25. *Experiments on the Synthesis of the Pyrethrins. Part X.** *Intermediates for the Synthesis of* cis-*Pyrethrolone.*†

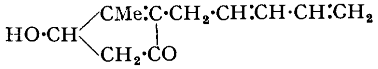
By L. Crombie, S. H. Harper, F. C. Newman, D. Thompson, and (in part) R. J. D. Smith.

The reactions of the toluene-*p*-sulphonates of pent-2-yne-1 : 5-diol with sodium hydroxide, sodium ethoxide, and ethyl sodioacetoacetate are investigated. Pent-4-en-2-yn-1-ol and oct-7-en-5-yn-2-one are obtained in poor yield as potential intermediates for the synthesis of *cis*-pyrethrolone by partial hydrogenation of the enyne system. Pent-4-en-2-yn-1-ol, however, is more readily prepared from the Grignard derivative of vinylacetylene and paraformaldehyde. Thence, by the acetoacetic ester ketone synthesis, pent-4-en-2-ynyl chloride gives a better yield of oct-7-en-5-yn-2-one.

Extension of these reactions to the preparation of *cis*-octa-5 : 7-dien-2-one from toluene-*p*-sulphonyl derivatives of *cis*-pent-2-ene-1 : 5-diol is studied, since construction of the *cis*-system by an elimination reaction would avoid difficulties encountered on hydrogenation of an enyne intermediate. However, *cis*-octa-5 : 7-dien-2-one is obtained in only poor yield; the predominant reaction with ethyl sodioacetoacetate is cyclisation to 4-acetyl*cyclo*hexene.

The possibility of using this cyclisation to prepare *cyclo*heptene and *cyclo*octene analogues of 4-acetyl*cyclo*hexene, from homologues of *cis*-pent-2-ene-1 : 5-diol, is explored.

The degradative experiments and stereospecific synthesis of (±)-*trans*-pyrethrolone described in Part VII (Crombie, Harper, and Thompson, *J.*, 1951, 2906) established the structure of pyrethrolone as 4-hydroxy-3-methyl-2-(*cis*-penta-2 : 4-dienyl)*cyclo*pent-2-en-1-one (I). Attention is now directed to the synthesis of (±)-*cis*-pyrethrolone utilising the routes previously devised for alkyl- and alkenyl-rethrolones (Crombie, Edgar, Harper, Lowe, and Thompson, *J.*, 1950, 3552; Schechter, Green, and LaForge, *J. Amer. Chem. Soc.*, 1949, **71**, 3165). In this and a later communication we describe a study of the introduction of the *cis*-penta-2 : 4-dienyl system into suitable intermediates.

(I) 

$$\mathrm{HO{\cdot}CH}\begin{cases}\mathrm{CMe{:}C{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH{:}CH_2}\\ \mathrm{CH_2{\cdot}CO}\end{cases}$$

The discovery by Eglington and Whiting (*J.*, 1950, 3650; 1953, 3052) that the toluene-*p*-sulphonates of two βγ-acetylenic alcohols, but-3-yn-1-ol and pent-4-yn-2-ol, lose toluene-*p*-sulphonic acid on treatment with strong alkali to form the vinylacetylene in high yield, while with sodiomalonic ester substitution occurs only to the extent of 3%, suggested means by which a $\cdot CH_2{\cdot}C{\vdots}C{\cdot}CH{:}CH_2$ side-chain could be introduced, subsequently to be selectively

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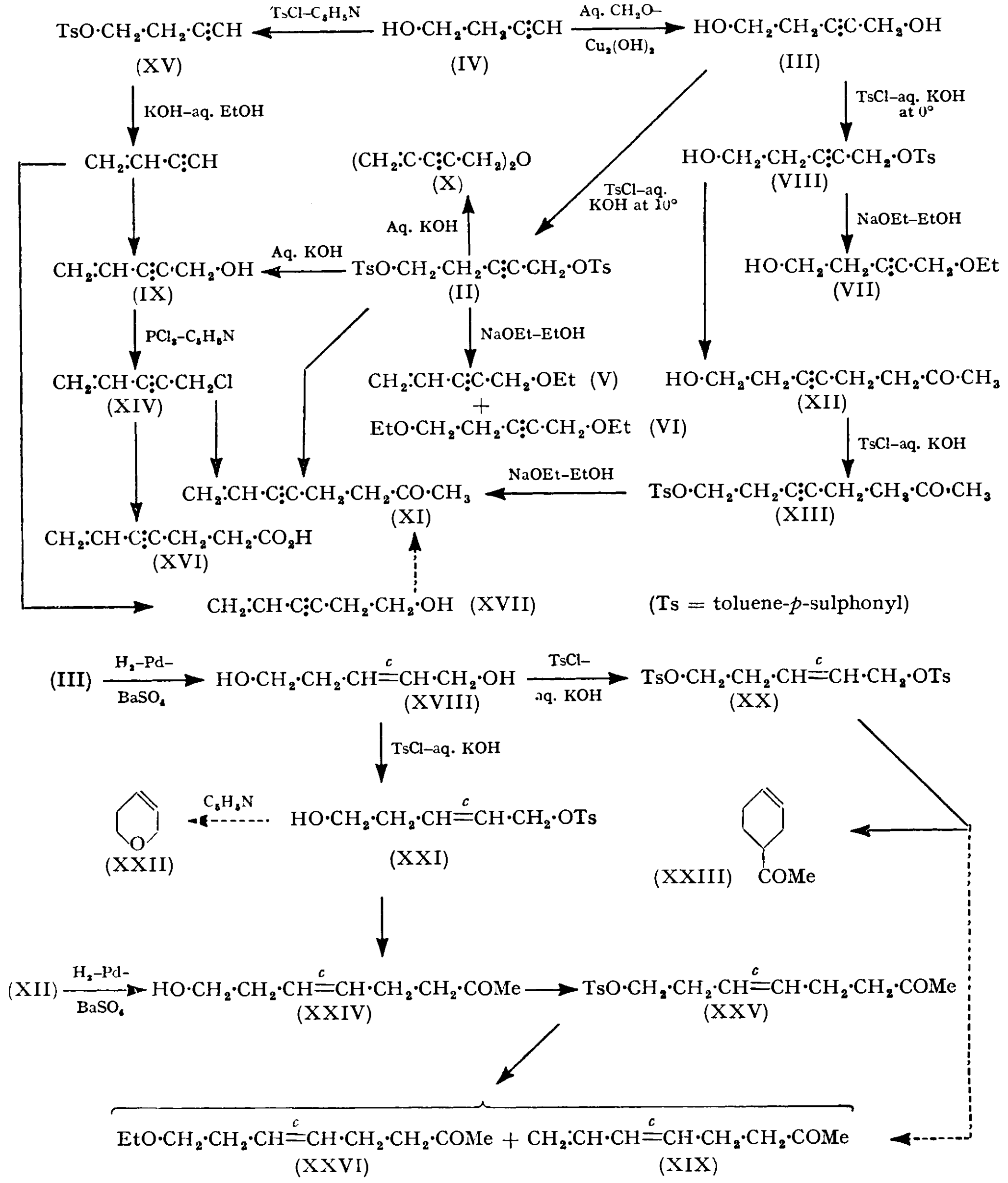
hydrogenated to the *cis*-penta-2 : 4-diene system. For this purpose the ditoluene-*p*-sulphonate (II) of pent-2-yne-1 : 5-diol (III) appeared particularly suitable for the β-sulphonyloxy-group should undergo elimination and the α-(propargylic)sulphonyloxy-group, owing to its pseudohalogen character, should undergo nucleophilic replacement.



