545. *Researches on Acetylenic Compounds. Part XXXVIII.* A New Method for the Introduction of the Acetylenic Linkage.*

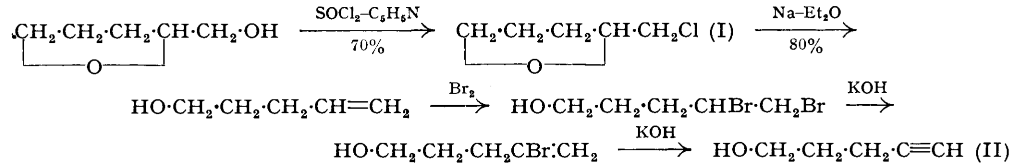
By G. EGLINTON, E. R. H. JONES, and M. C. WHITING.

Some β-halogenated ethers are converted into acetylenic compounds by treatment with sodamide in liquid ammonia; when the ether is cyclic an acetylenic alcohol may be formed by ring-scission. The scope and limitations of this reaction have been examined and some conclusions about its mechanism can be drawn.

The behaviour of the now readily accessible γ-acetylenic alcohol, pent-4-yn-1-ol, towards acidic and basic reagents has also been investigated.

The ultra-violet light absorption properties of the vinyl ethers encountered in this work have been determined.

THIS contribution, like Part XXVII (Eglinton and Whiting, *J.*, 1950, 3650), arises out of an attempt to prepare a series of compounds containing a free ethynyl group and a functional group separated by a short aliphatic chain. An obvious starting point for the synthesis of such ω-acetylenic compounds is pent-4-yn-1-ol (II). Lespieau (*Compt. rend.*, 1932, **194**, 287) prepared this alcohol by an eight-stage process starting from allyl bromide and malonic ester, but one of his intermediates, pent-4-en-1-ol, has since been obtained more conveniently (Paul, *Bull. Soc. chim.*, 1935, **2**, 745; *Org. Synth.*, 1945, **25**, 84), thus leading to the following five-stage synthesis of the acetylenic alcohol from tetrahydrofurfuryl alcohol:



$$\underbrace{CH_2\cdot CH_2\cdot CH_2\cdot CH}_{O}\cdot CH_2\cdot OH \xrightarrow[70\%]{SOCl_2-C_5H_5N} \underbrace{CH_2\cdot CH_2\cdot CH_2\cdot CH}_{O}\cdot CH_2Cl\ (I) \xrightarrow[80\%]{Na-Et_2O}$$

$$HO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH{=}CH_2 \xrightarrow{Br_2} HO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHBr\cdot CH_2Br \xrightarrow{KOH}$$

$$HO\cdot CH_2\cdot CH_2\cdot CH_2CBr{:}CH_2 \xrightarrow{KOH} HO\cdot CH_2\cdot CH_2\cdot CH_2\cdot C{\equiv}CH\ (II)$$

In preliminary attempts further to improve the accessibility of (II) it was found that the ring scission could be effected more conveniently with sodium in liquid ammonia, and that the last two stages could be combined by treating the dibromopentanol with sodamide in liquid ammonia, giving an overall yield of 30% for the four stages. The action of sodamide on (I) itself was then investigated and (II) was directly obtained in 85% yield (60% overall). Pent-4-yn-1-ol thus becomes one of the most accessible of the acetylenic alcohols.

During the present work, Paul and Tchelitcheff (*Compt. rend.*, 1950, **230**, 1473; see also *ibid.*, 1951, **232**, 2230) described an ingenious three-stage synthesis of (II) from 2 : 3-dihydropyran (III) *via* the 2 : 3-dibromide and 3-bromo-4 : 5-dihydropyran, the latter giving a good yield of the alcohol on treatment with butylsodium. We believe, however, that the present method is more convenient.

The reaction between tetrahydrofurfuryl chloride and sodamide is potentially a general route to acetylenes which would parallel the olefin synthesis of Boord *et al.* (*J. Amer. Chem. Soc.*, 1930, **52**, 651, 3396 *et seq.*). Systematic attempts were made, therefore, to extend it. Epichlorohydrin, a ring homologue, reacted with sodamide, but isolation of the product, propargyl alcohol, was difficult, and only a 46% yield could be obtained; this method is nevertheless probably the most convenient for its preparation in the laboratory. Oxidative coupling before isolation (Part XXXIV, *J.*, 1952, 1998) gave a 65% overall yield of hexa-2 : 4-diyne-1 : 6-diol. Two by-products were formed in the reaction of sodamide with epichlorohydrin: hexamethylenetetramine and pent-2-en-4-yn-1-ol. These probably result from the partial dissociation of the monosodiopropargyl alcohol into

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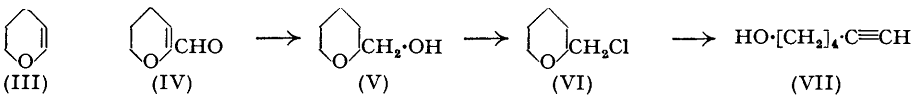
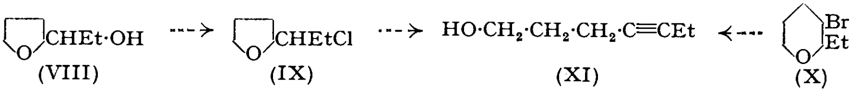
* Part XXXVII, *J.*, 1952, 2014.

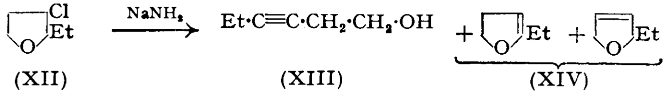
formaldehyde and sodium acetylide, the latter then reacting with epichlorohydrin as described by Haynes, Heilbron, Jones, and Sondheimer (*J.*, 1947, 1583).



For the next extension of the reaction, (V) was made by the preparation (Schultz and Wagner, *Angew. Chem.*, 1950, **62**, 105) and hydrogenation (Helberger, Ulubay, and Civelekoglu, *Annalen*, 1949, **561**, 215) of acraldehyde dimer (IV). Both stages gave difficulty and evidently need further study. Direct reaction with thionyl chloride and pyridine proved the best route to (VI), but from impure (V) the chloride may be prepared by the action of calcium chloride in 2-2′-ethoxyethoxyethanol on the crystalline and easily isolable toluene-*p*-sulphonate. The final conversion of (VI) into (VII) proceeded very smoothly in 80% yield, but at present the preferred route to (VII) would be from 6-chlorohex-1-yne (Newman and Wotiz, *J. Amer. Chem. Soc.*, 1949, **71**, 1294).



