

786. *Studies in the Polyene Series. Part XLIV.* The Preparation of Oct-4-ene-2 : 7-dione and Octa-3 : 5-diene-2 : 7-dione, Intermediates for the Synthesis of Carotenoids. The Anionotropic Rearrangement of Some Hexa-2 : 5-diene-1 : 4-diols.*

By R. AHMAD, F. SONDHEIMER, B. C. L. WEEDON, and R. J. WOODS.

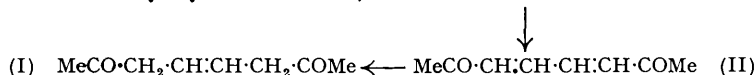
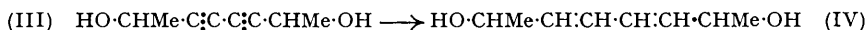
Routes to oct-4-ene-2 : 7-dione (I) and octa-3 : 5-diene-2 : 7-dione (II) from readily available materials have been developed. The diketone (II) is most conveniently prepared from octa-3 : 5-diyne-2 : 7-diol (III) by a two-stage process giving an overall yield of 40%.

Anionotropic rearrangement of the hexa-2 : 5-diene-1 : 4-diols (XII; R¹ = H, R² = Me and Prⁿ; R¹ = R² = Me) gives mixtures of conjugated diene 1 : 2- and 1 : 6-glycols, the former predominating.

THE investigations described in this paper were undertaken to develop routes to oct-4-ene-2 : 7-dione (I) and octa-3 : 5-diene-2 : 7-dione (II), neither of which had been described when this work was initiated. These diketones, possessing carbon skeletons identical with that of the central portion of β -carotene, offered promise as intermediates for the synthesis of various carotenoids. This view has recently been substantiated by the elegant syntheses from (I) of β -carotene, lycopene, and other polyene hydrocarbons by the Karrer and the Inhoffen school (Karrer and Eugster, *Helv. Chim. Acta*, 1950, **33**, 1172, 1952; 1951, **34**, 28, 1805; Karrer, Eugster, and Tobler, *ibid.*, 1950, **33**, 1349; Karrer, Eugster, and Faust, *ibid.*, 1951, **34**, 823; Inhoffen, Pommer, and Bohlmann, *Annalen*, 1950, **569**, 237; Inhoffen, Pommer, and Westphal, *ibid.*, 1950, **570**, 69; cf. Milas, Davis, Belič, and Fleš, *J. Amer. Chem. Soc.*, 1950, **72**, 4844).

Karrer and Eugster (*Helv. Chim. Acta*, 1949, **32**, 1934; cf. Karrer, Eugster, and Perl, *ibid.*, p. 1013) condensed glyoxal with acetoacetic acid to give (II), in \approx 4% yields, and then reduced (II) to (I) with zinc and acetic acid in pyridine in 70–75% yield; conditions for the initial condensation were stated to be highly critical. This publication led two of us (Sondheimer and Weedon, *Nature*, 1950, **165**, 483) to give a preliminary account of the preparation of (I) and (II), in 15 and 2% yields, respectively, by the action of dimethylcadmium on the acid chlorides of dihydromuconic and muconic acids, the dihydromuconic acid being conveniently prepared from butadiene *via* 1 : 4-dibromo- and 1 : 4-dicyano-but-2-ene (see p. 4092).

Later Inhoffen, Pommer, Winkelmann, and Aldag (*Chem. Ber.*, 1951, **84**, 87) hydrogenated, by a poisoned palladium catalyst, the readily available diacetylenic glycol (III) (Bowden, Heilbron, Jones, and Sargent, *J.*, 1947, 1579; Armitage, Jones, and Whiting, *J.*, 1951, 44) to a mixture which with *tert.*-butyl chromate (cf. Oppenauer, *Anal. Asoc. Quim. Argentina*, 1949, **37**, 246) gave (II) in 5% overall yield. The intermediate glycol (IV) was isolated as a crystalline solid, m. p. 100°, after regeneration from the dibenzoate, m. p. 140°.



The yields in all published methods for the preparation of (I) and (II) leave much to be desired, but a convenient method for the conversion of (III) into (II) in 40% overall yield has now been devised.

Reduction, with lithium aluminium hydride, of alcohols $\text{>C}\cdot\overset{\downarrow}{\text{C}}\cdot\text{C}\cdot\overset{\leftarrow}{\text{C}}\cdot\text{OH}$ to the corresponding diene alcohols (Chanley and Sobotka, *J. Amer. Chem. Soc.*, 1949, **71**, 4140; Raphael and Sondheimer, *J.*, 1950, 3185; Bharucha and Weedon, forthcoming publication) and of 2 : 7-dimethylocta-3 : 5-diyne-2 : 7-diol to the diene glycol (Professor E. R. H. Jones and Dr. M. C. Whiting, personal communication) suggested the use of this reagent. Treat-

* Part XLIII, *J.*, 1952, 2657.

ment of (III) with 1.3 mol. proportions of lithium aluminium hydride gave an oil (74%) which was estimated by light-absorption data to contain 64% of the required glycol (IV). By increasing the proportion of hydride to 3.5 mols., the purity of the product was raised to 83% but the yield was only 41%. Since the crude glycol can be oxidised to the diketone (II) almost quantitatively (see below), the former procedure is much preferred. After regeneration from its dibenzoate, m. p. 80°, the diunsaturated glycol (IV) was obtained as a solid of m. p. 45°. These melting points vary greatly from those of the products reported by Inhoffen *et al.*, a fact which may be ascribed to a difference in configuration about the double bonds. Whereas catalytic hydrogenation, employed by the German workers, would be expected to give mainly a *cis-cis*-diene (cf. Campbell and Campbell, *Chem. Reviews*, 1942, **31**, 148; Inhoffen, Bohlmann, Aldag, Bork, and Leibner, *Annalen*, 1951, **573**, 1; Bohlmann, *Chem. Ber.*, 1951, **84**, 545), reduction with lithium aluminium hydride probably gives the *trans-trans*-isomer since reduction of but-2-yn-1-ol with this reagent yields *trans*-crotyl alcohol (Bharucha and Weedon, *loc. cit.*).

Further support for the *trans-trans*-configuration of the glycol, m. p. 45°, comes from a consideration of its ultra-violet absorption properties and those of the *cis*- and the *trans*-form of hexa-3 : 5-dien-2-ol and piperylene (see Table 1). In piperylene no steric inhibition

TABLE 1.

