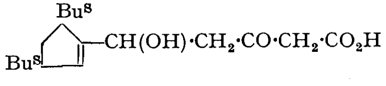
569. *Researches on Acetylenic Compounds. Part XXI. Reformatsky Reactions with Propargyl Bromides.*

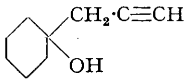
By H. B. Henbest,* E. R. H. Jones, and I. M. S. Walls.

It has been shown that propargyl bromide undergoes a Reformatsky type of reaction with a variety of carbonyl compounds to give $\beta\gamma$-acetylenic carbinols in good yields. These carbinols are required as intermediates for syntheses of compounds related to the plant-growth hormones, auxin-a and auxin-b. Substituted propargyl bromides also undergo this reaction with carbonyl compounds.

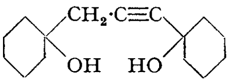
In an earlier publication from these laboratories it has been shown (Jones and Whiting, this vol., p. 1419) that $\beta\gamma$-acetylenic carbinols of the general formula $HO\cdot CHR\cdot CH_2\cdot C{\vdots}CH$, prepared from 1 : 2-epoxides and sodium acetylide, can be converted into 4-hydroxy-5 : 6-dihydro-2-pyrones. The importance of these pyrones is that they possess structures analogous to the lactone of auxin-b (I) as formulated by Kögl, Haagen-Smit, and Erxleben (*Z. physiol. Chem.*, 1934, **225**, 215). However, as a route for the synthesis of auxin-b and analogues, the above method is seriously limited by the inaccessibility of appropriate 1 : 2-epoxides. Attention has therefore been directed towards finding more convenient methods for preparing $\beta\gamma$-acetylenic carbinols. Zeile and Meyer (*Ber.*, 1942, **75**, 356) reported that propargyl bromide condenses with *cyclo*hexanone in the presence of zinc to give the carbinol (II) in 50% yield. The ethynyl group evidently activates the α-bromine atom in a similar manner to the ester group in the normal Reformatsky reaction. Two other products were also isolated, *viz.*, *cyclo*hexylidene*cyclo*hexanone, and the glycol (III), the latter presumably formed by condensation of the carbinol (II) with *cyclo*hexanone, catalysed by the basic BrZn-derivative of the carbinol (II).



(I.)



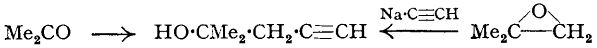
(II.)



(III.)

The generality of this reaction has been explored and it has now been shown that propargyl bromide condenses readily with aldehydes to give the required $\beta\gamma$-acetylenic carbinols in *ca.* 70% yields. *Carbinols* have been obtained where R = Pr^n, $Me\cdot CH{:}CH$, or Ph [and also p-C_6H_4Cl, $Ph\cdot CH{:}CH$, or *cyclo*pentenyl (forthcoming publications)]. It was not possible, however, to obtain a carbinol from acraldehyde, much polymerisation taking place. In these reactions with aldehydes, acetylenic glycols analogous to (III) (*i.e.*, $HO\cdot CHR\cdot CH_2\cdot C{\vdots}C\cdot CHR\cdot OH$) were formed in less than 10% yields; but only the crystalline *diphenyl* compound was isolated in a pure state.

The reaction between propargyl bromide and ketones has also been investigated. *cyclo*-Hexanone yielded the crystalline 3-1′-hydroxy*cyclo*hexylprop-1-yne (II) as described by Zeile and Meyer (*loc. cit.*), and acetone gave 2-*methylpent*-4-*yn*-2-*ol* (IV) in 40% yield, compared with a 19% yield obtained from *iso*butylene oxide and sodium acetylide. Acetophenone, benzophenone, and methylheptenone gave good yields of the acetylenic *carbinols* with only small amounts of the corresponding glycols.



$$Me_2CO \longrightarrow HO\cdot CMe_2\cdot CH_2\cdot C\equiv CH \xleftarrow{Na\cdot C\equiv CH} Me_2C\overset{O}{—}CH_2$$

(IV.)