Extension of the reaction to halides such as (IX) was then contemplated; this, however, was frustrated by the great difficulty of preparing (IX) from (VIII), as has recently been noted *inter al.* by Paul and Riobe (*Compt. rend.*, 1947, **224**, 474) and Crombie and Harper (*J.*, 1950, 1707). An attempt to substitute the toluene-*p*-sulphonate was contra-indicated by the failure of tetrahydrofurfuryl toluene-*p*-sulphonate itself to react smoothly with sodamide. An alternative route to (XI) *via* (X) (cf. Paul and Riobe, *loc. cit.*) was examined; but (X) was much less reactive towards sodamide than was (I) or (VI), and although some of the expected alcohol was probably obtained the method was unsatisfactory. Alkylation of the 2-tetrahydropyranyl ether of (II), which was readily obtained by the condensation of (II) with (III), was also investigated, but once again difficultly separable mixtures were encountered, so that alcohols of type (XI) remain somewhat inaccessible.



The action of sodamide on 3-chloro-2-ethyltetrahydrofuran (XII) was then investigated; the latter was prepared according to Crombie and Harper's method (*J.*, 1950, 1715) but the separation into the two stereoisomeric forms described by these authors was not attempted. Upon treatment with sodamide the desired hex-3-yn-1-ol (XIII) was obtained in 30% yield. From a preparative standpoint, however, this method does not rival in convenience that recently described by Sondheimer (*J.*, 1950, 877). A lower-boiling fraction, also obtained in 30% yield, apparently consisted of the two isomeric ethyldihydrofurans (XIV); it was hydrolysed by dilute acids to 6-hydroxyhexan-3-one, isolated as its phenylurethane. Straightforward dehydrohalogenation without simultaneous splitting of the ether linkage is thus a possible competing reaction.

$$\mathrm{Bu{\cdot}MgBr + Br{\cdot}CH(OEt){\cdot}CH_2Br \longrightarrow \underset{(XV)}{Bu{\cdot}CH(OEt){\cdot}CH_2Br} \xrightarrow{NaNH_2} Bu{\cdot}C{\equiv}CH + Bu{\cdot}C(OEt){:}CH_2}$$

$$\mathrm{Bu{\cdot}MgBr + Br{\cdot}CH(OEt){\cdot}CHEtBr \longrightarrow \underset{(XVI)}{Bu{\cdot}CH(OEt){\cdot}CHEtBr} \xrightarrow{NaNH_2} Bu{\cdot}C(OEt){:}CHEt}$$

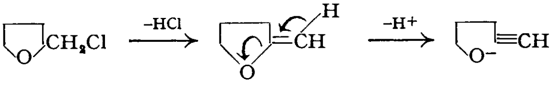
Finally the reactions between two acyclic β-halogeno-ethers and sodamide were examined. The ether (XV) gave a 45% yield of hex-1-yne together with 18% of 2-ethoxyhex-2-ene. The secondary bromo-ether (XVI) gave a 70% yield of 4-ethoxyoct-3-ene (probably containing some 4-ethoxyoct-2-ene) as the only isolable product; even a small amount of the acetylenic compound would have been isolated if formed.

Attention was next turned to the mechanism of the reaction:

$$-H + -Cl + NH_2^- \longrightarrow NH_3 + Cl^-$$
$$-H + -OR + NH_2^- \longrightarrow NH_3 + RO^-$$

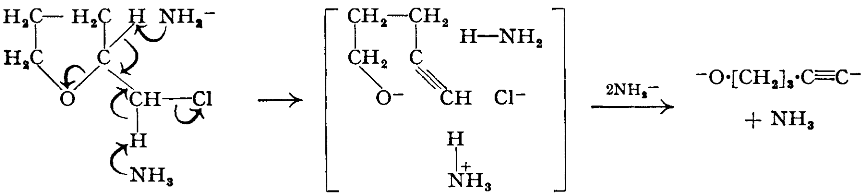
Energetically favourable processes, such as the above, are always necessary for the endothermic formation of a triple bond. It was therefore hardly to be expected that bases of moderate strength, such as alkoxides, would be effective. A base of intermediate strength was therefore examined, *viz.*, sodium acetylide. This was found to have no action on tetrahydrofurfuryl chloride, which was recovered in 75% yield after 50 hours at −33°, whereas sodamide reacts almost to completion within a few minutes. Since alkoxides and even sodium acetylide fail to effect the reaction, it was to be expected that the use of less than three molecular proportions of sodamide would result in incomplete reaction, since the disodium derivative of pentynol would similarly be insufficiently basic. This was verified in the case of (I) which on treatment with sodamide (2 mols.) gave a heterogeneous product.

In the typical case of the synthesis of pentynol two mechanisms might be considered plausible: (*a*) the reaction might occur in two stages, dehydrohalogenation first giving tetrahydro-2-methylenefuran (XVII) (which is in fact formed when the chloride reacts with potassium hydroxide), ring fission then giving the alcohol, *i.e.*:



(XVII)

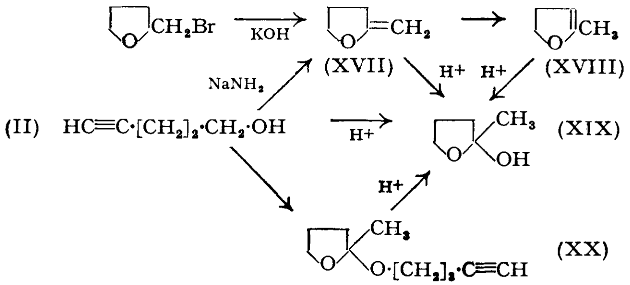
or (*b*) a " double-elimination reaction " might take place, such as was proposed by Crane and Rydon (*J.*, 1947, 766) for the formation of acetylene from 2-benzoyloxyethyldimethylsulphonium salts and alkalis:



Both seem reasonable; in fact Mamalis and Rydon (*Nature*, 1950, **166**, 405) later found that a mechanism of type (*a*) is actually involved in their reaction. In the present instance, however, a genuine double-elimination reaction (*b*) is probably involved. In the first place it was found that treatment of the chloride with one molecular proportion of sodamide gave only a mixture of the chloride and the acetylenic alcohol; in the second, sodamide merely converts tetrahydro-2-methylenefuran into the isomeric 3 : 4-dihydro-2-methylfuran, upon which, as upon 2 : 3-dihydropyran, it has no action.