	$\lambda_{\max.}, \text{\AA}$	$\epsilon_{\max.}$		$\lambda_{\max.}, \text{\AA}$	$\epsilon_{\max.}$
HO-CHMe-CH:CH-CH:CH-CHMe-OH	2270	32,000	CHMe-CH-CH:CH ₂ (<i>trans</i>) ³	2235	23,000
	2340 *	24,500	CHMe-CH-CH:CH ₂ (<i>cis</i>) ²	2230	22,600
HO-CHMe-CH:CH-CH:CH ₂ (<i>trans</i>) ¹ ...	2230	28,000	CHMe-CH-CH:CHMe ³ ...	2270	22,500
HO-CHMe-CH:CH-CH:CH ₂ (<i>cis</i>) ²	2240	20,000			

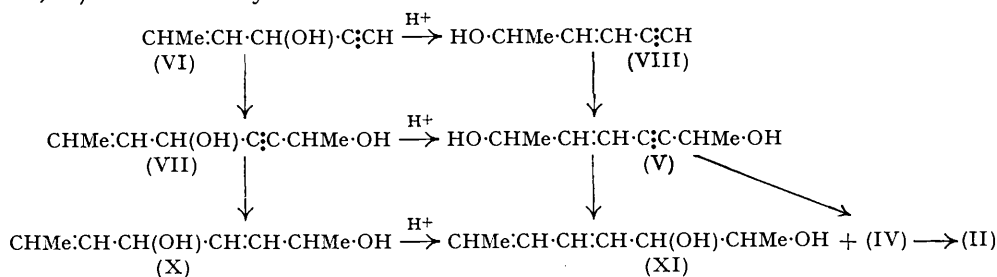
* Inflection. ¹ Heilbron, Jones, McCombie, and Weedon, *J.*, 1945, **88**. ² Braude and Coles, *J.*, 1951, 2085. ³ Booker, Evans, and Gillam, *J.*, 1940, 1453.

of coplanarity occurs in either the *cis*- or the *trans*-form, and the absorption of the two geometrical isomers is therefore identical. With the hexadienols, however, the intensity for the *cis*-form is reduced below that for piperylene and 1 : 4-dimethylbutadiene by steric interference between the CHMe-OH and the CH:CH₂ group (Braude and Coles, *J.*, 1951, 2085). A similar, or more pronounced, reduction would be expected with (IV) if this possessed a configuration other than *trans-trans*. The intensification which is actually observed with the glycol, m. p. 45°, may be attributed to the larger hyperconjugative properties of the C-OH compared with the C-H group, an effect noted previously with *trans*-hexa-3 : 5-dien-2-ol (*idem, loc. cit.*) and other ethylenic alcohols (Braude and Timmons, *J.*, 1950, 2000, 2007).

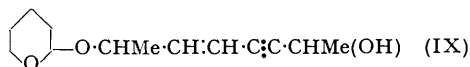
Independently of this work, the reduction with lithium aluminium hydride of (III), and other diacetylenic glycols, has been studied by the Manchester school (Bates, Jones, and Whiting, forthcoming publication). By using 4 mols. of hydride an oil was obtained in 45% yield which exhibited light-absorption properties similar to those observed in the present investigation for the 83%-pure diene glycol. The crystalline diene glycols obtained by similar reduction of some other diacetylenic glycols were shown by infra-red absorption measurements to possess a *trans-trans*-configuration.

Attention was next directed to the oxidation of the glycol (IV) to the required diketone (II). Of the methods studied by Inhoffen *et al.* (*loc. cit.*) only that using *tert.*-butyl chromate proved successful and gave the diketone in 13% yield from the crystalline glycol (IV), m. p. 100°. Oxidation of the glycol (IV), m. p. 45°, by shaking it with manganese dioxide in acetone (cf. Bharucha and Weedon, *loc. cit.*; Woods and Weedon, *J.*, 1951, 2687) gave the crystalline diketone (II) in 70% yield. A more valuable procedure, however, was oxidation of the crude reduction product of (III), containing *ca.* 64% of (IV), without isolation of the crystalline diene glycol. In this way (II) was obtained in 91% yield [based on the estimated content of (IV)], *i.e.*, in 35% overall yield from (III). Similar oxidation of the crude product formed by catalytic hydrogenation of (III) according to Inhoffen *et al.* (*loc. cit.*) gave (II) in 4% overall yield. Reduction of (II) by Karrer and Eugster's method (*loc. cit.*) gave crystalline (I) (80%) identical with that prepared from dihydro-muconic acid.

The diketone (II) has also been prepared *via* the glycol (V). Reaction of the Grignard complex of the readily available hex-4-en-1-yn-3-ol (VI) (Heilbron, Jones, and Weedon, *J.*, 1945, 81) with acetaldehyde led to the glycol (VII) in 70% yield. This, on treatment with dilute sulphuric acid, underwent anionotropic rearrangement to (V) which was also obtained in 70% yield from hex-3-en-5-yn-2-ol (VIII) (Heilbron, Jones, Smith, and Weedon, *J.*, 1946, 54) and acetaldehyde.



Selective partial reduction of (V) to (IV) proved more difficult than that of (III). By both catalytic hydrogenation, a partly poisoned palladium catalyst being used, and reduction with lithium aluminium hydride, mixtures of glycols were formed which on oxidation (manganese dioxide) furnished the diketone (II) in 14 and 8% yields, respectively [based on (V)]. While (IX) on treatment with lithium aluminium hydride gave the corresponding



diene (73%), conversion of the latter into (II) could be accomplished in poor yield only.

The partial hydrogenation of (VII) to (X), and the anionotropic rearrangement of the latter, were also examined as a route to (IV). Although the partial reduction of acetylenic 1:4-glycols has been investigated extensively by Zal'kind and others (for review see Johnson, "Acetylenic Compounds," Vol. I, Ed. Arnold & Co., London, 1946), few examples containing an alkenyl substituent have previously been reported. As with (VI) and related compounds (Heilbron, Jones, McCombie, and Weedon, *J.*, 1945, 84), partial hydrogenation of the triple bond in (VII) proceeded smoothly, in ethyl acetate solution with a 0.3% palladium-calcium carbonate catalyst, to give (X) in 90% yield.

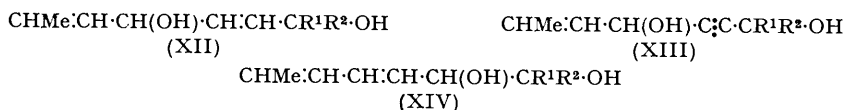
Anionotropic rearrangement of (X) occurred on treatment with 0.2% sulphuric acid for 1.5 hours giving, in almost quantitative yield, an oil which exhibited high-intensity light absorption in the 2230-Å region. The product, however, consisted of a mixture of the fully conjugated isomers (IV) and (XI), the latter predominating, which on oxidation (manganese dioxide) gave the diketone (II) in *ca.* 7% yield. Periodate oxidation of the mixture caused fission of the α -glycol to acetaldehyde and sorbaldehyde, the yield of the latter (as the semicarbazone) indicating that the initial mixture contained at least 50% of (XI). Catalytic hydrogenation of the rearranged glycols furnished a mixture of octane-2:7- and -2:3-diol, containing at least 60% of the former (periodate titration), which on oxidation with chromic acid yielded octane-2:7-dione (20%).