Pent-2-yne-1 : 5-diol (III), prepared by hydroxymethylation of but-3-yn-1-ol (IV) with formaldehyde in the presence of cuprous hydroxide and since described by Heuberger and Owen (*J.*, 1952, 910), was converted in good yield into the crystalline ditoluene-*p*-sulphonate (II). The crude ester with sodium ethoxide in ethanol gave, as main product though in only moderate yield, the expected 1-ethoxypent-4-en-2-yne (V), whose ultraviolet absorption (max. at 229 mμ, ε 9000) was characteristic of the enyne chromophore. A higher-boiling product appeared from analyses to be a mixture of 1 : 5-diethoxypent-2-yne (VI), derived by double replacement, and 5-ethoxypent-3-yn-1-ol (VII), formed by replacement from the monotoluene-*p*-sulphonate, a likely contaminant in the crude ditoluene-*p*-sulphonate. A liquid monotoluene-*p*-sulphonate was prepared by reaction of pent-2-yne-1 : 5-diol with 1 mol. of toluene-*p*-sulphonyl chloride in aqueous potassium hydroxide, and behaved as a mixture of the monoester (VIII), formed by more rapid reaction at the propargylic hydroxyl group, and the diester (II) : with sodium ethoxide in ethanol it gave the expected 5-ethoxypent-3-yn-1-ol (VII), together with, probably, 1-ethoxypent-4-en-2-yne (V) derived from the ditoluene-*p*-sulphonate.

The ditoluene-*p*-sulphonate (II) with potassium hydroxide in 50% aqueous ethanol still gave 1-ethoxypent-4-en-2-yne (V) as the main product. With aqueous potassium hydroxide pent-4-en-2-yn-1-ol (IX) was formed in low yield : the main product was tentatively identified as dipent-4-en-2-ynyl ether (X), formed by the preferential reaction of the pent-4-en-2-yne oxide anion with unhydrolysed propargylic toluene-*p*-sulphonate; pent-2-yne-1 : 5-diol may have been formed by solvolysis but would have remained in the unexamined aqueous layer.

Reaction of the ditoluene-*p*-sulphonate (II) with 2 mols. of ethyl sodioacetoacetate, followed by ketonic fission, gave the expected oct-7-en-5-yn-2-one (XI) isolated as the sole steam-volatile product, though in low yield. The crude monotoluene-*p*-sulphonate (VIII) with 1 mol. of ethyl sodioacetoacetate gave, as products of ketonic fission, the same ketone (XI), presumably derived from the ditoluene-*p*-sulphonate present, and 8-hydroxyoct-5-yn-2-one (XII), both in low yield. The identity of the hydroxy-ketone (XII) was confirmed by its infrared spectrum [hydroxyl 3390 (s), 1037 (s), unconjugated disubstituted acetylene 2247 (w), and α-saturated carbonyl 1704 (s) cm.$^{-1}$]. Conversion of the hydroxy-ketone (XII) into the toluene-*p*-sulphonate (XIII) and treatment with ethanolic sodium ethoxide gave oct-7-en-5-yn-2-one (XI) as the sole product, though only in moderate yield.

Although a suitable intermediate in oct-7-en-5-yn-2-one (XI) had been found, the poor overall yield (7%) from pent-2-yne-1 : 5-diol rendered this approach to *cis*-pyrethrolone unattractive. However, oct-7-en-5-yn-2-one should be more readily accessible from pent-4-en-2-ynyl chloride (XIV) by an acetoacetic ester ketone synthesis though this required a better route to pent-4-en-2-yn-1-ol (IX) than that provided by the ditoluene-*p*-sulphonate (II). Eglington and Whiting (*J.*, 1950, 3650) had obtained pent-4-en-2-yn-1-ol in low yield by the reaction of sodiovinylacetylene in liquid ammonia, prepared *in situ* from but-3-ynyl toluene-*p*-sulphonate (XV) with paraformaldehyde. However, interaction of the Grignard reagent of redistilled vinylacetylene with paraformaldehyde gave pent-4-en-2-yn-1-ol (IX) in satisfactory yield (50%). Pent-4-en-2-ynyl chloride, prepared with phosphorus trichloride, was condensed with ethyl sodioacetoacetate and after ketonic fission gave a fair yield of oct-7-en-5-yn-2-one (XI), identical with the previous sample, hydrogenated to octan-2-one with an uptake of 3 mols. of hydrogen, and posesssing the expected ultraviolet and infrared absorption [conjugated disubstituted acetylene 2231 (w), conjugated vinyl 976 (s) and 921 (s), carbonyl stretching 1720 (s), acetyl 1365 (s) cm.$^{-1}$]. A substantial by-product (20%) in this ketone synthesis was hept-6-en-4-ynoic acid (XVI), which on hydrogenation gave heptanoic acid with an uptake of 3 mols. of hydrogen and whose ultraviolet light absorption showed an enyne chromophore. To prepare an authentic specimen of the acid, ethyl sodiomalonate was condensed with pent-4-en-2-ynyl chloride : even after crystallisation the malonic acid appeared from analysis to be a 2 : 1 mixture of hex-5-en-3-yne-1 : 1- and undeca-1 : 10-diene-3 : 8-diyne-6 : 6-dicarboxylic acid; nevertheless, decarboxylation and crystallisation gave the desired hept-6-en-4-ynoic acid identical with that obtained from the acetoacetic ester reaction. The formation of a substantial proportion of substituted acetic acid when a propargylic halide is used in the acetoacetic ester ketone synthesis, with hydrolysis by aqueous alkali, appears likely to be general, for Gaudemar (*Compt. rend.*, 1953, **237**, 71) obtained equal amounts of hex-5-yn-2-one and pent-4-ynoic acid with propargyl bromide itself, while we have made a similar observation with but-2-ynyl chloride (Harper and Kazi, unpublished work).

As a further potential intermediate for subsequent chain extension by routes *B* or *E* (Crombie *et al.*, *loc. cit.*, 1950; Crombie, Harper, Stedman, and Thompson, *J.*, 1951, 2445), hex-5-en-3-yn-1-ol (XVII) was prepared from ethylene oxide and sodiovinylacetylene in liquid ammonia.