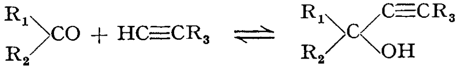
In these " modified " Reformatsky reactions it was found that the type of solvent employed was of some importance. The zinc complexes formed in the reaction are sometimes precipitated from solution, partly on to the zinc surface, thus inhibiting further reaction. Mixtures of ether and benzene, and especially of ether and tetrahydrofuran, were generally the most useful. An attempt to employ propargyl chloride in place of the bromide in these Reformatsky reactions was not successful, even when the zinc was previously activated by immersion in copper sulphate solution or mixed with copper powder (cf. Nieuwland and Daly, *J. Amer. Chem. Soc.*, 1931, **53**, 1842, who were able to condense α-chloro-esters with carbonyl compounds by using the latter procedure).

As mentioned above, acetophenone and benzophenone gave smaller amounts of the glycol by-product than did *cyclo*hexanone, a result in agreement with the known relatively great reactivity of the carbonyl group in the latter ketone. The overall yield of the desired acetylenic

---

* Beit Scientific Research Fellow.

carbinol from *cyclo*hexanone could be considerably increased, however, by heating the glycol in the presence of barium hydroxide at 170°, whereupon nearly quantitative fission occurred to give (II) and *cyclo*hexanone. The formation of αβ-acetylenic carbinols from ketones is known to be reversible in the presence of alkaline catalysts (cf. Babayan, *Chem. Abs.*, 1938, **32**, 7894; 1939, **33**, 9283).



$$R_1R_2C{=}O + HC{\equiv}CR_3 \rightleftharpoons R_1R_2C(C{\equiv}CR_3)OH$$

The structure of the glycol (V) derived from benzaldehyde was confirmed by hydrogenation to the saturated glycol (VI), followed by oxidation of the latter to the crystalline 1 : 5-diphenylpenta-1 : 5-dione (VII), previously prepared by Wislicenus and Kuhn (*Annalen*, 1898, **302**, 216) and by Japp and Michie (*J.*, 1901, 1019). Since most of these acetylenic glycols possess two different centres of asymmetry it was not surprising to find that the glycol (V) was a mixture of

$$\underset{\text{(V.)}}{HO{\cdot}CHPh{\cdot}CH_2{\cdot}C{\equiv}C{\cdot}CHR{\cdot}OH} \xrightarrow{2H_2} \underset{\text{(VI.)}}{HO{\cdot}CHPh{\cdot}[CH_2]_3{\cdot}CHPh{\cdot}OH} \xrightarrow{CrO_3} \underset{\text{(VII.)}}{Ph{\cdot}CO{\cdot}[CH_2]_3{\cdot}CO{\cdot}Ph}$$

two racemates. This was shown most clearly by observation of the product under the microscope whereby two different crystalline forms could be seen; examination of the mixture on the Köfler block showed that the forms had different melting points. The diphenyl-glycol was separated into its two racemic forms, m. p. 105—108° and 143—146° respectively, by means of their different solubilities in ether.

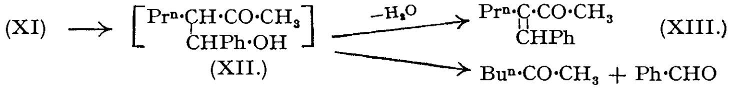
This type of Reformatsky condensation has been found to proceed equally well with the substituted propargyl bromides, 1-bromohept-2-yne (VIII), and the secondary bromide, 3-bromohex-1-yne (IX), which were prepared from the corresponding carbinols with phosphorus tribromide. Benzaldehyde thus gave the *carbinols* (X) and (XI) in 90 and 70% yields respectively. The bromide (VIII) gave higher yields than did propargyl bromide, with both benzaldehyde and

$$\underset{\text{(VIII.)}}{Bu^n{\cdot}C{\equiv}C{\cdot}CH_2Br} \longrightarrow \underset{\text{(X.)}}{Bu^n{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}CHPh{\cdot}OH} \qquad \underset{\text{(IX.)}}{Pr^n{\cdot}CHBr{\cdot}C{\equiv}CH} \longrightarrow \underset{\text{(XI.)}}{\begin{matrix}Pr^n{\cdot}CH{\cdot}C{\equiv}CH\\ CHPh{\cdot}OH\end{matrix}}$$

*cyclo*hexanone, the replacement of the reactive ethynyl hydrogen atom by an alkyl group preventing the formation of glycols. The good yield obtained from the secondary bromide (IX) may be compared with the similarly high yields given by α-bromopropionic ester in the normal Reformatsky reaction.