While the precise mechanism of the reaction has not been established, that suggested, involving one NH_2^- ion and one solvent molecule, seems more probable than one requiring two amide ions. A saturated solution of sodamide in liquid ammonia is only 0·025M, so that it seems unlikely that such a termolecular reaction would be fast at −33°, as this evidently is. The use of three stoicheiometric proportions of sodamide would still, of course, be necessary to allow for the removal of NH_2^- by the acidic species NH_4^+ and ≡CH. In inert solvents (even at 140°) sodamide fails to react with (I), whereas Paul (*Bull. Soc. chim.*, 1935, **2**, 745) stated that the corresponding bromide yields (III) and (XVII) with sodamide at 140°; evidently the double-elimination reaction proceeds only in an ionic medium.

Double-elimination reactions of type (*b*), involving a termolecular mechanism, might be expected to occur in liquid ammonia in preference to consecutive bimolecular single-elimination reactions of type (*a*), since the ammonia molecule itself has a considerable proton affinity and can participate as one reactant. Thus the very smooth dehydrohalogenation of vicinal dihalides by sodamide in liquid ammonia may well proceed in this manner, although the analogous reaction in aqueous or alcoholic solutions is known to involve two stages. On the other hand termolecular double-elimination reactions in aqueous solution are not impossible and, in the case of the dehydrohalogenation of 1 : 4-dichlorobut-2-yne to diacetylene by aqueous alkalis, the marked difference between sodium and calcium hydroxide (Armitage, Jones, and Whiting, *J.*, 1951, 44) suggests that a third-order termolecular reaction of this type may be involved. The alternative mechanism would in this case lead first to 1-chlorobuta-1 : 2 : 3-triene, and might therefore be less favoured.

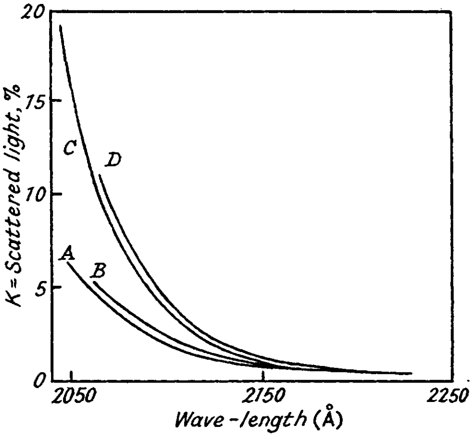


Some aspects of the chemistry of pent-4-yn-1-ol (II) are of interest; thus Paul and Tchelitcheff (*Compt. rend.*, 1950, **230**, 1872) have shown that treatment of the alcohol with a trace of sodamide, followed by distillation, gives a mixture of (XVII) and (XVIII). Repetition of this work resulted in the isolation of (XVIII) and also confirmed the formation of fairly pure (XVII) from tetrahydrofurfuryl bromide and potassium hydroxide and its subsequent rearrangement to (XVIII), when refluxed in the absence of alkali. The pentynol was also found to undergo unusually easy hydration in aqueous sulphuric acid, giving either (XIX), shown by its light-absorption properties to exist essentially in the cyclic form, as indicated, or under different conditions the glycoside-like product (XX). A solution of ammonium chloride in liquid ammonia, however, was without action on (II).

The reactions discussed above presumably result from the attack of the terminal $-O^-$ or $-OH_2^+$ groupings on the ethynyl group, and intramolecular proximity so alters the temperature-independent factor of the rate equation as to permit the reactions to proceed at a much greater rate than would be the case with intermolecular reactions between similar species at such low concentrations (cf. Paul, *Angew. Chem.*, 1951, **63**, 301).

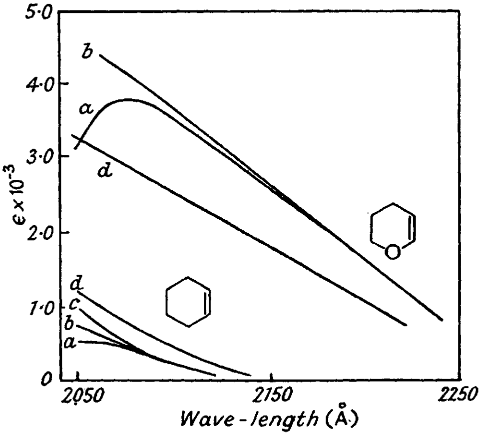
The ultra-violet light absorption properties of a number of vinyl ethers, prepared in connection with the above studies, have been examined in the 2050—2400-Å region, employing a "Unicam" S.P. 500 spectrophotometer. In this region scattered light within the instrument can cause serious errors. Two alternatives for the presentation of the results are available. Either the conditions can be carefully standardised, and the results used empirically without correction (cf., *e.g.*, Bladon, Henbest, and Wood, *J.*, 1952, 2737; Halsall, *Chem. and Ind.*, 1951, 467) or the usual technique for correcting this error, extensively used in infra-red spectroscopy, can be employed (see Opler, *J. Amer. Opt. Soc.*, 1950, **40**, 401). The latter method, used in the present work, has the advantage that results are reproducible even if the efficiency of the light source varies, as in practice it does; a somewhat similar method has recently been described by Saidel, Goldfarb, and Kolt (*Science*, 1951, **113**, 683). It is first necessary to find the percentage of scattered light at each setting of the wave-length scale, which can be done by using a filter opaque to light of the wave-length in question but transparent to almost all the remainder of the spectrum; a 0·5% solution (1-mm. cell) of α-ergostene in hexane, or α-ergostenol in alcohol, is satisfactory (cf. Bladon *et al.*, *loc. cit.*). The results, for various cells and solvent combinations, are then plotted (Fig. 1), and the instrument readings are corrected with the aid of the tables published by Opler (*loc. cit.*). The proportion of scattered light, and hence the magnitude of the correction necessary, varies widely with the condition of the hydrogen lamp used, and with the general condition of the instrument, and must be checked frequently. The effects of the correction are evident in Fig. 2, which shows the light absorption of *cyclo*hexene (*a*) uncorrected and (*b*) corrected, with the results obtained by Bateman and Koch (*J.*, 1944, 601) and by Platt, Klevens, and Price (*J. Chem. Phys.*, 1949, **175**, 466) using methods not liable to vitiation by this error, included for comparison. The present results for 2 : 3-dihydropyran are similarly compared with those of the latter authors. It will be seen that the magnitude of the scattered-light error varies so rapidly with wave-length (owing to the steep cut-off of solvent, quartz, and perhaps oxygen in this region), that the shape of the curve is seriously distorted and a spurious maximum, with our instrument always in the 2045—2080-Å region, is introduced. Incidentally, the " A " maximum observed at 2010—2080 Å by Moser and Kohlenberg (*J.*, 1951, 804) for substituted benzoic acids, which is ascribed by them to a displacement of the 1870-Å band in benzene, is almost certainly a consequence of the same phenomenon, and the attempts made to interpret its position electronically are unnecessary.