The observations of Ferns and Lapworth (*J.*, 1912, **101**, 273), of Hückel *et al.* (*Annalen*, 1938, **533**, 1; 1939, **537**, 113; 1940, **543**, 191), and of Owen *et al.* (*J.*, 1949, 315, 320; 1950, 2103, 2108; 1952, 910; 1953, 404) that the toluene-*p*-sulphonates of saturated primary and secondary alcohols give rise to olefin by elimination with strongly basic reagents suggested that in the system $TsO{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}$ elimination, with concomitant formation of a conjugated diene, would be the preponderating reaction. The behaviour of the mono- and the di-toluene-*p*-sulphonate of *cis*-pent-2-ene-1 : 5-diol (XVIII), therefore, was examined as providing a possible route to *cis*-octa-5 : 7-dien-2-one (XIX) not requiring partial hydrogenation of an enyne system.

Semihydrogenation of an isolated acetylenic bond yields *cis*-ethylenes of higher purity than partial hydrogenation of an enyne. Pent-2-yne-1 : 5-diol was selectively hydrogenated over both palladised barium sulphate and palladised calcium carbonate (cf. Heuberger and Owen, *loc. cit.*) to the required *cis*-diol (XVIII). With 1 and 2 mols. of toluene-*p*-sulphonyl chloride in aqueous potassium hydroxide, this gave a liquid " ditoluene-*p*-sulphonate " (XX) and " monotoluene-*p*-sulphonate " that resisted purification. The " monotoluene-*p*-sulphonate " is considered to be predominantly (XXI) formed through more rapid reaction at the allylic hydroxyl group. Attempts to prepare the ditoluene-*p*-sulphonate in pyridine failed. This may be due to instability of the monotoluene-*p*-sulphonate in the presence of pyridine, ring closure occurring between the favourably disposed (*cis*-)hydroxyl and sulphonyloxy-groups, with the formation of 5 : 6-dihydro-2-pyran (XXII). While this work was in progress Haggis and Owen (*J.*, 1953, 391) recorded difficulty in preparing the ditoluene-*p*-sulphonate of 1 : 2-bishydroxymethyl*cyclo*hexane, showing that the monotoluene-*p*-sulphonate cyclised in the presence of pyridine to form 8-oxa[4 : 3 : 0]*bicyclo*nonane.

As for the ditoluene-*p*-sulphonate of pent-2-yne-1 : 5-diol, the crude ditoluene-*p*-sulphonate (XX) was treated with ethyl sodioacetoacetate and subjected to ketonic fission. Although analysis showed the steam-volatile ketonic product to have the formula $C_8H_{12}O$ expected for the octadienone (XIX), the ultraviolet (no absorption in the 227-mμ region) and infrared absorption (no conjugated vinyl absorption, acyclic α-saturated carbonyl 1708 cm.$^{-1}$) established the absence of a conjugated diene system. Furthermore, catalytic hydrogenation showed the presence of only one ethylenic bond. The product, therefore, was monocyclic and comparison of its physical properties and those of its derivatives (Table) with data for 4-acetyl*cyclo*hexene (XXIII) [Petrov, *J. Gen. Chem.* (*Russia*), 1941, **11**, 309; *Chem. Abs.*, 1941, **35**, 5873] pointed beyond doubt to their identity. It was evident that after replacement of the allylic sulphonyloxy-group by acetoacetate anion the proximity of the β-sulphonyloxy-group, arising from the *cis*-configuration, favoured intramolecular replacement rather than elimination. Isolation of the total ketonic product by ether-extraction gave also a small amount of *cis*-8-hydroxyoct-5-en-2-one (XXIV) [infrared bands: hydroxyl 3425 (s), 1046 (s); unconjugated *cis*-CHR:CHR′ 1656 (w); α-saturated acyclic carbonyl, 1709 (s) cm.$^{-1}$; no absorption in the 970-cm.$^{-1}$ region (*trans*-CHR:CHR′)]. An identical ketone was prepared by semihydrogenation of 8-hydroxyoct-5-yn-2-one (XII) over palladised barium sulphate. The hydroxy-ketone (XXIV) presumably arose from the monotoluene-*p*-sulphonate (XXI) present as a contaminant in the crude ditoluene-*p*-sulphonate and in confirmation of this it was obtained in low yield, accompanied by 4-acetyl*cyclo*hexene, by reaction of the " monotoluene-*p*-sulphonate " of *cis*-pent-2-ene-1 : 5-diol with ethyl sodioacetoacetate followed by ketonic fission. These findings suggest that the " ditoluene-*p*-sulphonate " and the " monotoluene-*p*-sulphonate " were, in fact, mixtures of comparable composition.

	4-Acetyl*cyclo*hexene	Our product
B. p.	80°/20 mm.	74°/16 mm.
n_D^{20}	1·4698	1·4697
Semicarbazone, m. p.	165—166°	168·5—169°
p-Nitrophenylhydrazone, m. p.	142—143°	141—143°
2 : 4-Dinitrophenylhydrazone, m. p.	—	148·5—149°

The crude toluene-*p*-sulphonate (XXV) of *cis*-8-hydroxyoct-5-en-2-one (XXIV) was treated with ethanolic sodium ethoxide to effect elimination (and replacement), yielding *cis*-8-ethoxyoct-5-en-2-one (XXVI) [semicarbazone; infrared C–O stretching frequency for the alkyl ether, 1108 (vs) cm.$^{-1}$], and smaller amounts of desired *cis*-octa-5 : 7-dien-2-one (XIX) (semicarbazone, 2 : 4-dinitrophenylhydrazone; the infrared absorption showed a small peak at 1106 cm.$^{-1}$, probably owing to a trace of the ethoxy-ketone). The structure (XIX) was confirmed by the ultraviolet light absorption (max. at 228 mμ, ε 16,100), in agreement with a penta-2 : 4-*cis*-dienyl chromophore, and the infrared absorption spectrum [conjugated vinyl, 999 (s) and 910 (s) cm.$^{-1}$]. We consider this product to be stereochemically of high purity, but there was insufficient material for regeneration from the semicarbazone. Stereochemically slightly less pure diene-ketone was obtained in larger quantity by partial hydrogenation of oct-7-en-5-yn-2-one (unpublished experiments).

From the contrasting behaviour of the toluene-*p*-sulphonates of *cis*-8-hydroxyoct-5-en-2-one and 8-hydroxyoct-5-yn-2-one towards ethanolic sodium hydroxide it appears that there is a greater tendency for elimination to occur when the sulphonyloxy-group is β to an acetylenic bond than when it is β to an ethylenic bond.