Addition of 1-phenylbut-3-yn-1-ol ($OH{\cdot}CHPh{\cdot}CH_2{\cdot}C\vdots CH$) to 2 : 4-dinitrophenylhydrazine in methanol–sulphuric acid led to the rapid deposition of a red precipitate, which was identified as benzylideneacetone 2 : 4-dinitrophenylhydrazone. This derivative is clearly formed by a hydration–dehydration mechanism induced by the sulphuric acid. The reaction has been found to be of general applicability for the βγ-acetylenic carbinols derived from aromatic aldehydes and ketones, and provides a useful method of characterisation. No derivatives were obtained from the purely aliphatic carbinols even on warming the mixture.

Conversion of these βγ-acetylenic carbinols into the corresponding ethylenic ketones should occur in the presence of mercuric salts, and this reaction has been studied with 1-phenyl-2-propylbut-3-yn-1-ol (XI). This carbinol was recovered unchanged when heated with mercuric acetate in 60% acetic acid, conditions used by Venus-Danilova and Danilov (*J. Gen. Chem. Russia*, 1932, **2**, 645) to convert primary acetylenic carbinols ($R{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}OH$) into unsaturated ketones ($R{\cdot}CO{\cdot}CH{=}CH_2$). More vigorous hydration, *viz.*, by mercuric sulphate in methanol–sulphuric



$$\text{(XI)} \longrightarrow \underset{\text{(XII.)}}{\left[\begin{matrix}Pr^n{\cdot}CH{\cdot}CO{\cdot}CH_3\\ CHPh{\cdot}OH\end{matrix}\right]} \begin{matrix}\xrightarrow{-H_2O} \begin{matrix}Pr^n{\cdot}C{\cdot}CO{\cdot}CH_3\\ \Vert\\ CHPh\end{matrix} \quad \text{(XIII.)}\\ \longrightarrow Bu^n{\cdot}CO{\cdot}CH_3 + Ph{\cdot}CHO\end{matrix}$$

acid, gave a 35% yield of the expected ketone, 4-*phenyl*-3-*propylbut*-3-*en*-2-*one* (XIII). Rather surprisingly, there was also obtained a considerable quantity of low-boiling material which proved to be a mixture of methyl *n*-butyl ketone and benzaldehyde, each isolated in 35% yield as its 2 : 4-dinitrophenylhydrazone. These had obviously been formed by a reverse aldol condensation of the intermediate hydration product (XII). Another example of this type of reaction was encountered by Braude, Jones, Koch, Richardson, Sondheimer, and Toogood (this vol., p. 1890), who observed that hydration of 2-methyl-1-ethynyl*cyclo*hexene gave some nona-2 : 8-dione as well as the expected 1-acetyl-2-methyl*cyclo*hexene.

Some difficulty has been encountered with analysis of these βγ-acetylenic carbinols for carbon, low values having been obtained under the usual conditions of combustion. The reason for this is at present unknown and careful combustion methods are necessary to obtain correct analyses. The values for hydrogen on the other hand have been consistently good.

EXPERIMENTAL.

(All m. p.s were taken on a Köfler block and are corrected.)

General Conditions used for the Reformatsky Reactions.—Propargyl bromide was prepared from propargyl alcohol and phosphorus tribromide by the method of Kirrman (*Bull. Soc. chim.*, 1926, **39**, 618). The aldehydes and ketones employed were freshly distilled before use and were generally used in *ca.* 10% excess over that required for reaction with the more valuable propargyl bromide.

When the other reactants were ready, the zinc wool (in excess of the theoretical quantity) was etched with dilute hydrochloric acid, washed successively with water, methanol, and dry ether, and covered with dry benzene, and most of the benzene was removed by distillation. The reactants dissolved in the appropriate dry solvent were added immediately to the warm zinc. With this procedure, which ensured anhydrous conditions, the reaction usually commenced immediately and exothermally. The remainder of the reactants were added at such a rate as to maintain gentle refluxing—some external cooling was also often employed. Occasionally, when the reaction was difficult to start, the addition of *ca.* 50 mg. of mercuric chloride proved effective.

