours. The dioxan was removed by distillation

in vacuo, the residue dissolved in ether and extracted with hydrochloric acid (20 c.c. of concentrated acid in 150 c.c. of water), and the aqueous acid layer basified with 10N-sodium hydroxide. The gummy precipitate was extracted with ether, and, after drying ($MgSO_4$) and evaporation, crystallised from methanol to give 4-morpholino-1 : 1-diphenylbut-2-yn-1-ol (0·3 g., 1%) as needles, m. p. 150—152°, identical with those obtained under (a), above.

4-*Dimethylamino*-1 : 1-*diphenylpent*-2-en-1-*ol*.—4-Dimethylamino-1 : 1-diphenylpent-2-yn-1-ol (5 g.), dissolved in methyl alcohol (100 c.c.), was hydrogenated at ordinary temperature and atmospheric pressure by using palladium on calcium carbonate as catalyst. After 40 minutes, absorption was complete (410 c.c.; calc. for H_2, 405 c.c.). After evaporation of the filtered solution *in vacuo*, the residue was recrystallised from light petroleum (b. p. 40—60°), giving 4-*dimethylamino*-1 : 1-*diphenylpent*-2-*en*-1-*ol* (4 g.) as colourless plates, m. p. 72—74° (Found: C, 81·0; H, 7·95; N, 4·9. $C_{19}H_{23}ON$ requires C, 81·1; H, 8·2; N, 5·0%). The *methiodide* formed colourless prisms, m. p. 229—230° (decomp.; bath preheated to 210°), from water (Found: C, 56·55; H, 6·1; N, 3·25. $C_{20}H_{26}ONI$ requires C, 56·7; H, 6·1; N, 3·3%).

4-*Dimethylamino*-1 : 1-*diphenylpentan*-1-*ol*.—4-Dimethylamino-1 : 1-diphenylpent-2-yn-1-ol (5 g.), dissolved in methyl alcohol (100 c.c.), was hydrogenated at ordinary temperature and pressure by means of Raney nickel catalyst. The reduction proceeded in two stages, 415 c.c. (theory for H_2, 405 c.c.) being absorbed in one hour and 820 c.c. (theory for $2H_2$, 810 c.c.) in 12 hours, absorption then ceasing. Evaporation of the filtered solution *in vacuo* and crystallisation of the residue from light petroleum (b. p. 40—60°) gave 4-*dimethylamino*-1 : 1-*diphenylpentan*-1-*ol* (3·6 g.) as colourless prisms, m. p. 79—80° (Found: C, 80·7; H, 8·65; N, 5·4. $C_{19}H_{25}ON$ requires C, 80·5; H, 8·8; N, 4·95%). The *methiodide* formed colourless prisms, m. p. 237—238°, from methanol (Found: C, 56·4; H, 6·5; N, 3·05. $C_{20}H_{28}ONI$ requires C, 56·5; H, 6·6; N, 3·3%).

4-*Diethylamino*-1 : 1-*diphenylpent*-2-*en*-1-*ol*.—This was obtained by reduction of 4-diethylamino-1 : 1-diphenylpent-2-yn-1-ol as described above for the dimethylamino-analogue. The *base* (61% yield) formed colourless plates, m. p. 68—70°, from light petroleum (b. p. 40—60°) (Found: C, 81·2; H, 8·5; N, 4·2. $C_{21}H_{27}ON$ requires C, 81·5; H, 8·7; N, 4·5%). The *methiodide* formed colourless plates, m. p. 190—192° (decomp.), from methyl alcohol (Found: C, 58·25; H, 6·35; N, 2·95. $C_{22}H_{30}ONI$ requires C, 58·5; H, 6·7; N, 3·1%).