FIG. 1.



A, Hexane, 1-*mm. cell.*
B, Ethanol, 1-*mm. cell.*
C, Hexane, 1-*cm. cell.*
D, Ethanol, 1-*cm. cell.*

FIG. 2. *Light absorption of* cyclo*hexene and dihydropyran.*



a, Present work, uncorrected.
b, ,, corrected.
c, Bateman and Koch, *loc. cit.*
d, Platt, Klevens, and Price, *loc. cit.*

It should be pointed out that this procedure for correcting for " false energy " is only accurate if the solution of the substance examined does not absorb the scattered light (mainly 2300—4500 Å) to a very appreciable extent. It is also necessary that the wave-length scale should be accurately calibrated in this region. (" Unicam " S.P. 500 spectrophotometers issued before September 1951 were fitted with scales, inaccurate at short wave-lengths, which are now being replaced. The present results have been corrected by means of a provisional table kindly supplied by Unicam Instruments Ltd.)

The light-absorption properties of the vinyl ethers studied are illustrated in Fig. 3. It is at once evident that the vinyl ether chromophore, $-O-CR^1=CR^2R^3$, is affected by alkyl substitution in much the same way as the diene grouping; thus, butyl vinyl ether (*B*) has $\varepsilon = 3000$ at 2075 Å, while in 2-ethoxyhex-1-ene (*F*) the ε is 3000 at 2155 Å. When with the same degree of substitution the double bond becomes exocyclic (*e.g.*, *E*), the usual bathochromic shift (cf. Woodward, *J. Amer. Chem. Soc.*, 1942, **64**, 72) is observed, λ_{3000} moving to 2225 Å ($\Delta\lambda = + 70$ Å). The cyclic ether (*D*) has $\lambda_{3000} = 2230$ Å, and shows a somewhat flatter curve, while 2 : 3-dihydropyran (*C*) differs fundamentally from the other ethers studied, just as *cyclo*hexene does from other olefins (Platt, Klevens, and Price, *loc. cit.*). It is unfortunate that this, the only simple vinyl ether investigated by the latter authors over a wider range of wave-lengths, should be atypical. The present results, however, permit the easy differentiation of vinyl ethers from most olefins, since unlike the tri- and tetra-substituted olefins common among steroids and triterpenes (Bladon, Henbest, and Wood, *loc. cit.*; Halsall, *loc. cit.*), *cyclo*hexene, monoalkylethylenes, and *cis*- and *trans*-1 : 2-dialkylethylenes show absorption only of low intensity at 2040 Å (Platt, Klevens, and Price, *loc. cit.*; and unpublished work from these laboratories). One may also deduce values of $\lambda_{max.}$ and $\varepsilon_{max.}$ of 1940 Å and *ca.* 7000 respectively for the parent chromophoric system, and incremental values of about +75 Å for alkyl substituents.

Platt, Klevens, and Price (*loc. cit.*) reported a shoulder and a maximum, respectively, at 2225 Å (ε = 120 and 160) for oct-1- and -2-yne, though they did not rule out the possibility that these might be attributable to impurities. Such is evidently the case, for hex-3-yn-1-ol was found to have ε = only 70 at 2150 Å, the intensity of absorption falling sharply to longer wave-lengths, while behenolic acid (which can be purified, by crystallisation, much more easily than hex-3-yn-1-ol or the lower acetylenic hydrocarbons) showed light absorption very similar to that of stearic acid ($\Delta\varepsilon \ngtr 20$) down to 2050 Å. Extrapolation of the series $CH_3{\cdot}[C{\equiv}C]_n{\cdot}CH_3$ to $n = 1$ suggests that absorption of but-2-yne will probably begin below 1950 Å, with a band at *ca.* 1860 Å. (ε *ca.* 300), but the significance of this extrapolation is difficult to estimate.

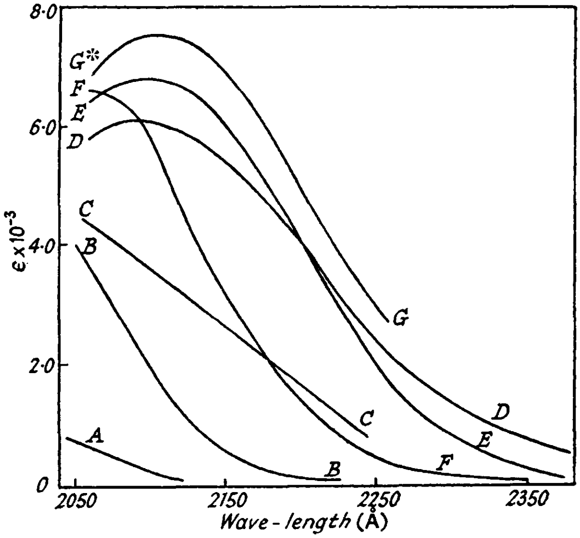
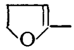
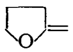
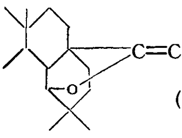


FIG. 3. *Light absorption of vinyl ethers (in hexane)*

A, cyclo*Hexene.*
B, *Butyl vinyl ether.*
C, *Dihydropyran.*
D,

E,

F, $CH_2 = C(OEt){\cdot}C_4H_9$*
G,


(cf. *J.*, 1951, 2698.)

