320. *Studies in the Polyene Series. Part XLVIII.* The Preparation and Rearrangement of Some Dialkenylmethanols.*

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Reduction of but-2-yn-1-ol with lithium aluminium hydride gives *trans*-crotyl alcohol.

Similar reduction of alcohols obtained by reaction of ethynyl*cyclo*hexene with crotonaldehyde and crotonylideneacetone, and of the latter with pent-2-en-4-yne, gives the corresponding polyene alcohols. These rearrange readily to fully conjugated isomers, mixtures being obtained from the two unsymmetrically substituted compounds.

Previous papers in this series have described the preparation of acetylenic analogues of vitamin A and vitamin A acid from ethynyl*cyclo*hexenes. Partial hydrogenation of the triple bond in suitable intermediates in these syntheses offered promising routes to polyenes of the vitamin A type. These possibilities prompted the study now described of the reduction of some vinyl acetylenic alcohols derived from crotonaldehyde and crotonylideneacetone, and of the anionotropic rearrangement of the resulting polyene alcohols.

The method of reduction used was developed by Chanley and Sobotka (*J. Amer. Chem. Soc.*, 1949, **71**, 4140), who showed that 4-*cyclo*hex-1′-enylbut-3-yn-2-ol (I) is converted into the diene alcohol (II) in good yield with lithium aluminium hydride. Reduction of an acetylenic alcohol with this reagent would be expected, by analogy with other chemical methods (Campbell and Campbell, *Chem. Reviews*, 1942, **31**, 148), to give the *trans*-isomer of the corresponding olefin. However, to enable comparisons to be made between the polyenes prepared in the present work and those obtained previously by routes not based on acetylene (preceding paper; Braude, Bruun, Weedon, and Woods, *J.*, 1952, **1414**), it was desirable to confirm the stereochemical course of the reaction. Since both *cis*- and

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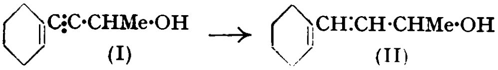
* Part XLVII, preceding paper.

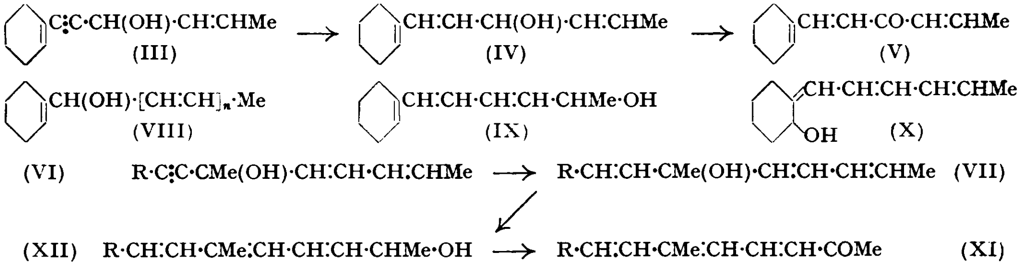
trans-forms of crotyl alcohol are readily characterised (Hatch and Nesbitt, *J. Amer. Chem. Soc.*, 1950, **72**, 727), but-2-yn-1-ol was reduced with lithium aluminium hydride; only *trans*-crotyl alcohol was detected in the product.



Similar treatment of the alcohol (III) from ethynyl*cyclo*hexene and crotonaldehyde (Heilbron, Jones, Lewis, Richardson, and Weedon, *J.*, 1949, 742) furnished a product which on oxidation (manganese dioxide) was converted in almost quantitative yield into the crystalline ketone (V). This exhibited the expected light absorption properties and on catalytic hydrogenation gave the known 1-*cyclo*hexylhexan-3-one. There is therefore no doubt that reduction of (III) occurred exclusively at the triple bond to give (IV). Similarly the alcohols (VI*a* and *b*), obtained by reaction of crotonylideneacetone with ethynyl*cyclo*hexene (Heilbron, Jones, and Richardson, *J.*, 1949, 287) and pent-2-en-3-yne, respectively, yielded the tetraenols (VII*a* and *b*).

Anionotropic rearrangement of the alcohols (IV) and (VII*a*) can conceivably take place by migration of the hydroxyl group either along the side chain or into the ring. Previously it has been found that the hydroxyl group in unsymmetrically substituted dialkenylmethanols migrates initially to the terminal carbon atom of the unsaturated system at which electron accession is the greater (Braude and Coles, *J.*, 1950, 2014; Braude and Forbes, *J.*, 1951, 1755). It was expected that the hydroxyl group of (IV) and (VII*a*), like that of the alcohols (VIII; $n = 1$ and 2) (Braude and Coles, *loc. cit.*, Braude, Bruun, Weedon, and Woods, *loc. cit.*), would migrate along the side chain almost exclusively. However rearrangement of (IV), under conditions identical with those used previously with the isomeric alcohol (VIII; $n = 1$), gave a product which had light-absorption properties in good agreement with those of (IX) but was shown to be a mixture of conjugated triene alcohols, presumably (IX) and (X).