4-*Diethylamino*-1 : 1-*diphenylpentan*-1-*ol*.—4-Diethylamino-1 : 1-diphenylpent-2-yn-1-ol (7 g.) in methyl alcohol (100 c.c.) was hydrogenated at room temperature and pressure in presence of Raney nickel catalyst. Absorption of 510 c.c. (theory for H_2, 513 c.c.) took 15 minutes, and that of 1400 c.c. 11 hours, after which the experiment was stopped although absorption was still occurring. The solvent was distilled from the filtered solution, and the presence of diethylamine in the distillate was established by isolation of its hydrochloride and picrolonate, and by the formation of *N*-α-naphthyl-*N'N'*-diethylurea, identical with authentic specimens. The residue after removal of methyl alcohol was dissolved in ether and extracted with dilute hydrochloric acid, the aqueous acid extract basified with 10N-sodium hydroxide, and the precipitated amine isolated with ether. Crystallisation of the residue from light petroleum (b. p. 40—60°) gave 4-*diethylamino*-1 : 1-*diphenylpentan*-1-*ol* (3·0 g.) as colourless plates, m. p. 92—94° (Found: C, 81·05; H, 8·9; N, 4·25. $C_{21}H_{29}ON$ requires C, 81·0; H, 9·3; N, 4·5%). The *methiodide* formed prisms, m. p. 178—180° (decomp.), from aqueous methyl alcohol (Found: C, 55·9; H, 7·1; N, 3·25. $C_{22}H_{32}ONI,H_2O$ requires C, 56·05; H, 7·2; N, 2·9%). Attempts to carry out the complete reduction with platinum or with palladium under pressure gave low yields of product and much fission to diethylamine.

4-*Morpholino*-1 : 1-*diphenylpent*-2-*en*-1-*ol*.—4-Morpholino-1 : 1-diphenylpent-2-yn-1-ol (5 g.) was reduced with a palladium–calcium carbonate catalyst as described for the dimethylamino-analogue. The *base* (4·4 g.) formed colourless elongated prisms, m. p. 93—94°, from light petroleum (b. p. 60—80°) (Found: C, 77·6; H, 7·6; N, 4·35. $C_{21}H_{25}O_2N$ requires C, 78·0; H, 7·7; N, 4·3%). The *methiodide* formed colourless prisms, m. p. 232° (decomp.; bath preheated to 210°), from methyl alcohol (Found: C, 56·35; H, 5·8; N, 2·7. $C_{22}H_{28}O_2NI$ requires C, 56·7; H, 6·0; N, 3·0%). Attempts to effect the saturation of the acetylenic linkage by means of platinum oxide gave a 16% yield of the ethylenic amine, and much morpholine. Raney nickel or palladium–calcium carbonate with hydrogen under pressure also gave a low yield of the ethylenic amine, and much fission occurred. Attempted further hydrogenation of the ethylenic amine gave the unchanged base in low yield and decomposition products, and reduction with sodium and liquid ammonia was also unsuccessful.

4-*Morpholino*-1 : 1-*diphenylbut*-2-*en*-1-*ol*.—4-Morpholino-1 : 1-diphenylbut-2-yn-1-ol (3·2 g.) was hydrogenated in dioxan (100 c.c.) at room temperature and atmospheric pressure with palladised calcium carbonate as catalyst. The hydrogenation was stopped after an absorption of 280 c.c. (absorption was still proceeding rapidly; theory for H_2, 240 c.c.), and after filtration and evaporation *in vacuo* gave a product (3 g.), m. p. 50—70°, which after three recrystallisations from methyl alcohol and two from light petroleum (b. p. 60—80°) gave 4-*morpholino*-1 : 1-*diphenylbut*-2-*en*-1-*ol* (2 g.) as needles, m. p. 88—89° (Found: C, 77·7; H, 7·4; N, 4·3. $C_{20}H_{23}O_2N$ requires C, 77·8; H, 7·4; N, 4·5%). The *methiodide* formed small prisms, m. p. 203° (decomp.; bath preheated to 190°), from water (Found: C, 55·7; H, 5·8; N, 3·1. $C_{21}H_{26}O_2NI$ requires C, 55·9; H, 5·8; N, 3·1%).

4-*Morpholino*-1 : 1-*diphenylbutan*-1-*ol*.—Hydrogenation was carried out as described for the semi-hydrogenation but the experiment was continued until absorption was complete. The *base* was obtained in 83% yield as silky needles, m. p. 128—130°, from light petroleum (b. p. 60—80°) (Found: C, 76·9; H, 8·0; N, 4·55. $C_{20}H_{25}O_2N$ requires C, 77·2; H, 8·0; N, 4·5%). The *methiodide* formed plates, m. p. 204° (decomp.; bath preheated to 190°), from water (Found: C, 55·5; H, 5·95; N, 3·4. $C_{21}H_{28}O_2NI$ requires C, 55·6; H, 6·2; N, 3·1%).