* In alcohol.

EXPERIMENTAL

Propargyl Alcohol.—Epichlorohydrin (360 g.) was added dropwise during 1½ hours to a well-stirred suspension of sodamide, prepared from ferric nitrate (1·2 g.) and sodium (270 g.), in liquid ammonia (2·5 l.) contained in a 4-l. vacuum-flask. After a further 12 hours' stirring dry ammonium chloride (550 g.) was carefully added. The mixture was poured into a stainless steel bucket and the greater part of the ammonia was allowed to evaporate (moisture being excluded by means of a "Cellophane" membrane, which is readily permeable to ammonia). Dry ether (1 l.) was added and most of the residual ammonia was driven off. The ethereal extract was filtered from the solid residue which was then further extracted with ether. The ether was removed from the combined extracts through a 20-cm. Dufton column, and the crude product dried (K_2CO_3). The upper layer, to which *ca.* 5 g. of succinic acid had been added (see Copenhaver and Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Pub. Corp., New York, 1949, p. 106), was carefully fractionated through a 50-cm. Fenske column, to give the pure alcohol (103 g., 46%), b. p. 53—55°/95 mm., n_D^{20} 1·4317 (Henne and Greenlee, *J. Amer. Chem. Soc.*, 1945, **67**, 485, give n_D^{20} 1·4320). Estimation of the ethynyl grouping by Hanna and Siggia's method (*Analyt. Chem.*, 1949, **21**, 1469) showed the material to be 99·5% pure. The phenylurethane separated from light petroleum (b. p. 60—80°) as laths, m. p. 63—64°, undepressed on admixture with a genuine specimen.

The high-boiling residue (37 g.) from the fractionation yielded substantial quantities of hexamethylenetetramine, obtained as rhombohedral crystals (which sublimed on heating) from ethanol (Found : C, 51·75; H, 8·7; N, 40·0. Calc. for $C_6H_{12}N_4$: C, 51·4; H, 8·65; N, 39·9%). In another experiment, on a larger scale, the high-boiling material was distilled. One fraction (10·5 g., 0·6%) had b. p. 65—67°/10 mm., n_D^{17} 1·4935, and showed light absorption : Max., 2195 Å, ε = 10,820; inflexion, 2280 Å, ε = 8500 (Haynes, Heilbron, Jones, and Sondheimer, *J.*, 1947, 1584, give b. p. 71—73°/19 mm., n_D^{19} 1·4972, for pent-2-en-4-yn-1-ol, and max., 2230 Å, ε = 15,000; inflexion, 2290 Å, ε = 10,000). It formed an α-naphthylurethane, m. p. 109—111°, undepressed on admixture with an authentic specimen.

Tetrahydrofurfuryl Toluene-p-*sulphonate.*—The ester, m. p. 38°, was prepared in 80% yield by the general method of Tipson (*J. Org. Chem.*, 1944, **9**, 235). Barger, Robinson, and Smith (*J.*, 1937, 720) obtained the ester in 68% yield by the less convenient procedure employing potassium hydroxide in dry ether.

Tetrahydrofurfuryl Bromide.—When the recorded method (*Org. Synth.*, 1943, **23**, 88) was employed the product contained pyridine and tetrahydrofurfuryl alcohol; washing ($NaHSO_4$ solution) and drying ($CaBr_2$) followed by redistillation gave a pure specimen, b. p. 63·5—64°/17 mm., n_D^{21} 1·4869, in 44% yield.

Tetrahydro-2-methylenefuran (XVII).—Two distillations of the above bromide from powdered potassium hydroxide followed by fractionation gave (XVII), b. p. 100—102°/764 mm., n_D^{19} 1·4490 (Paul and Tchelitcheff, *Bull. Soc. chim.*, 1950, **17**, 520, give b. p. 98—99°, n_D^{19} 1·4476).

4 : 5-*Dihydro-2-methylfuran* (XVIII).—Tetrahydro-2-methylenefuran (8·4 g.) was refluxed in nitrogen, the b. p. falling to *ca.* 80° during 4 hours. Distillation from a trace of quinol gave (XVIII) (5·2 g., 62%), b. p. 78—80°/760 mm., n_D^{23} 1·4323 (Paul and Tchelitcheff, *loc. cit.*, give b. p. 81—82°, $n_D^{18·5}$ 1·4328; Schniepp, Geller, and von Korff, *J. Amer. Chem. Soc.*, 1947, **69**, 672, give b. p. 80°, n_D^{25} 1·4290).

Tetrahydrofurfuryl Chloride.—(*a*) When the recorded method (*Org. Synth.*, 1945, **25**, 84) was employed, it was found that, unless the tetrahydrofurfuryl alcohol was redistilled before use, the chloride contained appreciable quantities of the starting material. This could not be removed without rigorous fractionation. When the reactants were purified, the product obtained had b. p. 55—56°/20 mm., n_D^{20} 1·4552, and the yield was 67—70%.

(*b*) A solution of anhydrous calcium chloride (15 g.) in 2-2′-ethoxyethoxyethanol (120 c.c.) was dried by distillation under reduced pressure through a 20-cm. Dufton column until the b. p. reached 130°/100 mm. Tetrahydrofurfuryl toluene-*p*-sulphonate (25·6 g.) was then added to the cooled (50°) residual solution. The mixture was homogenised by shaking and warmed to 130°, whereupon an exothermic reaction took place. After heating to 160° for 1½ hours, the distillation was resumed under reduced pressure (60 mm.) and continued until a b. p. of 105° was reached. The distillate (15 c.c.) was washed with water (15 c.c.), dried ($CaCl_2$), and redistilled, to give the chloride (7·3 g., 60%), b. p. 64°/40 mm., n_D^{20} 1·4551.

Pent-4-en-1-ol.—Tetrahydrofurfuryl chloride (12·1 g.) in dry ether (100 c.c.) was added dropwise to a solution of sodium (4·8 g.) in liquid ammonia (250 c.c.). After 3 hours, ammonium chloride (10 g.) and dry ether (150 c.c.) were added and the ammonia was allowed to evaporate. The residue was thoroughly extracted with ether, and the combined extracts were evaporated through a 20-cm. Dufton column. Distillation gave pent-4-en-1-ol (6·6 g., 76%), b. p. 73—81°/55 mm., n_D^{13} 1·4320—1·4330 (Paul, *Compt. rend.*, 1932, **195**, 1289, gives n_D^{16} 1·4322).