When the reactants had been added, the solution was heated under reflux for 5 minutes to complete the reaction; use of the correct solvent and amount of solvent led to the zinc complexes formed remaining in solution. The clear solution obtained was cooled and then decomposed with ice and 10% acetic acid, and the carbinol isolated in ether in the usual way. Distillation readily separated unchanged carbonyl compound from the carbinol; the glycol by-products were obtained as relatively non-volatile residues, which were not investigated further with the exception of those from *cyclo*hexanone and benzaldehyde, which were obtained crystalline.

3-1'-*Hydroxy*cyclo*hexylprop*-1-*yne* (II).—This compound was prepared from *cyclo*hexanone and propargyl bromide by using the procedure of Zeile and Meyer (*loc. cit.*). It crystallised from pentane in long needles, m. p. 57°. The glycol (m. p. 113°), the chief by-product in the above reaction, was obtained by triturating the residue from the distillation with ether. Zeile and Meyer give m. p.s 56·5° and 113° for the carbinol and glycol respectively. The glycol (5 g.), when mixed with powdered barium hydroxide (0·5 g.) and heated at 170° at 18 mm., gave a distillate, which was separated by subsequent fractional distillation into *cyclo*hexanone (1·8 g.) and 3-1'-hydroxy*cyclo*hexylprop-1-yne (2·1 g.).

2-*Methylpent*-4-*yn*-2-*ol* (IV).—(*a*) A mixture of propargyl bromide (48 g.) and dry acetone (30 g.) in dry ether (50 c.c.) was added to zinc (28 g.). The reaction started readily, but soon ceased owing to the separation of an insoluble complex. Dry dioxan (20 c.c.) was added, and the reaction recommenced on heating the mixture to gentle reflux; a clear brown solution was finally obtained. The 2-*methylpent*-4-*yn*-2-*ol* (15·7 g., 40%) had b. p. 124—127°/756 mm., n_D^{21} 1·4381 (Found : C, 73·1; H, 10·2. $C_6H_{10}O$ requires C, 73·4; H, 10·25%).

(*b*) [With L. J. HAYNES.]—A solution of sodium acetylide in liquid ammonia (500 c.c.) was prepared from sodium (23 g.) by the method of Vaughn, Vogt, and Nieuwland (*J. Amer. Chem. Soc.*, 1934, **56**, 2120). *iso*Butylene oxide (72 g.) was then added during 1 hour, and the reaction mixture was stirred overnight. After addition of ammonium chloride (60 g.), the carbinol was isolated in ether; removal of the ether gave 2-methylpent-4-yn-2-ol (18·8 g., 19%), b. p. 58—59°/50 mm., n_D^{18} 1·4380.

Hept-1-*yn*-4-*ol*.—A mixture of propargyl bromide (20 g.) and redistilled butaldehyde (15 g.) in tetrahydrofuran (40 c.c.) was added to zinc wool (12 g.) and warm tetrahydrofuran (20 c.c.). The mixture was warmed for 10 minutes after the completion of the reaction. The *hept*-1-*yn*-4-*ol* (13·1 g.) had b. p. 58—59°/11 mm., n_D^{20} 1·4443 (Found: C, 75·2; H, 10·9. $C_7H_{12}O$ requires C, 74·95; H, 10·8%). The 3 : 5-*dinitrobenzoate* separated from methanol in plates, m. p. 68° (Found : N, 9·2. $C_{16}H_{14}O_6N_2$ requires N, 9·15%).

Hept-5-*en*-1-*yn*-4-*ol*.—Zinc (30 g.) was covered with dry benzene (50 c.c.), and 15 c.c. of the latter were distilled off. A mixture of freshly distilled crotonaldehyde (40 g.) and propargyl bromide (48 g.) in dry ether (100 c.c.) was added to the zinc. The reaction started readily and finally gave a clear, pale brown solution. Isolation as before gave *hept*-5-*en*-1-*yn*-4-*ol* (29·5 g., 67%) as a pleasant-smelling liquid, b. p. 61°/15 mm., n_D^{19} 1·4667 (Found : C, 75·9; H, 9·0. $C_7H_{10}O$ requires C, 76·35; H, 9·15%). It showed no appreciable light absorption in the region 2200—4000 A.