(With R. J. D. SMITH.) Although the condensation of 1 : 2-, 1 : 3-, and 1 : 4-dihalides with active methylene-containing compounds of the type of acetoacetic ester has often been used since the time of W. H. Perkin, jun., for the preparation of substituted *cyclo*propanes, *cyclo*butanes, and *cyclo*pentanes respectively (see Rodd, " Chemistry of Carbon Compounds," Vol. IIA, Elsevier Pub. Co., Amsterdam), the formation of substituted *cyclo*hexanes and *cyclo*heptanes from 1 : 5- and 1 : 6-dihalides has rarely been observed. The conformation of the longer polymethylene chains favours inter- rather than intra-molecular condensation. However, the ready formation of 4-acetyl*cyclo*hexene from *cis*-pent-2-ene-1 : 5-diol di-toluene-*p*-sulphonate (p. 129) suggested that the presence of a *cis*-ethylenic bond in the polymethylene chain induces a conformation more favourable to ring closure: in this case substituted *cyclo*heptenes and *cyclo*octenes might be accessible from the readily prepared higher homologues of *cis*-pent-2-ene-1 : 5-diol.

$$\underset{\text{(XXVII)}}{\mathrm{HO{\cdot}[CH_2]_{\mathit{n}}{\cdot}C{\vdots}CH}} \longrightarrow \underset{\text{(XXVIII)}}{\mathrm{HO{\cdot}[CH_2]_{\mathit{n}}{\cdot}C{\vdots}C{\cdot}CH_2{\cdot}OH}} \longrightarrow \underset{\text{(XXIX)}}{\mathrm{HO{\cdot}[CH_2]_{\mathit{n}}{\cdot}CH\overset{\mathit{c}}{=}CH{\cdot}CH_2{\cdot}OH}}$$

Hydroxymethylation of pent 4-yn-1-ol and hex-5-yn-1-ol (XXVII; $n = 3$ and 4) by the formaldehyde–aqueous cuprous hydroxide method used for the lower homologue gave hex-2-yne-1 : 6-diol and hept-2-yne-1 : 7-diol (XXVIII; $n = 3$ and 4) in moderate yield. Semihydrogenation of these acetylenic diols over palladised barium sulphate then gave *cis*-hex-2-ene-1 : 6-diol and *cis*-hept-2-ene-1 : 7-diol (XXIX; $n = 3$ and 4).

As for *cis*-pent-2-ene-1 : 5-diol no crystalline ditoluene-*p*-sulphonate could be obtained from *cis*-hex-2-ene-1 : 6-diol and even under favourable conditions a liquid mixture of mono- and ditoluene-*p*-sulphonates was formed. A variety of methods (see Experimental section) was tried for the preparation of *cis*-1 : 6-dibromohex-2-ene before success was achieved by the method used by Johnson (*J.*, 1946, 1009) for but-2-yne-1 : 4-diol; even so the dibromide could not be purified by distillation.

Both the crude ditoluene-*p*-sulphonate and dibromide of *cis*-hex-2-ene-1 : 6-diol were treated under a variety of conditions with excess of ethyl sodioacetoacetate, but no definite ketonic product could be isolated. Experiments with *cis*-hept-2-ene-1 : 7-diol were therefore abandoned.

EXPERIMENTAL

Ultraviolet-light absorptions were determined for EtOH solutions by Mrs. A. I. Boston with a Hilger Medium Quartz Spectrograph. Infrared-light absorptions were determined partly with a Grubb Parsons single-beam spectrometer coupled to a Brown recorder and partly with a Grubb Parsons double-beam spectrometer, the pure liquids being used as capillary films.

p-Nitrophenylhydrazones and 2 : 4-dinitrophenylhydrazones were passed through a short column of alumina in benzene before final crystallisation. M. p.s are corrected.

But-3-*yn*-1-*ol*. By the procedure of *Inorg. Synth.*, 1946, **2**, 79, 128, sodium acetylide was prepared on a 12-molar scale in liquid ammonia and treated with a 10% excess of ethylene oxide to give but-3-yn-1-ol, b. p. 125—130°, n_D^{20} 1·438—1·441, in 42% yield (average of many runs) (cf. Hennion and Murray, *J. Amer. Chem. Soc.*, 1942, **64**, 1220; Campbell, Campbell, and Eby, *ibid.*, 1938, **60**, 2882).

Pent-2-*yne*-1 : 5-*diol.*—By a procedure similar to that of Heuberger and Owen (*J.*, 1952, 910; cf. Heilbron, Jones, and Sondheimer, *J.*, 1947, 1586) on a 0·75-molar scale, but-3-yn-1-ol was converted into pent-2-yne-1 : 5-diol, b. p. 107°/0·25 mm., n_D^{20}1·488—1·489, in 66% yield. Like Heuberger and Owen we had found that interaction of the Grignard reagent from but-3-yn-1-ol with paraformaldehyde gave a lower yield of pent-2-yne-1 : 5-diol.

Pent-2-*yne*-1 : 5-*diol Ditoluene*-p-*sulphonate.*—To a stirred solution of pent-2-yne-1 : 5-diol (20 g., 0·2 mole) and toluene-*p*-sulphonyl chloride (78 g., 0·4 mole) in acetone (150 ml.), kept at 10°, aqueous potassium hydroxide (33·6 g. in 60 ml.) was added dropwise during 1 hr. After further stirring at room temperature overnight, water was added. Ether-extraction followed by drying ($MgSO_4$) and evaporation then gave an oil which slowly but incompletely crystallised (60 g., 73% average yield). Trituration with methanol followed by crystallisation from methanol, gave *pent*-2-*yne*-1 : 5-*diol ditoluene*-p-*sulphonate*, m. p. 58° (Found : C, 55·1; H, 5·1; S, 16·1. $C_{19}H_{20}O_6S_2$ requires C, 55·85; H, 4·95; S, 15·7%). Crude ditoluene-*p*-sulphonate was used in the following experiments.

(*a*) Ditoluene-*p*-sulphonate (16·3 g., 0·04 mole) was added in portions with ethanol (20 ml.) to a solution of sodium ethoxide (from sodium, 2·3 g.) in ethanol (60 ml.). When the initial reaction had subsided the mixture was heated on the steam-bath under reflux for 30 min. and then most of the alcohol was boiled off. Addition of water to the paste and ether-extraction, followed by drying ($MgSO_4$) at 5° in the presence of quinol, and distillation, gave 1-*ethoxypent*-4-*en*-2-*yne* (0·81 g., 20%), b. p. 83—85°/100 mm., n_D^{20} 1·458 (Found : C, 76·3; H, 9·25. $C_7H_{10}O$ requires C, 76·3; H, 9·15%), possessing a celery-like odour. Light absorption : max. at 229 mμ (ε 9000). The unprotected ether polymerised within a few days at room temperature. Distillation of the residue gave a fraction (0·56 g.), b. p. 115—118°/15 mm., n_D^{20} 1·463 (Found : C, 67·1; H, 9·85. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4. Calc. for $C_9H_{16}O_2$: C, 69·2; H, 10·3%).

(*b*) Ditoluene-*p*-sulphonate (25 g.) was added during 15 min. to a hot solution of potassium hydroxide (10 g.) in 50% aqueous ethanol (20 ml.) containing a trace of Teepol detergent. After a further 15 minutes' heating under reflux steam-distillation followed by extraction of the distillate as in (*a*) and distillation gave 1-ethoxypent-4-en-2-yne (0·90 g., 13%), b. p. 80—82°/85 mm., n_D^{20} 1·459. A higher-boiling fraction (0·45 g.) had b. p. 104—112°/13 mm., n_D^{20} 1·494—1·505, and probably contained dipent-4-en-2-ynyl ether.