Pent-4-yn-1-ol (II).—(*a*) Tetrahydrofurfuryl chloride (242 g.) was added dropwise during 25 minutes to a stirred suspension of sodamide (from 161 g. of sodium) in liquid ammonia (3·5 l.). After a further 16 hours' stirring, dry ammonium chloride (350 g.) was slowly added, most of the ammonia allowed to evaporate, and the product thoroughly extracted with ether. Removal of the ether and distillation gave pent-4-yn-1-ol (142 g., 85%), b. p. 64—65°/16 mm., n_D^{19} 1·4451 (Paul and Tchelitcheff, *Compt. rend.*, 1950, **230**, 1473, record n_D^{19} 1·4432, and Lespieau, *Compt. rend.*, 1932, **194**, 287, gives $n_D^{22·5}$ 1·4450). A small sample was purified *via* the silver derivative and then had b. p. 77°/37 mm., n_D^{15} 1·4464. The pure alcohol was free from the pungent odour associated with the crude product, and had the characteristic sweetish odour of an acetylenic alcohol. Estimation of the ethynyl grouping by Hanna and Siggia's method (*loc. cit.*) gave inconsistent results (92—100%), presumably due to incomplete formation of the mercury derivative. Owing to the presence of traces of the hydroxy-ketone, 5-hydroxypentan-2-one (identified as its 2 : 4-dinitrophenylhydrazone, m. p. 154—155°; Paul and Tchelitcheff, *Compt. rend.*, 1950, **230**, 1872, give m. p. 150°), the silver nitrate–sodium hydroxide method of Chevastelon (*Compt. rend.*, 1897, **125**, 245) could not be employed. (See also Altieri, " Gas Analysis and Testing of Gaseous Materials," New York, American Gas Association, 1945.) The phenylurethane separated from light petroleum as needles, m. p. 56°, undepressed on admixture with the derivative of a sample prepared as described below (Paul and Tchelitcheff, *loc. cit.*, give m. p. 56°). The α-*naphthylurethane* formed clumps of needles, m. p. 79—80°, from light petroleum (b. p. 60—80°) (Found : C, 76·2; H, 5·8. $C_{16}H_{15}O_2N$ requires C, 75·85; H, 5·95%).

(*b*) (With T. Y. Shen) Pent-4-en-1-ol (111 g.; *Org. Synth.*, 1945, **25**, 84) was treated with the calculated amount of bromine in dry carbon tetrachloride (400 c.c.), the temperature being kept below 20°, to give 320 g. of 4 : 5-dibromopentan-1-ol (Paul, *Compt. rend.*, 1931, **192**, 1574). The dibromide (310 g.) was added dropwise during 1½ hours to a stirred suspension of sodamide (from sodium, 125 g.) in liquid ammonia (1·5 l.). After 3 hours, dry ether (1 l.) was added and the mixture hydrolysed with ammonium chloride. The product was isolated in the usual way and on fractionation gave pent-4-yn-1-ol (61 g., 56%), b. p. 68—69°/23 mm., n_D^{19} 1·4471, and a small quantity of higher-boiling material, probably essentially 4-bromopent-4-en-1-ol. The acetylenic alcohol gave a phenylurethane, m. p. 56°.

5-2′-*Tetrahydropyranyloxypent*-1-*yne*.—To a mixture of pent-4-yn-1-ol (8·4 g.) and 2 : 3-dihydropyran (8·4 g.) was added one drop of phosphorus oxychloride. The exothermic reaction was moderated by ice-cooling and, after the reaction mixture had been set aside for 2 hours at 20°, potassium hydroxide (0·3 g.) was added. Distillation then gave the *adduct* (15 g., 90%), b. p. 89—91°/19 mm., $n_D^{20\cdot5}$ 1·4575 (Found : C, 71·65; H, 9·9. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%).

Reactions of Pent-4-*yn*-1-*ol* (II).—(a) *Cyclisation to* 4 : 5-*dihydro*-2-*methylfuran* (XVII). Pentynol (15 g.), to which sodamide (*ca.* 0·5 g.; freshly prepared from sodium in liquid ammonia) had been added, was refluxed for 4 hours and then distilled through a 15-cm. Fenske column at such a rate that the b. p. did not exceed 90°. The crude product (9 g.) was freed from pentynol by redistillation, giving substantially pure 4 : 5-dihydro-2-methylfuran (7 g., 48%), b. p. 79—81°/746 mm., n_D^{18} 1·4340—1·4352 [Paul and Tchelitcheff, *Compt. rend.*, 1950, **230**, 1872, obtained a mixture of (XVII) and (XVIII), b. p. 82—100°, by repeated distillation from sodamide]. A small sample of (XVII) was hydrolysed with sulphuric acid and the solution of 5-hydroxypentan-2-one so formed treated with 2 :4-dinitrophenylhydrazine sulphate solution. After chromatographic purification the derivative of 5-hydroxypentan-2-one had m. p. 154—155°.

(b) *Action of dilute acid.* (i) A solution of the pentynol (5 g.) in 0·5N-sulphuric acid (35 c.c.) was heated under reflux for 6 hours. The cooled solution was neutralised and saturated with sodium chloride, and the mixture continuously extracted with ether for 24 hours. Removal of ether from the dried extract and fractional distillation gave unchanged pentynol (3·55 g.) and 5-*tetrahydro*-2′-*methyl*-2′-*furanyloxypent*-1-*yne* (0·8 g., 16%), b. p. 70—75°/7 mm., n_D^{16} 1·4505 (Found : C, 71·1; H, 9·65. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%). Estimation of the ethynyl grouping (see above) gave an approximate value of 179 for the equivalent weight ($C_{10}H_{16}O_2$ has *M*, 168). This compound was also isolated from a treatment of pentynol with sodamide. The ketal is insoluble in water, but is immediately hydrolysed by dilute acid. The resulting 5-hydroxypentan-2-one was again identified as its 2 : 4-dinitrophenylhydrazone, m. p. 154—155°.