4 : 8-*Dimethylnon*-7-*en*-1-*yn*-4-*ol*.—A mixture of propargyl bromide (24 g.) and methylheptenone (30 g., n_D^{22} 1·4453, as obtained from citral) in tetrahydrofuran (50 c.c.) was added to zinc (12 g.) in tetrahydrofuran (20 c.c.). The 4 : 8-*dimethylnon*-7-*en*-1-*yn*-4-*ol* (18·6 g.) had b. p. 53—54°/0·03 mm., n_D^{22} 1·4710 (Found : C, 79·25; H, 10·9. $C_{11}H_{18}O$ requires C, 79·5; H, 10·9%).

1-*Phenylbut*-3-*yn*-1-*ol*.—A mixture of benzaldehyde (24 g.) and propargyl bromide (24 g.) in dry ether (40 c.c.) was added to zinc (14 g.) covered with benzene (25 c.c.) so as to maintain gentle reflux. Isolation in the usual way gave 1-*phenylbut*-3-*yn*-1-*ol* (19·9 g.), b. p. 72°/0·4 mm., n_D^{20} 1·5482 (Found : C, 81·95; H, 7·1. $C_{10}H_{10}O$ requires C, 82·15; H, 6·9%).

Derivatives of 1-*Phenylbut*-3-*yn*-1-*ol*.—The carbinol was added to a solution of 2 : 4-dinitrophenylhydrazine sulphate in methanol and set aside at room temperature for 1 hour. The solid product was recrystallised from ethyl acetate to give deep-red needles of benzylideneacetone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. with an authentic sample, 229°. Light absorption in chloroform : Main maximum, 3950 A.; ε = 34,000.

Treatment of the carbinol with *p*-nitrobenzoyl chloride in pyridine gave the p-*nitrobenzoate*, m. p. 134—135°, as very pale yellow needles from methanol (Found : C, 69·15; H, 4·5; $C_{17}H_{13}O_4N$ requires C, 69·15; H, 4·45%).

1 : 5-*Diphenylpent*-2-*yne*-1 : 5-*diol* (V).—The high-boiling residue from the preparation of 1-phenylbut-3-yn-1-ol was dissolved in hot benzene; cooling gave 1 : 5-*diphenylpent*-2-*yne*-1 : 5-*diol* (2·6 g.). Examination of this glycol on the Köfler stage showed that it consisted of a mixture of two crystalline forms, one of which melted at 108—109°, and the other at 130—136° (Found, for the mixture : C, 80·9; H, 6·4. $C_{17}H_{16}O_2$ requires C, 80·95; H, 6·4%). The glycol (0·5 g.) was stirred with dry ether (20 c.c.); the insoluble part was recrystallised from aqueous methanol and then from benzene to give the higher-melting glycol, m. p. 143—146° (Found : C, 81·2; H, 6·25. $C_{17}H_{16}O_2$ requires C, 80·95; H, 6·4%). The ethereal filtrate was evaporated and the residue was recrystallised from benzene to give the lower-melting glycol, m. p. 105—108° (Found : C, 80·8; H, 6·25%).

Conversion of 1 : 5-*Diphenylpent*-2-*yne*-1 : 5-*diol* (V) *into* 1 : 5-*Diphenylpenta*-1 : 5-*dione* (VII).—The glycol (mixed isomers) (500 mg.) was hydrogenated in ethyl acetate (25 c.c.) containing acetic acid (5 c.c.) in the presence of platinic oxide (50 mg.). Hydrogenation ceased after 2·1 mols. of hydrogen had been absorbed. The catalyst was removed by filtration and the solvents in a vacuum. The residue was then treated with chromic acid (300 mg.) in acetic acid (20 c.c.). After the oxidation had proceeded for 3 hours at room temperature, the product was isolated by means of ether. Recrystallisation from light petroleum (b. p. 60—80°) and then aqueous methanol gave 1 : 5-diphenylpenta-1 : 5-dione (370 mg.), m. p. 66—67° (Wislicenus and Kuhn, *loc. cit.*, give m. p. 67·5°; Japp and Michie, *loc. cit.*, give m. p. 67·5°).

2-*Phenylpent*-4-*yn*-2-*ol*.—Propargyl bromide (24 g.) and acetophenone (33 g.), dissolved in dry tetrahydrofuran (50 c.c.), were added to zinc (12 g.) and tetrahydrofuran (20 c.c.). The reaction proceeded smoothly and gave the *carbinol* (15·1 g.), b. p. 77—79°/0·1 mm., 53—55°/0·01 mm., $n_{\rm D}^{21}$ 1·5406 (Found : C, 82·15; H, 7·8. $C_{11}H_{12}O$ requires C, 82·45; H, 7·6%).