Isomerisation of (VII*a*) also gave a mixture of alcohols, even under such mild conditions (0·001M-sulphuric acid for ½ hour) that further rearrangement of the initial product was extremely improbable (cf. Nazarov and Fisher, *Bull. Acad. Sci., U.R.S.S.*, 1948, 311; Braude and Timmons, *J.*, 1950, 2007). After Oppenauer oxidation of the mixture, and chromatographic purification, the *cyclo*hexenylmethyloctatrienone (XI*a*) was isolated as a 70% concentrate and characterised. The reason for the seemingly anomalous behaviour of (IV) and (VII*a*) on isomerisation is not apparent from existing theories on anionotropy (cf. Braude, *Quart. Reviews*, 1950, **4**, 404).



(*a*, R = *cyclo*hex-1-enyl; *b*, R = CHMe:CH)

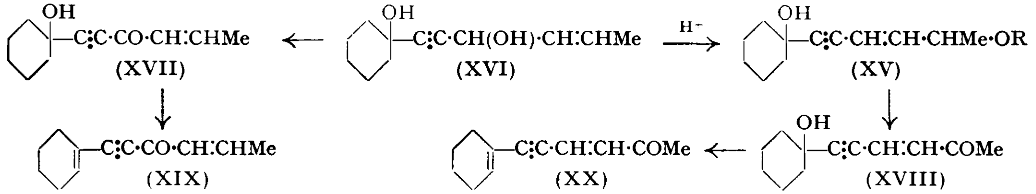
Rearrangement of the symmetrically substituted, acyclic analogue (VII*b*) of (VII*a*) gave the methylundecatetraenol (XII*b*), the structure of which was confirmed by oxidation to the known ketone (XI*b*) (preceding paper).

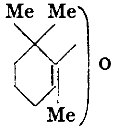
Attempts to prepare the *cyclo*hexenyl alcohol (IX) by rearrangement of the acetylenic alcohol (III) to (XIII), and reduction of the latter, were unsucessful; treatment of (XIII) with lithium aluminium hydride gave an isomer of the required trienol which, on the basis of its light absorption ($\lambda_{max.}$ 228 mμ; $\varepsilon = 23,000$), is believed to be formed by 1 : 4-addition of hydrogen to the vinylacetylenic system, and is provisionally assigned the allenic structure (XIV). On catalytic hydrogenation, and subsequent oxidation of the saturated alcohol, the known 6-*cyclo*hexylhexan-2-one (semicarbazone) was obtained. Structures analogous to (XIV) have previously been proposed for products obtained by catalytic hydrogenation of symmetrical divinylacetylenes (Thompson and Shaw, *J. Amer. Chem. Soc.*, 1942, **64**, 363).

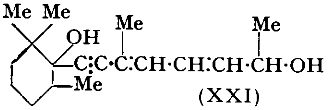
$$\text{(III)} \xrightarrow{\text{H}^+} \text{R·C⋮C·CH:CH·CHMe(OH)} \longrightarrow \text{R·CH:C:CH·CH}_2\text{·CHMe·OH}$$

(XIII) (R = *cyclo*hex-1-enyl) (XIV)

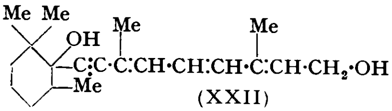
The last result indicated that for normal reduction to the corresponding olefin, an acetylene must possess a hydroxyl group on the α-carbon atom. Accordingly it seemed of interest to compare the reduction of the glycol (XV; R = H) with that of the alcohol (XIII). Reaction of the Grignard complex of ethynyl*cyclo*hexanol with crotonaldehyde gave the glycol (XVI) which on treatment with acid yielded the required conjugated isomer (XV; R = H). The latter was also obtained directly from hex-3-en-5-yn-2-ol and *cyclo*hexanone. The structures of the glycols (XVI) and (XV) were confirmed by oxidation (manganese dioxide) to the hydroxy-ketones (XVII) and (XVIII), which on dehydration with phosphorus oxychloride in pyridine yielded the ketones (XIX) and (XX), identical with those derived from ethynyl*cyclo*hexene. When lithium aluminium hydride was used, selective reduction of the triple bond could not be achieved with either the glycol (XV; R = H) or its monotetrahydropyranyl ether (as XV), prepared by reaction of *cyclo*hexanone with 2-(tetrahydro-2-pyranyloxy)hex-3-en-5-yne.