(ii) A solution of pentynol (9·5 g.) in 0·5N-sulphuric acid (100 c.c.) was heated under reflux for 13 hours. The solution was neutralised and the product isolated by continuous ether extraction. After removal of the ether, fractional distillation of the residue (8 g.) yielded a fore-run of unchanged pentynol (2·4 g.), followed by 5-hydroxypentan-2-one (4·3 g., 37%), b. p. 82—86°/7 mm., n_D^{13} 1·4402 (Schniepp, Geller, and von Korff, *loc. cit.*, give b. p. 75°/3 mm., n_D^{25} 1·4350). The 2 : 4-dinitrophenylhydrazone, after recrystallisation from benzene, had m. p. 154—155°, undepressed on admixture with an authentic specimen.

Tetrahydro-2-*pyranylmethyl Toluene*-p-*sulphonate*.—Crude tetrahydro-2-hydroxymethylpyran (52 g.; b. p. 75—83°/17 mm., n_D^{24} 1·4612—1·4572; obtained from a less successful experiment) was added to a stirred suspension of toluene-*p*-sulphonyl chloride (105 g.) in pyridine (80 c.c.) at such a rate that the temperature did not exceed 25°. The reaction mixture was set aside for 20 hours. Water (50 c.c.) was slowly added and the resultant suspension poured into a large volume of water, and the neutral fraction isolated with ether. The crude product (66 g.) solidified to a pasty solid on cooling. Crystallisation from light petroleum (b. p. 40—60°)–carbon tetrachloride gave the *ester* (53 g., 40%) as rhombic plates, m. p. 69—70°, raised to 72·5° after two further recrystallisations from light petroleum (Found : C, 57·75; H, 6·9. $C_{13}H_{18}O_4S$ requires C, 57·7; H, 6·7%).

2-*Chloromethyltetrahydropyran* (VI).—(*a*) Freshly distilled thionyl chloride (25 g.) was added dropwise with ice-cooling to a vigorously stirred solution of pure tetrahydro-2-hydroxymethylpyran (23 g.) in dry pyridine (17 g.). The mixture was stirred for 16 hours. Ice was then added and the product was isolated with ether. The *chloride* (13 g., 48%) had b. p. 62—64°/22 mm., n_D^{18} 1·4620 (Found: C, 53·7; H, 8·35. $C_6H_{11}OCl$ requires C, 53·6; H, 8·25%).

(*b*) A solution of calcium chloride (24 g.) in 2-2′-ethoxyethoxyethanol (300 c.c.) was dried by distillation. Tetrahydro-2-pyranylmethyl toluene-*p*-sulphonate (m. p. 69—70°, 27 g.) was added and the resultant solution heated at 150° for 2 hours. Distillation through a 20-cm. Dufton column yielded a mixture, b. p. 178—192°/760 mm., of the chloride and solvent. The distillate was dissolved in ether, and the ethereal solution was washed several times with small volumes of water, dried ($CaCl_2$), and evaporated. The residue, on distillation, gave the chloride (9 g., 68%), b. p. 120°/170 mm., n_D^{20} 1·4580—1·4600. Further purification by repeated washing and drying resulted in considerable losses.

Similar isolation difficulties were encountered when 2-ethoxyethanol was employed as solvent. The reaction was also carried out in dry methanol at 115° for 2 hours, but the product was again heterogeneous. Some of the corresponding methyl ether was probably present; 40% of the ester was recovered.

Hex-5-*yn*-1-*ol* (VII).—2-Chloromethyltetrahydropyran (6·8 g.) was added dropwise with occasional agitation to a suspension of sodamide (from sodium, 3·45 g.) in liquid ammonia (150 c.c.). After 36 hours ammonium chloride (6 g.) was added. After addition of ether (200 c.c.) the ammonia was allowed to evaporate. Evaporation and distillation gave hex-5-yn-1-ol (4·0 g., 80%), b. p. 75°/16 mm., n_D^{16} 1·4510 (analytical results were erratic: Found: C, 72·3; H, 10·1. Calc. for $C_6H_{10}O$: C, 73·4; H, 10·2%. The alcohol probably contained a little tetrahydro-2-hydroxymethylpyran). The 3 : 5-*dinitrobenzoate* formed plates, m. p. 58°, from light petroleum (b. p. 40—60°) (Found: C, 53·0; H, 4·1. $C_{13}H_{12}O_6N_2$ requires C, 53·4; H, 4·15%), and gave an α-*naphthylamine adduct* as bright red needles, m. p. 89·5°, from alcohol (Found: C, 63·65; H, 4·75. $C_{23}H_{21}O_6N_3$ requires C, 63·4; H, 4·85%). The *phenylurethane* crystallised in long needles, m. p. 55·5°, from light petroleum (b. p. 40—60°) (Found: C, 71·75; H, 6·6. $C_{13}H_{15}O_2N$ requires C, 71·9; H, 6·95%).

Hex-3-*yn*-1-*ol* (XIII).—3-Chloro-2-ethyltetrahydrofuran (45 g.; Crombie and Harper, *J.*, 1950, 1707) was added during 10 minutes to a stirred suspension of sodamide (from sodium, 25 g.) in liquid ammonia (1 l.), and the resulting suspension was stirred for 20 hours. Dry ether (150 c.c.) was added, followed by ammonium chloride (40 g.). Evaporation of the ethereal extract through a 10-cm. Fenske column and distillation gave two fractions: (*a*) b. p. 90—97° and (*b*) b. p. 83—87°/120 mm. Redistillation of (*a*) gave 2-ethyldihydrofuran (XIV) (10·2 g., 30%), b. p. 95—97°/751 mm., n_D^{15} 1·4392—1·4406. The structure of the vinyl ether was confirmed by hydrolysis with 2N-sulphuric acid to 6-hydroxyhexan-3-one, b. p. (bath-temp.) 130°/10 mm. The phenylurethane crystallised in flat needles, m. p. 86°, from light petroleum (b. p. 60—80°) (Wohlgemuth, *Compt. rend.*, 1914, **159**, 80, gives b. p. 115—116°/21 mm., for the hydroxyketone and m. p. 84° for the phenylurethane). Redistillation of (*b*) gave hex-3-yn-1-ol (10 g., 30%), b. p. 93—94°/52 mm., n_D^{16} 1·4561. It formed a 3 : 5-dinitrobenzoate as rosettes of feathery needles, m. p. 77° after two recrystallisations from light petroleum (b. p. 60—80°). The α-naphthylurethane crystallised in clusters of laths, m. p. 107°, from light petroleum (b. p. 60—80°) (Found: C, 76·7; H, 6·6. Calc. for $C_{17}H_{17}O_2N$: C, 76·4; H, 6·4%). [Sondheimer (*loc. cit.*) records n_D^{17} 1·4579 for the alcohol and m. p.s 73—74° and 84—85° for the 3 : 5-dinitrobenzoate and the α-naphthylurethane respectively. Stoll and Commarmont (*Helv. Chim. Acta*, 1949, **32**, 597) give m. p. 75—76° for the 3 : 5-dinitrobenzoate.] In view of the discrepancies in the m. p.s of the α-naphthylurethanes the structure of the alcohol was rigidly proved. Total hydrogenation with platinic oxide catalyst in ethyl acetate (uptake 92% of calculated amount) gave *n*-hexanol, which formed a 3 : 5-dinitrobenzoate, m. p. 59—60° (lit., 61°). Oxidation with an alkaline solution of potassium permanganate gave propionic acid, identified as the *p*-phenylphenacyl ester, which formed plates, m. p. 101° (lit., 102°), from ethanol.