Addition of the carbinol to a solution of 2 : 4-dinitrophenylhydrazine sulphate in methanol gave 4-*phenylpent*-3-*en*-2-*one* 2 : 4-*dinitrophenylhydrazone*, purplish-red needles (from ethyl acetate), m. p. 182° (Found: N, 16·4. $C_{17}H_{16}O_4N_4$ requires N, 16·45%). Light absorption in chloroform : Main maximum, 3920 A.; ε = 29,000.

1 : 1-*Diphenylbut*-3-*yn*-1-*ol*.—Propargyl bromide (15 g.) and benzophenone (15 g.) dissolved in tetrahydrofuran (35 c.c.) were added to zinc (7 g.) in tetrahydrofuran (15 c.c.). The reaction mixture was finally warmed for 10 minutes; isolation with ether gave a product which nearly all distilled at *ca.* 90°/10^{-5} mm. from a short-path still. The distillate was chromatographed on a column of activated alumina (90 × 3·8 cm.) in order to separate unchanged benzophenone; development was effected with light petroleum (b. p. 40—60°). The carbinol was retained at the top of the column; elution of this zone with ether–methanol (9 : 1) gave 1 : 1-*diphenylbut*-3-*yn*-1-*ol* (7·6 g.), b. p. 85—90° (bath temp.)/10^{-5} mm., $n_{\rm D}^{20}$ 1·5970 (Found : C, 86·1; H, 6·6. $C_{16}H_{14}O$ requires C, 86·45; H, 6·35%).

Treatment with 2 : 4-dinitrophenylhydrazine sulphate gave 4 : 4-*diphenylbut*-3-*en*-2-*one* 2 : 4-*dinitrophenylhydrazone*, dark red crystals [from methanol–ethyl acetate (9 : 1)], m. p. 155° (Found : N, 14·5. $C_{22}H_{18}O_4N_4$ requires N, 14·85%). Light absorption in chloroform : Main maximum, 3960 A.; ε = 34,00.

1-*Bromohept*-2-*yne* (VIII).—This was prepared as described by Bartlett and Rosen (*J. Amer. Chem. Soc.*, 1942, **64**, 543). The product had b. p. 67°/2 mm., $n_{\rm D}^{16}$ 1·4572 (Bartlett and Rosen give b. p. 93·6°/22 mm., $n_{\rm D}^{20}$ 1·4552).

1-*Phenyloct*-3-*yn*-1-*ol* (X).—A mixture of 1-bromohept-2-yne (8 g.) and benzaldehyde (6 g.) in tetrahydrofuran (30 c.c.) was added slowly to zinc (4 g.). The reaction was initiated by the addition of a trace of mercuric chloride and completed by heating under reflux for 15 minutes. The 1-*phenyloct*-3-*yn*-1-*ol* (8·4 g.) had b. p. 99°/0·2 mm., $n_{\rm D}^{16}$ 1·5320 (Found : C, 82·65; H, 8·6. $C_{14}H_{18}O$ requires C, 82·95; H, 8·95%).

Treatment of this carbinol with 2 : 4-dinitrophenylhydrazine sulphate reagent gave 1-*phenyloct*-1-*en*-3-*one* 2 : 4-*dinitrophenylhydrazone* as dark red prisms (from ethyl acetate), m. p. 162—163° (Found : N, 14·3. $C_{20}H_{22}O_4N_4$ requires N, 14·7%). Light absorption in chloroform : Main maximum 3890 A.; ε = 30,000.

1-1′-*Hydroxy*cyclo*hexylhept*-2-*yne*.—This was prepared in a similar manner to the preceding compound from 1-bromohept-2-yne (8 g.), *cyclo*hexanone (6·5 g.), and zinc (4 g.) in tetrahydrofuran (30 c.c.). The *alcohol* (6·9 g.) had b. p. 82°/0·1 mm., $n_{\rm D}^{19}$ 1·4913 (Found : C, 79·9; H, 11·15. $C_{13}H_{22}O$ requires C, 80·3; H, 11·4%).