(*c*) Ditoluene-*p*-sulphonate (25 g.) was added in portions to a stirred boiling solution of potassium hydroxide (10 g.) in water (25 ml.) containing a trace of Teepol detergent with simultaneous distillation. Finally the mixture was steam-distilled, to give an oil which rapidly discoloured in air (quinol was added to prevent this). Saturation of the distillate with salt, extraction with ether, drying as in (*a*), and distillation gave (i) pent-4-en-2-yn-1-ol (0·22 g., 5%), b. p. 72°/15 mm., n_D^{20} 1·493, and (ii) *dipent*-4-*en*-2-*ynyl ether* (0·76 g., 17%), b. p. 106°/12 mm., n_D^{20} 1·520—1·5215 (Found : C, 81·0; H, 7·05. $C_{10}H_{10}O$ requires C, 82·1; H, 6·9%). The pent-4-en-2-yn-1-ol gave a phenylurethane, needles [from light petroleum (b. p. 80—100°)], m. p. 80·5—81°, raised to 80·5—81·5° on admixture with the specimen described on p. 132.

(*d*) Ditoluene-*p*-sulphonate (40·8 g., 0·1 mole) was added during 5 min. to a stirred hot solution of ethyl sodioacetoacetate (0·2 mole) in ethanol. After a further hour's stirring and heating under reflux most of the ethanol was distilled off. The residue was stirred with 5% aqueous sodium hydroxide (200 ml.) at room temperature overnight. Next day a little oil was removed, the alkaline solution acidified to methyl-orange with concentrated hydrochloric acid and warmed to 50° to bring about decarboxylation. An oil separated. Steam-distillation, saturation of the distillate with salt, extraction with ether, and washing of the extract with sodium hydrogen carbonate solution, followed by drying as in (*a*) and distillation, gave *oct*-7-*en*-5-*yn*-2-*one* (0·85 g., 7%), b. p. 84—89°/15 mm., n_D^{20} 1·475—1·478. A much larger amount of oil was not steam-volatile but was not examined; it probably contained 8-hydroxyoct-5-yn-2-one. Oct-7-en-5-yn-2-one gave a semicarbazone, m. p. 142°, raised to 142·0—142·5° on admixture with the specimen described on p. 133, and a 2 : 4 dinitrophenylhydrazone, m. p. 80·0—80·7°, raised to 81° on admixture with the specimen described on p. 133.

Pent-2-*yne*-1 : 5-*diol Monotoluene*-p-*sulphonate.*—To a stirred ice-cooled solution of pent-2-yne-1 : 5-diol (20 g., 0·2 mole) and toluene-*p*-sulphonyl chloride (39 g., 0·2 mole) in acetone (100 ml.), aqueous potassium hydroxide (16·8 g. in 30 ml.) was added slowly. Then, by the procedure used for the ditoluene-*p*-sulphonate, pent-2-yne-1 : 5-diol monotoluene-*p*-sulphonate (36·5 g.) was obtained as a yellow oil and stored at 5°. This crude monotoluene-*p*-sulphonate was used in the following experiments.

(*e*) Monotoluene-*p*-sulphonate (7·7 g.) in ethanol (10 ml.) was added to a solution of sodium ethoxide (from sodium, 0·85 g.) in ethanol (10 ml.). Then, proceeding as in (*a*), distillation gave 5-*ethoxypent*-3-*yn*-1-*ol* (1·28 g., 24% overall yield from pentynediol), b. p. 107—113°/9 mm., mainly 112°, n_D^{20} 1·463—1·4605 (Found : C, 65·9; H, 9·25. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4%), preceded by a forerun (0·16 g.), b. p. up to 50°/10 mm., n_D^{20} 1·459, probably largely 1-ethoxypent-4-en-2-yne.

(*f*) Monotoluene-*p*-sulphonate (107 g., 0·42 mole) dissolved in ethanol (120 ml.) was added during 90 min. to a stirred boiling solution of ethyl sodioacetoacetate (0·4 mole) in ethanol (240 ml.) under reflux. Then, proceeding as in (*d*) and with 5% aqueous sodium hydroxide (400 ml.), the acid solution after decarboxylation was made alkaline (to pH 9), saturated with salt, extracted with ether, and the extract was dried (Na_2SO_4) and concentrated. Distillation then gave (i) oct-7-en-5-yn-2-one (4·16 g., 5·5% overall yield from pentynediol), b. p. 75—79°/7 mm., n_D^{20} 1·478—1·481, and (ii) 8-*hydroxyoct*-5-*yn*-2-*one* (7·63 g., 10% overall yield), b. p. 104—110°/0·2 mm., mainly 107°, n_D^{20} 1·479—1·481 (Found : C, 68·15; H, 8·5. $C_8H_{12}O_2$ requires C, 68·5; H, 8·6%). Oct-7-en-5-yn-2-one gave a semicarbazone, m. p. 140·5—141·5°, not depressed on admixture with the specimens described below and on p. 133. The *semicarbazone of* 8-hydroxyoct-5-yn-2-one was prepared in aqueous solution and recrystallised from water; it formed transparent plates, m. p. 141·5—142·5° (Found : C, 54·95; H, 7·6. $C_9H_{15}O_2N_3$ requires C, 54·8; H, 7·65%); the yellow 2 : 4-*dinitrophenylhydrazone* crystallised from ethanol as needles, m. p. 111—112° (Found : C, 52·5; H, 4·95. $C_{14}H_{16}O_5N_4$ requires C, 52·5; H, 5·05%).

8-Hydroxyoct-5-yn-2-one (1·12 g.) and toluene-*p*-sulphonyl chloride (1·55 g.) were shaken in acetone (4 ml.) at room temperature whilst aqueous potassium hydroxide (0·67 g. in 2 ml.) was added during 90 min. After a further 2 hours' shaking the crude toluene-*p*-sulphonate (1·85 g.) was isolated as for the ditoluene-*p*-sulphonate above and to it sodium ethoxide (from sodium, 0·37 g.) in ethanol (12 ml.) was added. Then, proceeding as in (*a*), distillation finally gave oct-7-en-5-yn-2-one (0·37 g., 38% yield from hydroxy-ketone), b. p. 76—80°/7 mm., n_D^{20} 1·481. The semicarbazone had m. p. 141·5—142·5°, not depressed on admixture with the specimens described above and on p. 133.

In another experiment the crude toluene-*p*-sulphonate from 8-hydroxyoct-5-yn-2-one (1·12 g.) was boiled under reflux with potassium hydroxide (2·5 g.) in 50% aqueous ethanol (5 ml.) for 30 min. Steam-distallation and addition of Brady reagent to the first 20 ml. of distillate gave impure oct-7-en-5-yn-2-one 2 : 4-dinitrophenylhydrazone (0·56 g., 27%), m. p. 77—78° after crystallisation, raised on admixture with the specimen described on p. 133.