Under the conditions employed for the isomerisation of (X), conversion of the symmetrical glycol (IV) into the α -glycol (XI) occurred to only a small extent (<2%). The initial rearrangement of (X) therefore gives mainly (XI) rather than (IV) which would be the thermodynamically more stable product in view of the strong hyperconjugative effects of the C-OH groups. Isomerisation of (X) under more vigorous conditions was accompanied by extensive polymerisation but the composition of the resulting mixture of glycols showed no marked change.

Previous investigations of the rearrangement of unsymmetrical dialkenylcarbinols show that the hydroxyl group migrates initially to the γ -carbon atom at which electron accession is greatest (Heilbron, Jones, McCombie, and Weedon, *J.*, 1945, 84; Braude and Timmons, *J.*, 1950, 2007, Braude and Coles, *J.*, 1950, 2014). This principle seems inadequate, however, to account for the formation mainly of (XI) on isomerisation of (X), since the dissociation

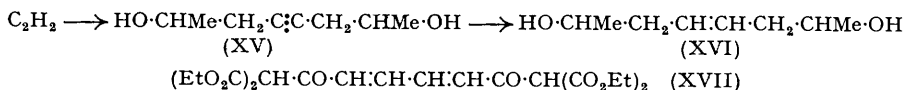
constants of acetic acid (1.75×10^{-5}) and lactic acid (1.38×10^{-4}) indicate that the electron-releasing properties of the methyl group are greater than those of CHMe·OH. Furthermore electronic interaction (hyperconjugation) between the CHMe·OH group and the adjacent double bond would be expected to take place by way of contributions to the resonance hybrid of forms such as $-\text{CH}:\overset{+}{\text{C}}\text{H}\cdot\overset{-}{\text{C}}\text{HMe}\cdot\overset{-}{\text{O}}\text{H}$ and $-\overset{+}{\text{C}}\text{H}:\text{CH}:\overset{-}{\text{C}}\text{HMe}\cdot\overset{-}{\text{O}}\text{H}$, which again would not favour α -glycol formation. A possible explanation is that a cyclic intermediate is involved (cf. Braude and Coles, *J.*, 1951, 2085); the *cis*-configuration of the double bond in (X) introduced by catalytic hydrogenation may then be a determining factor. This and other aspects of the reaction will be investigated as opportunity permits.

The novel formation of an α -glycol by isomerisation of an ethylenic 1 : 4-glycol has been further exemplified by rearrangement of (XII; $\text{R}^1 = \text{R}^2 = \text{Me}$) and (XII; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Pr}^n$), prepared in 90 and 65% yields, respectively, by partial hydrogenation of the corresponding acetylenic glycols (XIII). The presence of the α -glycols (XIV) in the



rearranged products was established by treatment with periodate and isolation of sorbaldehyde. In the conversion of the acetylenic glycols into sorbaldehyde the isolation of the intermediates may be omitted. Thus sorbaldehyde (as the semicarbazone) was obtained from (XIII; $\text{R}^1 = \text{R}^2 = \text{Me}$) and (XIII; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Pr}^n$) in 25 and 82% overall yields, respectively.

Other routes examined did not lead to (I) and (II). The acetylenic glycol (XV) was prepared from propylene oxide and the Grignard complex of both acetylene and pent-4-yn-2-ol and on catalytic hydrogenation gave (XVI). The latter could not, however, be oxidised to (I).



Condensation of muconyl chloride with ethyl malonate readily gave (XVII), which had light-absorption properties indicating that it existed in the dienolic form. Attempts to convert this tetra-ester into (II) by hydrolysis and decarboxylation were unsuccessful, only muconic acid being isolated. This result is in keeping with the recently reported behaviour of related β -ketomalonates (Eisner, Elvidge, and Linstead, *J.*, 1951, 1501).

EXPERIMENTAL

M.p.s are uncorrected. Light-absorption data were determined in ethanol.

Commercial lithium aluminium hydride (*ca.* 80% pure) was used without purification.

For the oxidation experiments manganese dioxide was selected from various commercial sources (cf. Weedon and Woods, *J.*, 1951, 2687). Acetone was treated with potassium permanganate and dried (K_2CO_3). Unless stated otherwise, oxidations of (IV) were performed by shaking a solution of the crude distilled product in acetone (100 vols.) with manganese dioxide (20 parts by weight) at room temperature.

All chromatograms were carried out on alumina (Grade II—III; cf. Brockmann and Schodder, *Ber.*, 1941, 74, 73) which had been pretreated as described in Part XXXV (*J.*, 1949, 3120).

Syntheses from Dihydromuconic and Muconic Acids.— Δ^{β} -Dihydromuconic acid. A mixture of 1 : 4-dibromobut-2-ene (360 g.), acetonitrile (720 c.c.; technical), and cuprous cyanide (360 g.) was heated under reflux (steam-bath) until reaction commenced, then cooled (ice-bath; until the vigorous reaction had subsided), and finally heated under reflux for 1 hour, again cooled, and, when cuprous bromide began to separate, poured into ether. The suspension was filtered and the filtrate evaporated, giving a mixture (*ca.* 130 g.) of 1 : 2 : 3 : 4-tetrabromobutane and 1 : 4-dicyanobut-2-ene. This was added to concentrated hydrochloric acid (750 c.c.), and the mixture was boiled for 3 hours whereupon the tetrabromide steam-distilled and collected in the condenser.

The clear red acid solution was cooled in ice; Δ^{β} -dihydromuconic acid (76 g.) which separated had m. p. 193—194°, raised to 195° by one recrystallisation from water (Bode, *Annalen*, 1889, 256, 26, gives m. p. 195°).

In one experiment (from 80 g. of dibromobutene) the crude dinitrile was crystallised from benzene-light petroleum (b. p. 40—60°), giving 1 : 4-dicyanobut-2-ene (20 g., 50%) as needles, m. p. 76—77° (Hager, U.S.P. 2,462,388, gives m. p. 75—77°).

Oct-4-ene-2 : 7-dione. Dihydromuconic acid (40 g.) and thionyl chloride (240 c.c.), heated under reflux for 4 hours, gave dihydromuconyl chloride (47 g.), b. p. 83—84°/10⁻³ mm., n_D^{20} 1.4920.

Powdered cadmium chloride (20 g.; dried by heating it just below the m. p. for 20 minutes) was added in several portions to a stirred solution of methylmagnesium bromide (from 4.5 g. of magnesium) in ether (150 c.c.), and the suspension was heated under reflux for $\frac{1}{2}$ hour. (A small portion gave no colour with the Gilman reagent, indicating complete conversion of the Grignard complex into dimethylcadmium; cf. Cason, *Chem. Reviews*, 1947, 40, 15.) The ether was then distilled off and benzene (140 c.c.) was added. The above acid chloride (4.7 g.) in benzene (20 c.c.) was added dropwise, and the mixture was heated under reflux for 1 hour and then cooled (ice-bath). Dilute sulphuric acid was added, and the benzene layer was separated, washed with sodium hydrogen carbonate solution, dried, and evaporated under reduced pressure. A portion (1.6 g.) of the residue (2.0 g.) was distilled and the fraction (0.6 g.), b. p. 75—85°/10⁻³ mm., was collected; on cooling this solidified. Two crystallisations from light petroleum (b. p. 60—80°) gave oct-4-ene-2 : 7-dione as plates, m. p. 35—36° (Found: C, 68.4; H, 9.0. Calc. for C₈H₁₂O₂: C, 68.55; H, 8.65%) (Karrer and Eugster, *Helv. Chim. Acta*, 1949, 32, 1934, give m. p. 31°). The *bis-2 : 4-dinitrophenylhydrazone* crystallised from nitromethane in orange plates, m. p. 208—209° (Found: C, 48.1; H, 4.15; N, 22.55. C₂₀H₂₀O₈N₈ requires C, 48.0; H, 4.05; N, 22.4%).