3-*Bromohex*-1-*yne* (IX).—A mixture of hex-1-yn-3-ol (propylethynylcarbinol) (50 g.) and dry pyridine (5 c.c.) was treated with phosphorus tribromide (48 g.) in ether (40 c.c.) at a temperature not exceeding −10°. The reaction mixture was allowed to attain room temperature and then stirred for 1½ hours. Isolation with ether gave 3-*bromohex*-1-*yne* (38·3 g.), b. p. 82—83°/110 mm., $n_{\rm D}^{21}$ 1·4731 (Found : C, 45·1; H, 5·9. C_6H_9Br requires C, 44·75; H, 5·65%).

1-*Phenyl*-2-*propylbut*-3-*yn*-1-*ol* (XI).—A mixture of 3-bromohex-1-yne (10 g.) and benzaldehyde (7 g.) in tetrahydrofuran (25 c.c.) was caused to react with zinc (5 g.) in tetrahydrofuran (10 c.c.). This gave 1-*phenyl*-2-*propylbut*-3-*yn*-1-*ol* (7·1 g.), b. p. 87—89°/0·2 mm., 65°/0·01 mm., $n_{\rm D}^{20}$ 1·5232 (Found: C, 82·65; H, 8·85. $C_{13}H_{16}O$ requires C, 82·9; H, 8·55%).

Addition of the carbinol to 2 : 4-dinitrophenylhydrazine sulphate in warm methanol gave the 2 : 4-*dinitrophenylhydrazone* of 4-phenyl-3-propylbut-3-en-2-one in poor yield; it crystallises from methanol–ethyl acetate (5 : 1) as red needles, m. p. 186—187° (Found : N, 15·35. $C_{19}H_{20}O_4N_4$ requires N, 15·2%). Light absorption in chloroform : Main maximum, 3950 A.; ε = 29,000.

Hydration of 1-*Phenyl*-3-*propylbut*-3-*yn*-1-*ol*. (XI).—The carbinol (3 g.) was heated under reflux in a solution of mercuric sulphate (1 g.) in methanol (12 c.c.) and 3% sulphuric acid (8 c.c.) for 24 hours. Isolation in ether, followed by distillation, gave 3 fractions : (*a*) methyl *n*-butyl ketone, b.p. 30—31°/25 mm., $n_{\rm D}^{21}$ 1·4005 (*lit.*, $n_{\rm D}^{17}$ 1·3970), (*b*) benzaldehyde (0·6 g.), b. p. 26—27°/0·1 mm., $n_{\rm D}^{21}$ 1·5450 (lit., $n_{\rm D}^{17}$ 1·5463), and (*c*) 4-*phenyl*-3-*propylbut*-3-*en*-2-*one* (XIII) (1·0 g.), b. p. 85°/0·3 mm., $n_{\rm D}^{20}$ 1·5450 (Found : C, 82·7; H, 8·65. $C_{13}H_{16}O$ requires C, 82·9; H, 8·55%). Light absorption : Maximum, 2780 A.; ε = 13,000. Fraction (*a*) on treatment with 2 : 4-dinitrophenylhydrazine sulphate in methanol gave methyl *n*-butyl ketone 2 : 4-dinitrophenylhydrazone, needles (from methanol), m. p., 106°, undepressed on admixture with an authentic sample. Fraction (*b*) similarly gave benzaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 239°. Fraction (*c*) gave the 2 : 4-dinitrophenylhydrazone of (XIII), m. p. and mixed m. p. with a sample prepared directly from the carbinol (XI) (see above), 186—187°.

3-1′-*Hydroxy*cyclo*hexylhex*-1-*yne.*—3-Bromohex-1-yne (16 g.) and *cyclo*hexanone (12·7 g.) in tetrahydrofuran (45 g.) were made to react with zinc (7 g.) in tetrahydrofuran (15 c.c.). This gave 3-1′-*hydro*cyclo*hexylhex*-1-*yne* (8·0 g.), b. p. 54°/0·01 mm., n_D^{16} 1·4820 (Found : C, 80·1; H, 11·05. $C_{12}H_{20}O$ requires C, 79·95; H, 11·2%).

One of us (I. M. S. W.) thanks the Department of Scientific and Industrial Research for a Maintenance Grant.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
S. KENSINGTON, LONDON, S.W.7.
THE UNIVERSITY, MANCHESTER, 13.

[*Received, July* 13*th*, 1949.]