Reaction between 1-*Bromo*-2-*ethoxyhexane* (XV) *and Sodamide*.—(*a*) 1-Bromo-2-ethoxyhexane (37 g.; Swallen and Boord, *J. Amer. Chem. Soc.*, 1930, **52**, 654, 3400) was added dropwise during 1 hour to a stirred suspension of sodamide (from 13 g. of sodium) in liquid ammonia (400 c.c.), and the resulting suspension was stirred for a further 20 hours. Liquid butane (200 c.c.) was then added, followed by ammonium chloride (22 g.). Most of the ammonia was allowed to evaporate, water (200 c.c.) was gradually added, the butane layer was decanted, and the aqueous layer was further extracted with butane. Butane was slowly removed from the combined dried extracts through a 20-cm. vapour-jacketed Fenske column using a carbon dioxide–methanol condenser for partial reflux. On distillation the residual liquid gave two fractions:

(i) hex-1-yne (6·5 g., 45%), b. p. 72—76°/755 mm., n_D^{18} 1·4008 (Hurd and Christ, *J. Org. Chem.*, 1936, **1**, 143, give b. p. 71·3°, n_D^{12} 1·402), and (ii) 2-*ethoxyhex*-1-*ene* (4·1 g., 18%), b. p. 78°/100 mm., n_D^{17} 1·4172 (Found : C, 74·35; H, 12·7. $C_8H_{16}O$ requires C, 74·95; H, 12·6%). Treatment of (ii) with aqueous 2 : 4-dinitrophenylhydrazine sulphate solution resulted in an immediate precipitate of hexan-2-one 2 : 4-dinitrophenylhydrazone, which from ethanol gave feathery orange needles, m. p. 107° (lit., 106°). Hydrolysis of a further quantity of the vinyl ether with dilute acid, followed by isolation of the ketone and treatment with semicarbazide hydrochloride, gave the corresponding semicarbazone, crystallising from aqueous ethanol in prismatic needles, m. p. 123° (lit., 122°).

4-*Ethoxyoct*-3-*ene*.—3-Bromo-4-ethoxyoctane was prepared by the method of Wibaut and Gitsels (*Rec. Trav. chim.*, 1940, **59**, 947). The bromo-ether (33 g.) was added during 10 minutes to a stirred suspension of sodamide (from sodium, 12 g.) in liquid ammonia (400 c.c.) and dry ether (50 c.c.). After 20 hours, ether (100 c.c.) was added, followed by ammonium chloride (20 g.). Water (150 c.c.) was then cautiously added and the aqueous layer extracted with ether. The ether was carefully removed from the dried extract through a 15-cm. Fenske column. The residual liquid (17 g.) on fractionation gave a negligible forerun (which would contain any oct-3-yne present) and 4-*ethoxyoct*-3-*ene* (14·5 g., 67%), b. p. 74—76°/31 mm., n_D^{19} 1·4240 (Found : C, 76·75; H, 12·45. $C_{10}H_{20}O$ requires C, 76·85; H, 12·9%). Light absorption measurements (2120 Å, ε = 2250) indicated that some of the isomeric ether, 4-ethoxyoct-2-ene, was present. Its structure was confirmed by acid hydrolysis to octan-4-one, b. p. 98°/97 mm., n_D^{20} 1·4172, identified as the 2 : 4-dinitrophenylhydrazone which formed orange crystals, m. p. 37—38°, from light petroleum (b. p. 60—80°) (Found : C, 54·45; H, 6·3. Calc. for $C_{14}H_{20}O_4N_4$: C, 54·55; H, 6·5%). Hargreaves and Owen (*J.*, 1947, 752) quote n_D^{14} 1·4173 for the ketone and m. p. 41° for the 2 : 4-dinitrophenylhydrazone. The semicarbazone crystallised from aqueous methanol and had m. p. 96—96·5° (Woods and Schwartzman, *J. Amer. Chem. Soc.*, 1949, **71**, 1396, record 95—97°).

Ultra-violet Light Absorption Measurements.—Purified hexane was used as solvent unless otherwise stated. Care was taken to minimise evaporation losses from the cells (preferably 1-mm.). Measurements were commenced at the shortest wave-length and continued systematically. The slit was initially set at maximum width, and the sensitivity control at least two turns from the maximum position. As the wave-length was increased the slit was used to zero the instrument until the normal slit width was reached (0·4—0·6 mm.), operation then being as usual (zero with sensitivity control). As far as possible, concentrations of solutions were adjusted so that the observed values of E were in the region 0·2—0·4. The values were then corrected for the scattered light, Opler's table (*loc. cit.*) being used to calculate the actual value of E.

All the ethers were distilled from potassium hydroxide immediately before examination; commercial 2 : 3-dihydropyran and *cyclo*hexene were purified by refluxing them with sodium and distillation, and by washing with sodium hydrogen sulphite and distillation over sodium, respectively. In our experience these precautions are necessary for consistent results, and the discrepancies between the results illustrated and those recorded by Platt, Klevens, and Price (*loc. cit.*) are possibly due to differences in the methods of purification.

The authors thank Mr. E. S. Morton for microanalyses. One of them (G. E.) is indebted to the Department of Scientific and Industrial Research for a Maintenance Grant.

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[*Received, February 5th*, 1952.]