Since these investigations were completed, the reaction of some related acetylenic alcohols and glycols with lithium aluminium hydride has been reported (Attenburrow, Cameron, Chapman, Evans, Hems, Jansen, and Walker, *J.*, 1952, 1094). Selective reduction of the triple bond was not observed with VI; R =  or its fully conjugated isomer. The failure in the first case, in which the αβ-double bond was stated to be preferentially reduced, is probably due to inability of the reagent to form the necessary cyclic intermediate with the triple bond, owing to steric interference by the ring-methyl groups. Both the glycols (XXI) and (XXII) were successfully reduced to the corresponding polyenes.



(XXI)



(XXII)

EXPERIMENTAL

(See notes preceding the Experimental section in Part XLV.)

Reduction of Acetylenic Alcohols.—The following general method was used. A solution of the alcohol in ether was added during $\frac{1}{2}$—1 hour to a stirred solution of lithium aluminium hydride (*ca.* 80% pure) in ether. The mixture was heated under reflux for 3 hours and then cooled. Ethyl acetate (*ca.* 7 c.c./g. of hydride used) was added, to decompose any excess of hydride, followed by a saturated solution of ammonium chloride (*ca.* 12 c.c./g. of hydride). The mixture was filtered and the ethereal solution was washed with water, dried (Na_2SO_4 + trace of K_2CO_3), and evaporated under reduced pressure. The various products were purified as indicated below.

trans-*Crotyl Alcohol.*—But-2-yn-1-ol (3·0 g.) in ether (25 c.c.) was reduced with lithium aluminium hydride (2·0 g.) in ether (150 c.c.). Distillation of the product gave *trans*-crotyl alcohol (1·6 g.), b. p. 122°, n_D^{23} 1·4278 (Hatch and Nesbitt, *J. Amer. Chem. Soc.*, 1950, **72**, 727, give n_D^{25} 1·4262). The 3 : 5-dinitrobenzoate, formed in 40% yield, crystallised from benzene–light petroleum (b. p. 40—60°) (1 : 1) in needles, m. p. 68—69°, undepressed on admixture with an authentic specimen [*idem, loc. cit.*, give m. p. 70° (corr.)].

The 3 : 5-*dinitrobenzoate* of but-2-yn-1-ol crystallised from the same solvents in plates, m. p. 107° (Found: C, 50·3; H, 3·3; N, 10·55. $C_{11}H_8O_6N_2$ requires C, 50·0; H, 3·05; N, 10·6%) (*idem, loc. cit.*, give m. p. 71° for this derivative).

1-cyclo*Hex-1'-enylhexa-*1 : 4-*dien-*3-*ol* (IV).—1-*cyclo*Hex-1'-enylhex-4-en-1-yn-3-ol (10·0 g.) (Heilbron, Jones, Lewis, Richardson, and Weedon, *J.*, 1949, 742), in ether (75 c.c.), was reduced with lithium aluminium hydride (2·7 g.), in ether (250 c.c.), giving an oil (9·5 g.), n_D^{24} 1·5348 Light absorption: max. 237 mμ; $E^{1\%}_{1\,\text{cm.}} = 1340$. A portion (0·52 g.) was distilled and gave the *alcohol* (0·44 g.), b. p. 60° (bath-temp.)/10^{-4} mm., n_D^{19} 1·5358 (Found: C, 81·05; H, 10·35 $C_{12}H_{18}O$ requires C, 80·85; H, 10·15%). Light absorption: max. 237 mμ; ε = 25,500 A solution of the alcohol (0·885 g.) in ethyl acetate (25 c.c.) was shaken in hydrogen in the presence of Adams's catalyst until absorption was complete. Hydrogen absorbed (346 c.c. at 20°/760 mm.) was equivalent to 2·9 double bonds.

1-cyclo*Hex-1'-enylhexa-*1 : 4-*dien-*3-*one* (V).—The preceding alcohol (1·7 g.; distilled) in light petroleum (b. p. 40—60°) (200 c.c.) was shaken with manganese dioxide (14 g.) at 20° for 2½ hours. Removal of oxide and solvent gave an oil (1·65 g.), n_D^{20} 1·5662, m. p. 51—54°. Crystallisation from light petroleum (b. p. 40—60°) gave the *ketone* as needles, m. p. 53—55° (Found: C, 82·0; H, 9·15. $C_{12}H_{16}O$ requires C, 81·75; H, 9·15%). Light absorption: max. 303 mμ; ε = 21,000. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in prisms, m. p. 142—144°, varying with the rate of heating (Found: N, 15·6. $C_{18}H_{20}O_4N_4$ requires N, 15·7%). Light absorption in $CHCl_3$ (main band only): max., 404 mμ; ε = 29,500.