Vinylacetylene.—By the procedure of Eglington and Whiting (*J.*, 1950, 3650) and on a similar scale, but-3-yn-1-ol was converted into the crude toluene-*p*-sulphonate and thence into vinylacetylene, which on redistillation was obtained in 75—80% overall yield. The use of a technical grade of pyridine in the preparation of the toluene-*p*-sulphonate resulted in tar formation and a reduced yield. Invariably, on redistillation of the vinylacetylene, a small amount of less volatile liquid was left in the first trap, perhaps 1-ethoxybut-3-yne formed by a replacement reaction.

Pent-4-*en*-2-*yn*-1-*ol.*—Redistilled vinylacetylene (41 g., 1 mol.) in cooled ether (240 ml.) was slowly added to a stirred ice-cooled Grignard solution prepared from ethyl bromide (88 g., 1 mol.) and magnesium (19·4 g.) in ether (240 ml.) under a solid carbon dioxide–ethanol reflux condenser. After the addition the reaction mixture was boiled for 3 hr., then cooled, and dried paraformaldehyde (36 g., 1·5 mol.) was sublimed in a stream of nitrogen on to the stirred surface of the solution, causing gentle boiling. The resinous complex was decomposed by the addition of dilute sulphuric acid with cooling, and the ethereal solution separated, washed, dried (Na_2SO_4), and concentrated. Distillation then gave pent-4-en-2-yn-1-ol (32 g., 50%), b. p. 67·5°/16 mm., 58°/12 mm., n_D^{20} 1·4940 (Found : C, 73·45; H, 7·25. Calc. for C_5H_6O : C, 73·15; H, 7·35%). Microhydrogenation : 3·0 mol. uptake. Light absorption : max. at 227 mμ (ε 12,000). The phenylurethane formed needles, m.p. 82·5°, from light petroleum. The alcohol formed a gel at room temperature during 14 days. Nazarov and Torgov (*Chem. Abs.*, 1948, **42**, 7735g) prepared pent-4-en-2-yn-1-ol (described as " vinylethinylcarbinol ") by a similar method in 65% yield but used a 30% excess of vinylacetylene.

Pent-4-*en*-2-*ynyl Chloride.*—On a 0·5—1·0-molar scale and by the procedure used for *trans*-penta-2 : 4-dien-1-ol (Part VII, *J.*, 1951, 2906), pent-4-en-2-yn-1-ol was converted into *pent*-4-*en*-2-*ynyl chloride* (55—60%), b. p. 60°/65 mm., n_D^{20} 1·5505 (Found : Cl, 35·5. C_5H_5Cl requires Cl, 35·1%). It was necessary to add a Silicone antifoaming agent before distillation of the chloride.

The distilled chloride darkened quickly even at 0° but a solution in light petroleum with a trace of quinol was stable at this temperature.

Oct-7-en-5-yn-2-one.—By the procedure recorded in Part VII (*loc. cit.*) for *trans*-oct-5-en-7-yn-2-one, on a 0·25-molar scale, pent-4-en-2-ynyl chloride was converted into *oct-7-en-5-yn-2-one* (29—31% yield), b. p. 87—90°/16 mm., 75°/7 mm., n_D^{20} 1·4805 (Found : C, 78·4; H, 8·2. $C_8H_{10}O$ requires C, 78·6; H, 8·25%). Light absorption : max. at 222 and 232 mμ (ε 12,200 and 11,000). The ketone could be stored without deterioration in the presence of quinol at 0°. The *semicarbazone* of oct-7-en-5-yn-2-one formed plates (from ethanol), m. p. 141·5° (Found : C, 59·9; H, 7·35. $C_9H_{13}ON_3$ requires C, 60·3; H, 7·3). The 2 : 4-*dinitrophenylhydrazone* was obtained first as red plates (from ethanol), m. p. 67·5° (Found : C, 54·6; H, 4·7; N, 18·6. $C_{14}H_{14}O_4N_4$ requires C, 55·6; H, 4·7; N, 18·55%), and later as orange needles, m. p. 81° (Found : C, 55·5; H, 4·5%); a mixed m. p. of the two forms was 76—77·5°.

On hydrogenation in ethanol over Adams catalyst oct-7-en-5-yn-2-one (106 mg.) absorbed 2·90 mols. of hydrogen. Filtration and treatment of the hot solution with 2 : 4-dinitrophenylhydrazine and a drop of concentrated hydrochloric acid gave octan-2-one 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 58°.

Hept-6-en-4-ynoic Acid.—Overnight the cold residue from the steam-distillation above deposited crystals. These were taken up in ether and shaken with aqueous sodium hydrogen carbonate. This alkaline extract was combined with the sodium hydrogen carbonate washings of the ether extract of the steam-distillate and acidified, *hept-6-en-4-ynoic acid* (20%) separating. On recrystallisation from water or from light petroleum (b. p. 40—60°) at 0° the acid formed plates, m. p. 57·5° (Found : C, 67·7; H, 6·65. $C_7H_8O_2$ requires C, 67·75; H, 6·5%). Coloured impurities which could not be removed with activated carbon were removed by warming in solution with silica gel. Light absorption : max. at 224 and 233 mμ (ε 11,300 and 10,400). The acid was light-sensitive and unstable but in a refrigerator in a vacuum or under water or light petroleum could be stored without deterioration. The p-*bromophenacyl ester* formed plates (from aqueous ethanol), m. p. 99·5—100·5° (Found : C, 55·6; H, 4·1. $C_{15}H_{13}O_3Br$ requires C, 56·0; H, 4·1%).

On hydrogenation in ethyl acetate over 5% palladised barium sulphate hept-6-en-4-ynoic acid (0·50 g.) absorbed 3·0 mols. of hydrogen. Distillation then gave heptanoic acid (0·36 g., 72%), b. p. 121—123°/20 mm., n_D^{20} 1·4245, characterised as the *p*-bromophenacyl ester, m. p. 70·2—71·2°, in agreement with literature data.

Pent-4-en-2-ynyl chloride (5·5 g.) was added to a stirred boiling solution of ethyl sodiomalonate (0·05 mole) in ethanol. By proceeding in the usual way the undistilled malonic ester (9·6 g.) was hydrolysed with aqueous sodium hydroxide, and the malonic acid (6·2 g.) isolated with ether. Recrystallised from benzene the *acid* was microcrystalline with no m. p. but sintering above 140° (Found : C, 60·7; H, 4·9. $C_8H_8O_4$ requires C, 57·2; H, 4·8. $C_{13}H_{21}O_4$ requires C, 67·2; H, 5·2%). The acid decomposed in a few days at room temperature. The acid (3 g.) was heated at 140—150° for 2·5 hr. and the brown sintered mass thoroughly extracted with light petroleum (b. p. 40—60°), to give crude hept-6-en-4-ynoic acid (0·80 g.) which after repeated crystallisation from light petroleum had m. p. and mixed m. p. 57°.