In some experiments under conditions nearly identical with those described above, the diketone was obtained admixed with polymer and varying amounts of 2 : 7-dimethyloct-4-ene-2 : 7-diol. The latter crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 86° (Found: C, 69.4; H, 11.4. C₁₀H₂₀O₂ requires C, 69.7; H, 11.7%). Hydrogenation of this in ethyl acetate in the presence of Adams's catalyst gave 2 : 7-dimethyloctane-2 : 7-diol which crystallised from ether-light petroleum (b. p. 40—60°) in needles, m. p. 92—93°, and from water in plates, m. p. 58—59° (Zal'kind and Aizikovitch, *J. Gen. Chem., Russia*, 1937, 7, 227, give m. p. 88—89°, from light petroleum, and 57—59°, from water). The formation of a tertiary alcohol on reaction of an acid chloride with dimethylcadmium has also been reported by Pinson and Friess (*J. Amer. Chem. Soc.*, 1950, 72, 5333).

Octa-3 : 5-diene-2 : 7-dione. A mixture of muconic acid (7.1 g.) (Guha and Sankaran, *Org. Synth.*, 1946, 26, 57) and thionyl chloride (45 c.c.) was heated under reflux for 25 hours. The resulting solution was evaporated under reduced pressure, giving crude muconyl chloride (cf. Bailey and Ross, *J. Amer. Chem. Soc.*, 1949, 71, 2570). A solution of this in benzene (30 c.c.) was added to dimethylcadmium (from 4.9 g. of magnesium and 19.6 g. of cadmium chloride) in benzene (175 c.c.). The mixture was heated to ca. 60° for 1 hour and then cooled. Sulphuric acid (2N) was added and the crude product (4.6 g.) was isolated and distilled. The fraction, b. p. <80°/10⁻² mm., partly solidified. Recrystallisation from light petroleum (b. p. 60—80°) gave octa-3 : 5-diene-2 : 7-dione (100 mg.) as needles, m. p. 126—127°. Light absorption: max., 2720 and 2790 Å; ϵ , 31,000 and 32,000, respectively (Karrer, Eugster, and Perl, *Helv. Chim. Acta*, 1949, 32, 1013, give m. p. 126—126.5°; max., 2760 Å; ϵ , 33,000).

Ethyl 2 : 7-diketo-octa-3 : 5-diene-1 : 1 : 8 : 8-tetracarboxylate. Muconyl chloride (3.75 g.) in ether (50 c.c.) was added during 20 minutes to a stirred solution of sodiomalonate (from 3 g. of sodium and 30 c.c. of ethyl malonate) in ether (300 c.c.). The mixture was heated under reflux for 1.5 hours and then cooled. Sulphuric acid (2N) was added and the ethereal layer was separated, washed with sodium hydrogen carbonate solution, dried, and evaporated. The residue was triturated with light petroleum (b. p. 40—60°). The solid (6.1 g.), m. p. 124—128°, was recrystallised from alcohol, giving the *tetraester* as long yellow needles (5.1 g.), m. p. 132° (Found: C, 56.35; H, 6.25. C₂₀H₂₆O₁₀ requires C, 56.3; H, 6.15%). Light absorption: max., 3550 Å; ϵ , 51,000; inflexion, 3620 Å; ϵ , 45,000.

Syntheses from Octa-3 : 5-diyne-2 : 7-diol.—*Octa-3 : 5-diene-2 : 7-diol.* Octa-3 : 5-diyne-2 : 7-diol (10.0 g.; mixture of stereoisomers) (Bowden, Heilbron, Jones, and Sargent, *J.*, 1947, 1578) in ether (100 c.c.) was added during 45 minutes to a stirred solution of lithium aluminium hydride (4.5 g.) in ether (600 c.c.). The mixture was heated under reflux for 15 hours and the excess of hydride then destroyed by the addition of ethyl acetate. The mixture was cooled

(0°), a cold solution of ammonium chloride was added, and the ethereal layer was separated, washed with water, and dried (Na_2SO_4). Evaporation of the solvent and distillation of the residue gave the crude glycol as a viscous oil (7.6 g.), b. p. 90—100° (bath temp.)/ 10^{-4} mm., n_D^{25} 1.5085.

Similar reductions of octa-3 : 5-diyne-2 : 7-diol were also performed but with larger proportions of lithium aluminium hydride ; the results are given in the following table.

Mols. of hydride *	1.3	1.7	2.4	2.6	3.5
Product, b. p. 90—100° (bath)/ 10^{-4} mm.; yield, %	74	72	58	50	41
Product, b. p. 90—100° (bath)/ 10^{-4} mm.; octa-3 : 5-diene-2 : 7-diol content, % †	64	—	—	74	83

* Allowance has been made for impurities in the commercial hydride used.

† Estimated on the intensity of the 2270-Å absorption maximum, the pure glycol, m. p. 45°, having $E_{1\text{cm.}}^{1\%} = 2300$. The purity, 64%, for the product obtained by using 1.3 mols. of hydride was subsequently confirmed by oxidation, whereby (II) was isolated in 58% yield (*i.e.*, 91% based on the estimated amount of diene glycol).

The *dibenzoate* (*ca.* 20% yield) crystallised from methanol in needles, m. p. 80° (Found : C, 75.6; H, 6.45. $\text{C}_{22}\text{H}_{22}\text{O}_4$ requires C, 75.5; H, 6.35%). Light absorption : max. 2270 Å ; ϵ , 64,000. A mixture of the dibenzoate (1.0 g.) in benzene (5 c.c.) and methanolic potassium hydroxide (10% w/v; 5 c.c.) was heated under reflux for 10 minutes and then cooled. Water was added and the product isolated with ether, giving an oil, b. p. 90—95° (bath-temp.)/ 10^{-4} mm., which solidified at 0°. Crystallisation from *cyclohexane* gave *octa-3 : 5-diene-2 : 7-diol* (164 mg.) as needles, m. p. 45° (Found : C, 67.3; H, 9.95. $\text{C}_8\text{H}_{14}\text{O}_2$ requires C, 67.5; H, 9.95%). Light absorption : see Table 1.