4-*Dimethylamino*-1 : 1-*diphenylpent*-1-*en*-3-*one*.—4-Dimethylamino-1 : 1-diphenylpent-2-yn-1-ol (5 g.) was heated with dilute sulphuric acid (20 c.c. of concentrated acid in 100 c.c. of water) at 100° for 30 minutes. After cooling, 10N-sodium hydroxide (70 c.c.) was added, and the solution, after filtration from sodium sulphate, was extracted with ether to remove non-basic by-products. The aqueous layer was basified with 10N-sodium hydroxide and extracted with ether, and the ether dried ($MgSO_4$) and

evaporated. The product crystallised from light petroleum (b. p. 40—60°) to give 4-*dimethylamino*-1 : 1-*diphenylpent*-1-*en*-3-*one* as yellowish needles, m. p. 52—54° (2·9 g., 58%) (Found : C, 81·3; H, 7·55; N, 5·1. $C_{19}H_{21}ON$ requires C, 81·7; H, 7·5; N, 5·0%). The *methiodide* formed cream-coloured plates, m. p. 220° (decomp.; bath preheated to 205°), from methanol (Found : C, 57·5; H, 5·7; N, 3·5. $C_{20}H_{24}ONI$ requires C, 57·0; H, 5·7; N, 3·3%).

This amino-ketone was very unstable; purified specimens decomposed to a brown liquid in 72 hours, and impure specimens were even less stable. For this reason the complete preparation and the utilisation of the product were always carried out in one day. One of the products of decomposition was non-basic, and it was possible to recover some of the amino-ketone from a partly decomposed sample by extraction with acid.

3-*Chloro*-4-*dimethylamino*-1 : 1-*diphenylpent*-2-*en*-1-*ol*.—4-Dimethylamino-1 : 1-diphenylpent-2-yn-1-ol (1 g.) was heated at 100° for 5 minutes with water (10 c.c.) and 10N-hydrochloric acid (5 c.c.). After cooling to 45°, the insoluble hydrochloride was collected and crystallised from alcohol, giving 3-*chloro*-4-*dimethylamino*-1 : 1-*diphenylpent*-2-*en*-1-*ol hydrochloride* as white needles, m. p. 195° (decomp.) (0·5 g.) (Found : C, 63·25; H, 6·4. $C_{19}H_{22}ONCl,HCl,0{\cdot}5H_2O$ requires C, 63·15; H, 6·7%). The free *base* formed white prisms, m. p. 56—58°, from light petroleum (b. p. 40—60°) (Found : C, 72·7; H, 6·85; N, 4·4; Cl, 11·8. $C_{19}H_{22}ONCl$ requires C, 72·3; H, 7·0; N, 4·4; Cl, 11·3%). The *methiodide* formed white prisms, m. p. 227° (decomp.; bath preheated to 210°), from alcohol (Found : C, 52·55; H, 5·55; N, 2·95. $C_{20}H_{25}ONClI$ requires C, 52·5; H, 5·5; N, 3·0%).

The use of very dilute hydrochloric acid in this reaction gave only unchanged amino-alcohol after 24 hours' boiling; concentrated hydrochloric acid (15 minutes at 100°), however, caused disruption of the molecule and gave a non-basic tar from which benzophenone was isolated as its dinitrophenylhydrazone (m. p. and mixed m. p. 232°).

3-Chloro-4-dimethylamino-1 : 1-diphenylpent-2-en-1-ol regenerates the original acetylenic amine on treatment with 5% methanolic potassium hydroxide at 80° for 1½ hours. On catalytic reduction with Raney nickel and hydrogen at room temperature and pressure, 20% of the material is recovered unchanged, the rest being converted into a non-basic resin. When the alcohol is heated with 30% sulphuric acid, 4-dimethylamino-1 : 1-diphenylpent-1-en-3-one is formed.