Hex-5-en-3-yn-1-ol.—By the procedure of *Inorg. Synth.*, 1946, **2**, 128, sodamide was prepared from sodium (4·5 g.) in liquid ammonia (250 ml.), and cooled vinylacetylene (9·5 g.) added all at once in a little ether. After 40 minutes' stirring ethylene oxide (20 ml.) was added and stirring continued for 48 hr. After a further 36 hr. ether and ammonium chloride were added, followed by water. After thorough ether-extraction the extracts were washed, dried (Na_2SO_4), and distilled, to give *hex-5-en-3-yn-1-ol* (2·7 g.), b. p. 73—81°/12 mm., n_D^{20} 1·4975—1·4980 (Found : C, 74·95; H, 8·55. C_6H_8O requires C, 75·0; H, 8·4%). Microhydrogenation : 3·1 mols. uptake. Light absorption : max. at 226 mμ (ε 11,700).

cis-*Pent-2-ene-1 : 5-diol.*—On a 1-molar scale pent-2-yne-1 : 5-diol was hydrogenated in ethyl acetate at room temperature and atmospheric pressure over 5% palladised barium sulphate or palladised calcium carbonate until 1 mol. of hydrogen was absorbed. Filtration and distillation then gave *cis*-pent-2-ene-1 : 5-diol, b. p. 84°/0·1 mm., 91—92°/0·4 mm., n_D^{20} 1·4763—1·4769, in 80—85% yield.

cis-*Pent-2-ene-1 : 5-diol " Ditoluene-*p*-sulphonate."*—By the procedure used to prepare pent-2-yne-1 : 5-diol ditoluene-*p*-sulphonate (p. 131), *cis*-pent-2-ene-1 : 5-diol (10·2 g., 0·1 mole) was converted into a " ditoluene-*p*-sulphonate "(21 g.), obtained as an oil (Found: C, 54·5; H, 6·2; S, 13·6. $C_{19}H_{22}O_6S_2$ requires C, 55·6; H, 5·35; H, 5·35; S, 15·6. $C_{12}H_{16}O_4S$ requires C, 56·25; H, 6·25; S, 12·5%). This crude " ditoluene-*p*-sulphonate " was used in the following experiments.

(*g*) " Ditoluene-*p*-sulphonate " from 0·1 mole of diol was added to ethyl sodioacetoacetate

(0·08 mole) at 50—55° and the reaction completed at this temperature. Then, proceeding as in (*d*), distillation finally gave 4-acetyl*cyclo*hexene (1·33 g., 11% overall yield from diol), b. p. 69—74°/17 mm., which was converted into the semicarbazone and this was recrystallised from ethanol (Found : C, 59·8; H, 8·4. Calc. for $C_9H_{13}ON_3$: C, 59·7; H, 8·35%). Regeneration from the semicarbazone with hot aqueous oxalic acid gave pure 4-acetyl*cyclo*hexene (Found : C, 76·7; H, 9·8. Calc. for $C_8H_{12}O$: C, 77·35; H, 9·75%). The *p*-nitrophenylhydrazone formed yellow needles from ethanol (Found : C, 64·4; H, 6·8. Calc. for $C_{14}H_{17}O_2N_3$: C, 64·8; H, 6·6%), and the 2 : 4-*dinitrophenylhydrazone* orange-red laths (Found : C, 55·5, 55·3; H, 5·55, 5·75; N, 18·65. $C_{14}H_{16}O_4N_4$ requires C, 55·3; H, 5·3; N, 18·4%). For physical properties of the ketone and its derivatives see Table (p. 129).

On hydrogenation in ethyl acetate over 5% palladised barium sulphate 4-acetyl*cyclo*hexene (220 mg.) absorbed 1·0 mol. of hydrogen in 5 min.

In another condensation on the same scale but with 0·1 mole of ethyl sodioacetoacetate and isolation by ether-extraction after decarboxylation, distillation gave 4-acetyl*cyclo*hexene (2·21 g., 18% overall yield from diol), b. p. 64—70°/7 mm., n_D^{20} 1·4675—1·4682, and *cis*-8-hydroxyoct-5-en-2-one (1·06 g., 7·5% overall yield from diol), b. p. 88—93°/0·07 mm., n_D^{20} 1·466—1·467.

cis-*Pent*-2-*ene*-1 : 5-*diol* " *Monotoluene*-p-*sulphonate*."—By the procedure used to prepare pent-2-yne-1 : 5-diol monotoluene-*p*-sulphonate (p. 131), *cis*-pent-2-ene-1 : 5-diol (20·4 g., 0·2 mole) was converted into a " monotoluene-*p*-sulphonate " (24 g.), obtained as in an oil. This crude " monotoluene-*p*-sulphonate " was used in the following experiments.

(*h*) " Monotoluene-*p*-sulphonate " from 0·2 mole of diol was caused to react with ethyl sodioacetoacetate (0·09 mole) as in (*f*). Continuing as in (*f*), distillation finally gave 4-acetyl*cyclo*hexene (1·67 g., 7% overall yield from diol), b. p. 72—73°/13 mm., n_D^{20} 1·469, and cis-8-*hydroxyoct*-5-*en*-2-*one* (1·57 g., 6% overall yield from diol), b. p. 93—96°/0·08 mm., n_D^{20} 1·465—1·469, mainly 1·4684 (Found : C, 67·9; H, 10·25. $C_8H_{14}O_2$ requires C, 67·6; H, 9·9%). A semicarbazone of *cis*-8-hydroxyoct-5-en-2-one could not be obtained; the 2 : 4-*dinitrophenylhydrazone*, formed in only poor yield, was sparingly soluble in ethanol but, crystallised from ethyl acetate, had m. p. 203—204·5° (Found : C, 52·8; H, 5·2. $C_{14}H_{18}O_5N_4$ requires C, 52·2; H, 5·6%). The 4-acetyl*cyclo*hexene formed a semicarbazone, m. p. and mixed m. p. 169°.

8-Hydroxyoct-5-yn-2-one (4·20 g.) was hydrogenated in ethyl acetate over 5% palladised barium sulphate (0·25 g.). Uptake was interrupted when 1 mol. of hydrogen had been absorbed although no change in rate was observed. Filtration and distillation then gave *cis*-8-hydroxyoct-5-en-2-one (3·32 g., 78%), b. p. 85—88°/0·03 mm. (mainly 86°), n_D^{20} 1·468—1·469.

cis-*Octa*-5 : 7-*dien*-2-*one*.—By the procedure for the conversion of 8-hydroxyoct-5-yn-2-one into oct-7-en-5-yn-2-one, *cis*-8-hydroxyoct-5-en-2-one (3·58 g.) was converted into the crude toluene-*p*-sulphonate (5·1 g.) and to it sodium ethoxide (from sodium, 0·69 g.) in ethanol (25 ml.) was added. Then, proceeding as in (*a*), distillation finally gave (i) cis-*octa*-5 : 7-*dien*-2-*one* (0·34 g., 16% overall yield from hydroxy-ketone), b. p. 78—82°/9 mm., 70—72°/6 mm. on redistillation, n_D^{20} 1·470, 1·473 after redistillation (Found : C, 76·65; H, 9·6. $C_8H_{12}O$ requires C, 77·4; H, 9·75%), and (ii) cis-8-*ethoxyoct*-5-*en*-2-*one* (0·60 g., 21% overall yield from the hydroxy-ketone), b. p. 109—112°/7 mm., 106—107°/7 mm. on redistillation, n_D^{20} 1·451—1·448, 1·446 after redistillation (Found : C, 70·7; H, 10·65. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·65%).