Octa-3 : 5-diene-2 : 7-dione. (a) A solution of the crystalline 2 : 7-diol (150 mg.) in acetone (15 c.c.) was shaken with manganese dioxide (3 g.) at 20° for 24 hours. The mixture was filtered, the solid was washed thoroughly with acetone, and the combined filtrate and washings were evaporated. Crystallisation of the residue, m. p. 120—122°, from alcohol gave the diketone (106 mg.) as needles, m. p. 124° (Found : C, 69.5; H, 7.5. Calc. for $\text{C}_8\text{H}_{10}\text{O}_2$: C, 69.45; H, 7.3%). Light absorption : max., 2800 Å ; ϵ , 32,000 : inflexion, 2730 Å ; ϵ , 29,500.

Oxidation in the above manner of the liquid glycol (64%-pure) (10.0 g.), without regeneration from the dibenzoate, gave an oil from which the diketone (2.6 g.) separated. Re-oxidation of the residual oil gave more (3.0 g.) diketone. The total yield of crystalline diketone, m. p. 124°, was 58% (based on crude glycol). The bis-semicarbazone had m. p. 249° (Karrer, Eugster, and Perl, *loc. cit.*, give m. p. 249°).

In small-scale experiments (*ca.* 1—3 g. of crude glycol) carried out as described above but by using single reaction periods of 12, 24, and 70 hours, the yields of crystalline diketone were 35, 50, and 50%, respectively.

(b) A solution of the diacetylenic glycol (6.2 g.) in methanol (40 c.c.) was shaken in the presence of palladium-charcoal (0.5 g.; 4% of Pd), partially poisoned by quinoline (*cf.* Isler, Huber, Ronco, and Kofler, *Helv. Chim. Acta*, 1947, **30**, 1911), until 1.6 mols. of hydrogen had been absorbed (*cf.* Inhoffen, Pommer, Winkelmann, and Aldag, *Chem. Ber.*, 1951, **84**, 87). The reaction was interrupted, the catalyst and solvent were removed, and the residue was distilled, giving the crude diene glycol (4.8 g.), b. p. 90—100° (bath-temp.)/ 10^{-4} mm., n_D^{25} 1.4927. Light absorption : max., 2300 Å, $E_{1\text{cm.}}^{1\%}$ 850.

Oxidation (24 hours) of the crude glycol (4.2 g.) gave a dark brown oil (3.8 g.) which was purified by chromatographic adsorption on alumina from benzene solution. The oil (1.3 g.) thus obtained had a light absorption max. at 2750 Å ($E_{1\text{cm.}}^{1\%}$ 700). On cooling, it deposited octa-3 : 5-diene-2 : 7-dione (220 mg.), m. p. 124—126°.

Oct-4-ene-2 : 7-dione.—Octa-3 : 5-diene-2 : 7-dione (4.0 g.), reduced with zinc dust and acetic acid in pyridine by Karrer and Eugster's method (*Helv. Chim. Acta*, 1949, **32**, 1934), gave oct-4-ene-2 : 7-dione (3.2 g.), m. p. 31—32°. The bis-2 : 4-dinitrophenylhydrazone had m. p. 208—209°, undepressed on admixture with the specimen described above.

Syntheses from Oct-6-en-3-yne-2 : 5-diol.—Oct-6-en-3-yne-2 : 5-diol. Ether was displaced from a solution of ethylmagnesium bromide (from 24 g. of magnesium) in ether (400 c.c.) by distillation while benzene (600 c.c.) was added. The solution was cooled in an ice-bath and hex-4-en-1-yn-3-ol (40 g.) in benzene (120 c.c.) was added during $\frac{1}{2}$ hour. The mixture was stirred at 20° for 3 hours and then again cooled in an ice-bath. Acetaldehyde (44 g.) in benzene (100 c.c.) was added during $\frac{1}{2}$ hour. After the mixture had been stirred at 20° for 1 hour, the complex was decomposed by addition of a saturated aqueous solution of ammonium chloride. Isolation of the product gave (i) recovered alcohol (15.0 g.) and (ii) the *glycol* (49.8 g.), b. p. 124°/0.02 mm.

n_D^{20} 1.4960 (Found: C, 68.1; H, 8.6. $C_8H_{12}O_2$ requires C, 68.5; H, 8.65%). The glycol exhibited no light absorption of appreciable intensity in the 2000—4000-Å range.

When the suspension of the Grignard complex of hex-4-en-1-yn-3-ol in benzene was warmed, and the mixture heated to 70° for 1 hour after the addition of acetaldehyde, considerable polymerisation occurred and the yield of glycol was negligible.

Oct-3-en-5-yne-2:7-diol. (a) A solution of oct-6-en-3-yne-2:5-diol (3.9 g.) in sulphuric acid (135 c.c.; 15% wt./vol.) was kept at 20° for 1.5 hours. The solution was then neutralised by the addition of solid sodium hydrogen carbonate, and saturated with ammonium sulphate. The product was extracted with ether. Distillation gave the glycol (3.7 g.), b. p. 85—90° (bath-temp.)/10⁻⁴ mm., n_D^{21} 1.5130 (Found: C, 68.35; H, 8.7. $C_8H_{12}O_2$ requires C, 68.5; H, 8.65%). Light absorption: max., 2280 Å; ϵ , 12,500; inflexion, 2340 Å; ϵ , 9500.

(b) A solution of hex-3-en-5-yn-2-ol (44.0 g.) in benzene (100 c.c.) was added slowly to an ice-cooled solution of ethylmagnesium bromide (from 26.5 g. of magnesium) in benzene (900 c.c.). The solution was stirred for 3 hours at 20° and again cooled to 0°. Acetaldehyde (48.5 g.) in benzene (100 c.c.) was added during $\frac{1}{2}$ hour and the mixture stirred for 2 hours at 20°. Decomposition of the complex and isolation of the product gave (i) recovered alcohol (10.0 g.) and (ii) the glycol (34—39 g.), b. p. 107—110°/10⁻³ mm., b. p. 90° (bath-temp.)/10⁻⁴ mm., n_D^{19} 1.5141. Light absorption: max., 2270 Å; ϵ , 13,500; inflexion, 2350 Å; ϵ , 11,500.

Octa-3:5-diene-2:7-diol and octa-3:5-diene-2:7-dione. (a) A solution of oct-3-en-5-yne-2:7-diol (12.0 g.) in methanol (150 c.c.) was shaken in hydrogen in the presence of palladium-charcoal (1.5 g.; 4% of Pd), partly poisoned by quinoline (cf. Isler, Huber, Ronco, and Kofler, *loc. cit.*) until one mol. had been absorbed (2090 c.c. at 20°/760 mm.). After removal of catalyst and solvent the residue was distilled, giving the crude diene glycol (9.5 g.), b. p. 90—100° (bath-temp.)/10⁻⁴ mm., n_D^{26} 1.4997. Light absorption: max. 2270 Å; $E_{1\text{cm}}^{1\%}$ 700. (In other experiments performed similarly the product had $E_{1\text{cm}}^{1\%}$ up to 1300.)