4-*Diethylamino*-1 : 1-*diphenylpent*-1-*en*-3-*one*.—4-Diethylamino-1 : 1-diphenylpent-2-yn-1-ol hydrochloride (3·3 g.), dissolved in water (50 c.c.), was boiled under reflux for 24 hours. After cooling, some oil was removed by ether-extraction, the aqueous layer was basified with dilute sodium hydroxide solution, and the product (a sticky solid) extracted with ether. After drying ($MgSO_4$) and evaporation, a viscous yellow oil was obtained, which on crystallisation from light petroleum gave only a low yield of recovered diethylaminodiphenylpentynol, m. p. 81—83°. Methylation of the crude oil with methyl iodide in acetone, however, gave pale yellow needles, m. p. 193°, from alcohol. This was not identical with the methiodide of the original amine, and is probably 4-*diethylamino*-1 : 1-*diphenylpent*-1-*en*-3-*one methiodide* (Found : C, 58·5; H, 6·4; N, 3·6; I, 27·6. $C_{22}H_{28}ONI$ requires C, 58·8; H, 6·3; N, 3·1; I, 28·3%).

3-*Chloro*-4-*morpholino*-1 : 1-*diphenylpent*-2-*en*-1-*ol*.—4-Morpholino-1 : 1-diphenylpent-2-yn-1-ol (10 g.) was heated with hydrochloric acid (36%; 50 c.c.) and water (100 c.c.) at 80—90° for 5 minutes. After cooling to 40°, the precipitated hydrochloride (5 g., 41%) was collected and recrystallised from alcohol, giving 3-*chloro*-4-*morpholino*-1 : 1-*diphenylpent*-2-*en*-1-*ol hydrochloride* as needles, m. p. 176° (decomp.) (Found : C, 63·55; H, 6·3; N, 3·3. $C_{21}H_{24}O_2NCl,HCl$ requires C, 63·9; H, 6·3; N, 3·6%). The free *base*, regenerated from the hydrochloride with sodium hydroxide, separated from methyl alcohol in small plates, m. p. 105—106° (Found : C, 70·4; H, 6·9; N, 4·0; Cl, 10·7. $C_{21}H_{24}O_2NCl$ requires C, 70·6; H, 6·7; N, 3·9; Cl, 10·1%). The *methiodide* formed minute needles, m. p. 198° (decomp.), from methyl alcohol (Found : C, 52·5; H, 5·4; N, 2·5. $C_{21}H_{27}O_2NClI$ requires C, 52·8; H, 5·4; N, 2·8%).

Treatment of the base with methanolic potassium hydroxide regenerated 4-morpholino-1 : 1-diphenylpent-2-yn-1-ol, m. p. and mixed m. p. 140—142°. Reduction with Raney nickel and hydrogen at room temperature and pressure gave 20% of recovered chloro-amine and much unidentified tar.

4-*Morpholino*-1 : 1-*diphenylpent*-1-*en*-3-*one*.—4-Morpholino-1 : 1-diphenylpent-2-yn-1-ol (2 g.) was dissolved in dilute sulphuric acid (8 c.c. of concentrated acid and 40 c.c. of water), and the solution heated on the steam-bath for 30 minutes. The cooled solution was made strongly alkaline with 10N-sodium hydroxide, and the precipitated oil extracted with ether. The ethereal solution was extracted with 2N-hydrochloric acid, and the acidic extract basified (10N-NaOH), and again extracted with ether. Evaporation of the ether gave a yellow oil which could not be induced to crystallise. Addition of dry hydrogen chloride in ether afforded the *hydrochloride*, m. p. 184—185°, as white needles from alcohol (Found : C, 70·3; H, 6·75; N, 3·9. $C_{21}H_{23}O_2N,HCl$ requires C, 70·5; H, 6·7; N, 3·9%), which depressed the m. p. (186°) of the hydrochloride of the starting material. Treatment of the crude oil with methyl iodide gave the *methiodide* as yellow prisms, m. p. 197° (decomp.), from alcohol (Found : C, 57·2; H, 6·0; N, 2·9. $C_{22}H_{26}O_2NI$ requires C, 57·0; H, 5·7; N, 3·0%). The methiodide depressed the m. p. (202—203°) of the (white) methiodide of the starting material. The same material, identified as the hydrochloride and methiodide, was formed when 3-chloro-4-morpholino-1 : 1-diphenylpent-2-en-1-ol (above) was treated at 100° for 3 hours with 35% sulphuric acid.

IMPERIAL CHEMICAL INDUSTRIES LTD. (DYESTUFFS DIVISION),
BLACKLEY, MANCHESTER, 9.

[*Received, October 20th*, 1949.]