The infrared spectrum of *cis*-octa-5 : 7-dien-2-one was identical with that of a specimen obtained by another route (Part XI), except for a small band at 1106 cm.$^{-1}$ due to a trace of *cis*-8-ethoxyoct-5-en-2-one. The semicarbazone of *cis*-oct-5 : 7-dien-2-one crystallised from aqueous ethanol as plates, m. p. 115·0—115·5°, and the 2 : 4-dinitrophenylhydrazone, purified by crystallisation from ethanol, had m. p. 52·5—53·5°. These derivatives were identical (mixed m. p.) with those described in Part XI, where analytical data will be given.

The *semicarbazone* of *cis*-8-ethoxyoct-5-en-2-one crystallised from aqueous ethanol as plates, m. p. 98° (Found : C, 57·8; H, 9·4. $C_{11}H_{21}O_2N_3$ requires C, 58·1; H, 9·3%).

cis-*Hex*-2-*ene*-1 : 6-*diol*.—Tetrahydrofurfuryl alcohol was converted into tetrahydrofurfuryl chloride on a 6-mole scale by the procedure of *Org. Synth.* (1945, **25**, 84) in 58—78% yield and thence into pent-4-yn-1-ol on a 2-molar scale by a procedure similar to that of Eglington, Jones, and Whiting (*J.*, 1952, 2873; Stokes, unpublished work) in up to 85% yield. In the latter stage, when technical instead of pure dry ammonium chloride was used to decompose the sodium salts, the yield of pent-4-yn-1-ol dropped considerably. Even so this ring scission with sodamide in liquid ammonia is erratic and one run gave pent-4-en-1-ol (75%), b. p. 47—50°/11 mm., n_D^{20} 1·4322, as the product perhaps owing to incomplete conversion of the sodium into sodamide.

By the procedure used for pent-2-yne-1 : 5-diol (p. 131), on a 0·5—2·0-molar scale and with a reaction time of 24 hr. at 100°, pent-4-yn-1-ol was converted into hex-2-yne-1 : 6-diol, b. p.

131°/0·65 mm., 115°/0·1 mm., n_D^{20} 1·487 (Found, C, 62·7; H, 8·85. Calc. for $C_6H_{10}O_2$: C, 63·1; H, 8·85%), in up to 41% yield. Hex-2-yne-1 : 6-diol has since been prepared in a similar way by Paul and Tchelitcheff (*Bull. Soc. chim. France*, 1953, 417). The yield of diol appeared to decrease with increase in the scale of preparation. Hydrogenation of hex-2-yne-1 : 6-diol in ethyl acetate over 5% palladised barium sulphate on a 0·5-molar scale then gave cis-*hex*-2-*ene*-1 : 6-*diol* (up to 85%), b. p. 108°/0·25 mm., 89°/0·06 mm., n_D^{20} 1·473—1·476 (Found : C, 62·0; H, 10·6. $C_6H_{14}O_2$ requires C, 62·0; H, 10·4%). No crystalline derivatives could be obtained from this diol.

By the procedure used for pent-2-yne-1 : 5-diol, *cis*-hex-2-ene-1 : 6-diol (1 mol.) and toluene-*p*-sulphonyl chloride (2 mol.) in acetone were treated with aqueous potassium hydroxide to give an oil, considered to be a mixture of the mono- and di-toluene-*p*-sulphonate, from which no more than a trace of crystals could be isolated.

cis-1 : 6-*Dibromohex*-2-*ene*.—No dibromide was obtained by reaction of *cis*-hex-2-ene-1 : 6-diol with phosphorus tribromide at 0—20° in either the presence or absence of pyridine, or with 48% hydrobromic acid and cuprous bromide. A little dibromide (up to 12% yield) was obtained with 48% hydrobromic acid and sulphuric or toluene-*p*-sulphonic acid.

A satisfactory product was obtained by addition of phosphorus tribromide (27 g.) to a vigorously stirred suspension of *cis*-hex-2-ene-1 : 6-diol (11·6 g.) in benzene (100 ml.) at room temperature during 1 hr. Iced water was then added and the benzene layer separated, washed, and evaporated under reduced pressure without heating, to give cis-1 : 6-*dibromohex*-2-*ene* (15 g., 65%), n_D^{20} 1·527 (Found : Br, 63·0. $C_6H_{10}Br_2$ requires Br, 66·0%). Decomposition invariably ensued on attempted distillation.

cis-*Hept*-2-*ene*-1 : 7-*diol*.—The following preparation of tetrahydropyranylmethyl chloride devised by Mr. B. J. Stokes was preferred to that of Eglington, Jones, and Whiting (*loc. cit.*) : Thionyl chloride (130 g.) was added during 30 min. to a stirred mixture of tetrahydropyranylmethanol (116 g.) and pure pyridine (113 g.) heated in an oil-bath at 135°. After a further 2 hours' heating the cooled pasty mass was repeatedly extracted with ether. The combined ether extracts were washed, dried, and distilled, to give tetrahydropyranylmethyl chloride (up to 68%), b. p. 56—57°/15 mm., n_D^{20} 1·4617 (Found : C, 53·6; H, 8·4. Calc. for $C_6H_{11}OCl$: C, 53·6; H, 8·3%). Eglington, Jones, and Whiting obtained a 48% yield by reaction at 0° during 16 hr. Ring scission of tetrahydropyranylmethyl chloride by a procedure similar to that of these authors (*loc. cit.*; Stokes, unpublished work) on a 1-molar scale gave hex-5-yn-1-ol, b. p. 73—75°/15 mm., n_D^{20} 1·4502, in 88% yield.

By the procedure used for hex-2-yne-1 : 6-diol and on a 0·5-molar scale, hex-5-yn-1-ol was converted into *hept*-2-*yne*-1 : 7-*diol* (38%, one experiment only), b. p. 133°/1·0 mm., 105°/0·05 mm., n_D^{20} 1·4827 (Found : C, 64·45; H, 9·15. $C_7H_{12}O_2$ requires C, 65·5; H, 9·4%).

Hept-2-yne-1 : 7-diol (5·9 g.) was hydrogenated in methanol over 5% palladised barium sulphate (0·2 g.) until 0·98 mol. of hydrogen was absorbed. Interruption of the hydrogenation, filtration, and distillation then gave cis-*hept*-2-*ene*-1 : 7-*diol* (4·7 g., 81%), b. p. 105—106°/0·25 mm., n_D^{20} 1·4708 (Found : C, 64·2; H, 11·0. $C_7H_{14}O_2$ requires C, 64·6; H, 10·8%).

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Imperial College of Science and Technology,
South Kensington, S.W.7 (L. C.).
King's College (University of London),
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