Oxidation (72 hours) of the crude glycol (3.4 g.) and chromatographic purification of the product (3.4 g.) gave octa-3:5-diene-2:7-dione (180 mg., 5% overall yield), m. p. 124° undepressed on admixture with the above specimen from the diacetylenic glycol (III).

(b) The glycol (1.2 g.) in ethyl acetate (10 c.c.) was partly hydrogenated, giving the impure diene glycol (1.2 g.), b. p. 90—100° (bath-temp.)/10⁻⁴ mm., n_D^{20} 1.4935. Light absorption: max., 2300 Å; $E_{1\text{cm}}^{1\%}$ 1200. Oxidation (24 hours) gave the diketone (190 mg., 14% overall yield), m. p. and mixed m. p. 124—125°.

(c) A solution of oct-3-en-5-yne-2:7-diol (5.0 g.) in ether (50 c.c.) was added during $\frac{1}{2}$ hour to lithium aluminium hydride (1.2 g.) in ether (200 c.c.). The mixture was heated under reflux for 15 hours and then cooled. Isolation of the product gave the crude diene glycol (4.2 g.), b. p. 90—100° (bath-temp.)/10⁻⁴ mm., n_D^{25} 1.5065. Light absorption: max., 2270 Å; $E_{1\text{cm}}^{1\%}$ 1350; inflexion, 2330 Å; $E_{1\text{cm}}^{1\%}$ 1200. Oxidation (48 hours) gave the diketone (315 mg., 8% overall yield), m. p. and mixed m. p. 125°.

7-2'-Tetrahydropyran-5-en-3-yn-2-ol.—A solution of phenyl-lithium (from 1.6 g. of lithium) was added dropwise to a solution of 2-2'-tetrahydropyran-5-en-3-yn-2-ol (20 g.) [prepared from hex-3-en-5-yn-2-ol and dihydropyran (Bharucha and Weedon, *loc. cit.*)] in ether (150 c.c.), and the mixture stirred at 0° for 16 hours. Acetaldehyde (9 g.; freshly distilled) in ether (75 c.c.) was added slowly and the temperature of the mixture allowed to rise to 20° during 8 hours. The mixture was then heated under reflux for 10 minutes and cooled. Decomposition of the complex with ammonium chloride and isolation of the product with ether gave the alcohol (19.5 g.), b. p. 80—90° (bath temp.)/10⁻⁴ mm., n_D^{24} 1.4941 (Found: C, 70.3; H, 9.05. $C_{13}H_{20}O_3$ requires C, 69.65; H, 8.9%). Light absorption: max., 2270 Å; ϵ , 17,000.

7-2'-Tetrahydropyran-5-en-3-yn-2-ol. Lithium aluminium hydride (1.3 g.) in ether (75 c.c.) was added during 30 minutes to a solution of the preceding alcohol (10.0 g.) in ether (100 c.c.), and the mixture was heated under reflux for 3 hours and then cooled. Decomposition of the complex and isolation of the product gave the diene (7.2 g.), b. p. 80—85° (bath-temp.)/10⁻⁴ mm., n_D^{21} 1.4947 (Found: C, 68.75; H, 10.15. $C_{13}H_{22}O_3$ requires C, 69.0; H, 9.75%). Light absorption: max., 2270 Å; ϵ , 24,000.

Octa-3:5-diene-2:7-dione. A solution of the preceding diene (4.8 g.) in methanolic sulphuric acid (2N; 200 c.c.) was kept at 20° for 3 hours. The acid was neutralised by the addition of solid sodium carbonate, and the mixture was filtered. Evaporation of the filtrate and isolation of the product from the residue by ether gave an oil (1.9 g.), oxidation (24 hours) of which gave a product which on cooling (alcohol-carbon dioxide) deposited a solid (124 mg.), m. p. 117—120°. One recrystallisation from alcohol gave octa-3:5-diene-2:7-dione, m. p. and mixed m. p. 124°.

Octa-3:6-diene-2:5-diol. A solution of oct-6-en-3-yne-2:5-diol (8.5 g.) in ethyl acetate

(50 c.c.) was shaken in an atmosphere of hydrogen in the presence of palladium-calcium carbonate (1.0 g.; 0.27% of Pd) until one mol. of hydrogen had been absorbed (1480 c.c. at 17°/756 mm.). The catalyst and solvent were removed and the residue was distilled, giving the glycol (7.6 g.), m. p. 85°/0.006 mm., n_D^{25} 1.4859 (Found: C, 67.7; H, 9.75. $C_8H_{14}O_2$ requires C, 67.55; H, 9.95%).

When the hydrogenation was carried out in methanolic solution with 10% palladium-calcium carbonate, there was obtained a 60% yield of a liquid, b. p. 30—170°/10⁻³ mm., n_D^{20} 1.4480—1.5093, from which no pure compound could be isolated.

Rearrangement of octa-3 : 5-diene-2 : 5-diol. A solution of the unconjugated glycol (6.0 g.) in sulphuric acid (300 c.c.; 0.2% wt./vol.), containing a trace of quinol, was kept at 20° for 1.5 hours. The solution was neutralised with sodium hydrogen carbonate and saturated with ammonium sulphate, the product was extracted with ether, and the ethereal solution was washed with water, dried, and evaporated. This gave a mixture of the conjugated glycols, octa-3 : 5-diene-2 : 7-diol and octa-4 : 6-diene-2 : 3-diol, as an oil (5.5 g.), n_D^{20} 1.5100. A small portion was distilled for analysis and had b. p. 80° (bath-temp.)/10⁻⁴ mm., n_D^{20} 1.5102 (Found: C, 67.3; H, 9.85. Calc. for $C_8H_{14}O_2$: C, 67.55; H, 9.95%). Light absorption: max., 2290 Å; ϵ , 25,500.

When the rearrangement was carried out with 1% acid for 60 hours, an appreciable amount of low-boiling material was obtained and the yield of glycols was reduced to 40%.

Octa-3 : 5-diene-2 : 7-dione. Oxidation (24 hours) of the preceding mixture (1.0 g.) and chromatographic purification of the crude product gave octa-3 : 5-diene-2 : 7-dione (70 mg.), m. p. 125°.

Octane-2 : 7- and -2 : 3-diols. Hydrogenation (Adams's catalyst) of the mixture (2.6 g.) of glycols in methanol (30 c.c.) (absorption, 880 c.c. at 19°/765 mm., equiv. to 2.0 double bonds), removal of catalyst and solvent, and distillation gave mixed saturated glycols (2.2 g.), b. p. 95—96°/0.01 mm., n_D^{20} 1.4515 (Found: C, 65.5; H, 12.2. Calc. for $C_8H_{18}O_2$: C, 65.7; H, 12.4%).

A portion of the mixture was treated at 20° with an excess of sodium periodate solution. At intervals aliquots of the resulting solution were added to an excess of potassium iodide solution, and the iodine liberated was titrated with sodium thiosulphate solution. The titre became constant after 36 hours and indicated that the original mixture contained 58% of the α -glycol.

Octane-2 : 7-dione. (a) A solution of the saturated glycols (1.5 g.) in acetone (3 c.c.) was treated at 0° with a solution of chromium trioxide (0.8 g.) and concentrated sulphuric acid (0.8 c.c.) in water (2 c.c.). The product was extracted with ether, and the extract was washed thoroughly with sodium hydrogen carbonate solution and water, dried ($MgSO_4$), and evaporated. Of the residual crude octa-2 : 7-dione, one half was treated with methanolic semicarbazide acetate and the other with methanolic 2 : 4-dinitrophenylhydrazine sulphate. The bis-semicarbazone (255 mg.) crystallised from dimethylformamide and had m. p. 221.5° undepressed on admixture with a specimen from (b). The bis-2 : 4-dinitrophenylhydrazone (520 mg.) crystallised from nitromethane and had m. p. 208°, undepressed on admixture with a sample from (b).

(b) Hydrogenation (Adams's catalyst, 25 mg.) of octa-3 : 5-diene-2 : 7-diol (0.8 g.) in methanol (15 c.c.) (absorption, 630 c.c. at 18°/761 mm., equiv. to 4.5 double bonds), removal of catalyst and solvent, and oxidation of the residue as in (a), gave a crude diketone, whose bis-semicarbazone, crystallised from dimethylformamide, had m. p. 222° (Meerwein, *Annalen*, 1914, 405, 159, gives m. p. 223°). The bis-2 : 4-dinitrophenylhydrazone, crystallised from methanol-nitromethane (1 : 1), had m. p. 209° (Found: N, 22.55. $C_{20}H_{22}O_8N_8$ requires N, 22.3%).

Periodate fission of octa-4 : 6-diene-2 : 3-diol. (a) A solution of the mixed conjugated glycols, octa-3 : 5-diene-2 : 7-diol and octa-4 : 6-diene-2 : 3-diol (0.5 g.), and sodium periodate (2.0 g.) in water was steam-distilled. The distillate was collected in a solution of 2 : 4-dinitrophenylhydrazine sulphate in water, and distillation was continued until no more solid separated in the receiver. The solid was collected and dried (1.21 g., 70%). A benzene solution was poured on a column of alumina (200 g.) and the chromatogram developed with the same solvent. The main diffuse brown band yielded a red crystalline solid (0.91 g.), which was dissolved in boiling ethyl acetate and the solution cooled to ca. 30°, giving a dark red powder (350 mg.), m. p. 179—181°. This was filtered off and crystallised from ethyl acetate, giving sorbaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 192° undepressed on admixture with an authentic specimen, m. p. 193°. When the original ethyl acetate mother-liquors cooled, an orange powder (300 mg.), m. p. 153—157°, separated. This was crystallised first from light petroleum (b. p. 60—80°) and then from alcohol, giving acetaldehyde 2 : 4-dinitrophenylhydrazone as plates, m. p. 164° undepressed on admixture with an authentic specimen.

(b) A solution of the mixed conjugated glycols (3.7 g.) and sodium periodate (6.4 g.) in water

(100 c.c.) was steam-distilled. The aqueous distillate (175 c.c.) was neutralised with sodium hydrogen carbonate, saturated with ammonium sulphate, and extracted with ether. The extract was dried (MgSO_4) and evaporated, and the residual oil treated with an excess of methanolic semicarbazide acetate solution. The crude derivative was crystallised once from aqueous methanol, giving sorbaldehyde semicarbazone (2.0 g., 50% based on mixture of glycols) as plates, m. p. 205° undepressed on admixture with an authentic specimen, m. p. 206° .

(c) A solution of octa-3 : 6-diene-2 : 5-diol (7.6 g.) in sulphuric acid (400 c.c.; 0.2% wt./vol.) was kept at 20° for 90 minutes. Sodium periodate (10 g.) was added and the mixture steam-distilled. Isolation of the product as described in (b) and conversion of the crude sorbaldehyde (3.2 g.), n_D^{20} 1.530, into the semicarbazone gave plates (3.0 g., 37% based on the diol), m. p. 204° undepressed on admixture with an authentic specimen.

Rearrangement of the diol with 0.5% acid and subsequent treatment as detailed above gave sorbaldehyde semicarbazone in 29% yield.

Rearrangement of octa-3 : 5-diene-2 : 7-diol. A solution of octa-3 : 5-diene-2 : 7-diol (0.94 g., 64% pure), in sulphuric acid (50 c.c.; 0.2% wt./vol.), was kept at 20° for 90 minutes. Sodium periodate (2.5 g.) was added and the mixture was steam-distilled. The distillate was collected in aqueous 2 : 4-dinitrophenylhydrazine sulphate, and the resulting crude derivative was purified by chromatography on alumina, giving a red powder (20.4 g.), m. p. 178° . Crystallisation from ethyl acetate yielded sorbaldehyde 2 : 4-dinitrophenylhydrazone (10 mg.), m. p. 193° , undepressed on admixture with an authentic specimen.

Syntheses from 2-Methyloct-6-en-3-yne-2 : 5-diol.—2-Methylocta-3 : 6-diene-2 : 5-diol. 2-Methyloct-6-en-3-yne-2 : 5-diol was prepared in 85% yield from hex-4-en-1-yn-3-ol and acetone as described above for oct-6-en-3-yne-2 : 5-diol (cf. Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39). A solution of this glycol (15.5 g.) in ethyl acetate (75 c.c.) was shaken in hydrogen in the presence of a palladium-calcium carbonate catalyst (1.5 g.; 0.27% of Pd) until 1 mol. of hydrogen had been absorbed (2417 c.c. at $18^\circ/760$ mm.). The catalyst and solvent were removed and the residue distilled, giving the glycol (13.9 g.), b. p. $85-87^\circ/0.02$ mm., n_D^{25} 1.4742—1.4763 (Found: C, 69.35; H, 10.45. $\text{C}_9\text{H}_{16}\text{O}_2$ requires C, 69.2; H, 10.3%). Light absorption: max., 2280 and 2360 Å; $E_{1\text{cm}}^{1\%}$ 90 and 90.

Rearrangement of 2-methylocta-3 : 6-diene-2 : 5-diol. A solution of the glycol (10.2 g.) in sulphuric acid (500 c.c.; 0.2% wt./vol.) was kept at 20° for 90 minutes. Isolation of the product gave a mixture of the conjugated glycols (5.2 g.), b. p. $89^\circ/0.002$ mm., n_D^{26} 1.4929 (Found: C, 69.2; H, 10.5. Calc. for $\text{C}_9\text{H}_{16}\text{O}_2$: C, 69.2; H, 10.3%). Light absorption: max., 2280 Å; ϵ , 20,000; inflexion, 2340 Å; ϵ , 17,500.

Periodate fission of 2-methylocta-4 : 6-diene-2 : 3-diol. (a) A solution of the preceding conjugated glycols (3.0 g.) in ether (10 c.c.) was shaken with a solution of sodium periodate (4.5 g.) in water (150 c.c.) at 20° for 15 hours. The aqueous layer was saturated with ammonium sulphate and the product isolated with ether and treated with an excess of semicarbazide acetate in methanol. This gave sorbaldehyde semicarbazone which crystallised from methanol in plates (1.5 g., 51% based on mixture of glycols), m. p. 206° undepressed on admixture with an authentic specimen.

(b) The conjugated glycols (0.74 g.) were added to a solution of sodium periodate (1.1 g.) in water (30 c.c.), and the mixture was steam-distilled. The distillate was collected in a flask containing a solution of dimedone (1.5 g.) in alcohol (60 c.c.) and water (15 c.c.). The resulting yellow emulsion was kept at 20° for $\frac{1}{2}$ hour and then at 0° for 2 hours. The solid was filtered off and the filtrate was steam-distilled. The distillate was collected in aqueous 2 : 4-dinitrophenylhydrazine sulphate (from 1.5 g. of 2 : 4-dinitrophenylhydrazine); acetone 2 : 4-dinitrophenylhydrazone (590 mg.; 52% based on mixture of glycols), m. p. 128° undepressed on admixture with an authentic specimen, m. p. 129° , was obtained.

(c) 2-Methylocta-6-en-3-yne-2 : 5-diol (7.75 g.) was partially hydrogenated; the resulting crude ethylenic glycol was dissolved in sulphuric acid (350 c.c.; 0.2% wt./vol.), and the solution kept at 20° for 1.5 hours. Sodium periodate (8.0 g.) was added and the mixture steam-distilled. Isolation of the product with ether gave crude sorbaldehyde (1.45 g.; 30%), b. p. $47-49^\circ/15$ mm., n_D^{22} 1.536. Light absorption: max., 2800 Å; $E_{1\text{cm}}^{1\%}$ 1940, indicating a purity of 80—85%. The 2 : 4-dinitrophenylhydrazone had m. p. 193° , undepressed on admixture with an authentic specimen.

Syntheses from Dec-2-en-5-yne-4 : 7-diol.—Deca-2 : 5-diene-4 : 7-diol. Dec-2-en-5-yne-4 : 7-diol was prepared in 83% yield from hex-4-en-1-yn-3-ol and *n*-butaldehyde in the manner described above for oct-6-en-3-yne-2 : 5-diol (cf. Cymerman, Heilbron, Johnson, and Jones, *J.*, 1944, 141). A solution (7.1 g.) in ethyl acetate (75 c.c.) was shaken in hydrogen in the presence

of a palladium-calcium carbonate catalyst (1.0 g.; 0.27% Pd) until 1 mol. of hydrogen had been absorbed (1050 c.c. at 17°/750 mm.). Isolation of the product gave the *decadienediol* (4.5 g.), b. p. 117°/0.002 mm., n_D^{25} 1.4800—1.4830 (Found: C, 70.7; H, 10.8. $C_{10}H_{18}O_2$ requires C, 70.55; H, 10.65%). Light absorption: max., 2290 and 2630 Å; $E_{1\%}^{1\text{cm}}$ 90 and 55, respectively. The *bis-3:5-dinitrobenzoate* crystallised from methanol-benzene (1:1) and had m. p. 156° (Found: N, 10.05. $C_{24}H_{22}O_{12}N_4$ requires N, 10.05%).

Rearrangement of deca-2:5-diene-4:7-diol. A mixture of the decadienediol (4.0 g.), sulphuric acid (200 c.c.; 0.2% wt./vol.), and a trace of quinol was shaken at 20° for 2 hours. The mixture was neutralised by the addition of sodium hydrogen carbonate, and the aqueous layer was saturated with ammonium sulphate. Isolation of the product with ether and distillation gave a mixture of the isomeric conjugated glycols (3.1 g.), b. p. 98°/0.003 mm., n_D^{25} 1.4970 (Found: C, 70.8; H, 10.8. Calc. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.65%). Light absorption: max. 2290 Å; ϵ , 19,500.

Periodate fission of deca-6:8-diene-4:5-diol. Dec-2-en-5-yne-4:7-diol (18.9 g.) was partially hydrogenated and the crude product was rearranged by shaking it with sulphuric acid (800 c.c.; 0.2% wt./vol.) for 2 hours at 20°. Sodium periodate (26 g.) was added, the mixture steam-distilled, and the distillate was extracted with ether. The extract was dried and evaporated, finally at 35°/15 mm. for 15 minutes. The residue was treated with an excess of methanolic semicarbazide acetate, giving sorbaldehyde semicarbazone (plates from aqueous methanol) (14.1 g.; 82% based on the acetylenic glycol), m. p. 205° undepressed on admixture with an authentic specimen, m. p. 206°.

Synthesis from Oct-4-yne-2:7-diol.—Oct-4-yne-2:7-diol. (a) Acetylene was passed into a solution of ethylmagnesium bromide (from 36 g. of magnesium) in benzene (1 l.) for 3 hours; the mixture became warm and a grey solid separated. The suspension was cooled to 0°, propylene oxide (171 g.) was added dropwise, and the mixture was stirred for 2 hours at 20° and then for 15 minutes under reflux. After the mixture had cooled, the complex was decomposed by addition of a saturated aqueous ammonium chloride solution, and the product was isolated. Distillation gave the *octynediol* (46.2 g.), b. p. 102—106°/0.5 mm., n_D^{25} 1.4755 (Found: C, 66.9; H, 9.9. $C_8H_{14}O_2$ requires C, 67.5; H, 9.9%).

(b) Pent-4-yn-2-ol (8.4 g.) (Haynes and Jones, *J.*, 1949, 945) in benzene (50 c.c.) was added dropwise to a solution of ethylmagnesium bromide (from 4.85 g. of magnesium) in benzene (100 c.c.). The mixture was stirred for 1 hour at 20° and then for 2 hours under reflux, and cooled. A solution of propylene oxide (5.7 g.) in benzene (25 c.c.) was added during 15 minutes and the mixture was heated under reflux for 1 hour and then cooled. Decomposition of the complex and isolation of the product gave the glycol (4.6 g.), b. p. 95°/0.05 mm., n_D^{25} 1.4759.

cis-Oct-4-ene-2:7-diol. A solution of the octynediol (14.0 g.) in ethyl acetate (50 c.c.) was shaken in hydrogen in the presence of a palladium-calcium carbonate catalyst (1.0 g.; 0.3% Pd) until one mol. of hydrogen had been absorbed (2360 c.c. at 17°/757 mm.). The catalyst and solvent were removed and the residue distilled giving the *cis-octenediol* (12.6 g.), b. p. 74°/0.05 mm., n_D^{25} 1.4662 (Found: C, 66.9; H, 11.5. $C_8H_{16}O_2$ requires C, 66.6; H, 11.2%). [For the *trans*-isomer, Karrer and Eugster, *loc. cit.*, give b. p. 90—95° (bath temp.)/0.05 mm.]

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