1-cyclo*Hexylhexan-*3-*one*.—A solution of the preceding ketone (0·304 g.) in ethyl acetate (15 c.c.) was shaken in hydrogen in the presence of Adams's catalyst (0·03 g.) until absorption was complete (128 c.c. at 18°/768 mm., equiv. to 3·1 double bonds). Removal of catalyst and solvent gave the saturated ketone (0·25 g.). The semicarbazone crystallised from aqueous methanol in needles, m. p. 126°, undepressed on admixture with an authentic specimen (*idem, loc. cit.*, give m. p. 127·5°).

Rearrangement of 1-cyclo*Hex-1'-enylhexa-*1 : 4-*dien-*3-*ol*.—A 0·01N-solution of hydrochloric acid and 1-*cyclo*hex-1'-enylhexa-1 : 4-dien-3-ol (4·9 g.; undistilled) in acetone (132 c.c.) and water (66 c.c.) was kept at 20° for 20 hours. The solution was saturated with salt and the product isolated with ether, giving an oil (4·1 g.), n_D^{23} 1·5690. Light absorption: max., 270 and 280 mμ; $E^{1\%}_{1\,\text{cm.}} = 1560$ and 1560. Inflexion, 258 mμ; $E^{1\%}_{1\,\text{cm.}} = 1300$. A portion (0·5 g.) was distilled and gave a mixture of rearranged alcohols (0·225 g.), b. p. 75—80° (bath-temp.)/10^{-4} mm., n_D^{17} 1·5738 (Found: C, 81·0; H, 10·05. $C_{12}H_{18}O$ requires C, 80·85; H, 10·15%). Light absorption: max. 270 and 280 mμ; $E^{1\%}_{1\,\text{cm.}} = 1680$ and 1500 respectively, equiv. to ε = 30,000 and 26,500 respectively. (6-*cyclo*Hex-1'-enylhexa-3 : 5-dien-2-ol has max. at 270 and 279 mμ; ε = 33,500 and 27,500 respectively; inflexion, 259 mμ; ε = 25,000) (Braude, Bruun, Weedon, and Woods, *J.*, 1952, 1414). A solution of the mixed alcohols (1·162 g.; undistilled) in ethyl acetate (25 c.c.) was shaken in hydrogen in the presence of Adams's catalyst (0·106 g.) until absorption was complete. Hydrogen absorbed (425 c.c. at 20°/760 mm.) was equivalent to 2·7 double bonds.

The mixed alcohols (3·0 g.; undistilled) and aluminium *tert.*-butoxide (7·5 g.) in acetone (75 c.c.) and benzene (100 c.c.) were heated under reflux for 60 hours. Decomposition of the complex with dilute sulphuric acid and isolation of the product in the usual manner gave a red oil (3·5 g.) which was purified by chromatography on alumina (250 g.) from light petroleum (b. p. 40—60°). Elution of the main, yellow band gave an oil (1·15 g.), n_D^{24} 1·6000. Light absorption: max., 280 and 320 mμ; $E^{1\%}_{1\,\text{cm.}} = 600$ and 1200 respectively. Inflexion, 292 mμ; $E^{1\%}_{1\,\text{cm.}} = 750$. The crude product yielded a mixture of 2 : 4-dinitrophenylhydrazones which after several crystallisations from ethyl acetate had m. p. 181—194° (Found: N, 15·2. $C_{18}H_{20}O_4N_4$ requires N, 15·7%). Light absorption in $CHCl_3$ (main band only): max, 405 mμ; $E^{1\%}_{1\,\text{cm.}} = 1050$ (equiv. to ε = 37,500). Distillation of the crude product (0·8 g.) gave a mixture of ketones (0·223 g.), b. p. 70—80° (bath-temp.)/10^{-4} mm., n_D^{26} 1·6081, which was hydrogenated in ethyl acetate (20 c.c.) in the presence of Adams's catalyst (45 mg.) (hydrogen absorbed = 94 c.c. at 22°/762 mm., equiv. to 3 double bonds). After the catalyst and solvent had been removed, the residue was treated with methanolic semicarbazide acetate and gave a mixture of derivatives which after several crystallisations from methanol had m. p. 138—145° (50 mg.) (Found: N, 17·1. $C_{13}H_{25}ON_3$ requires N, 17·55%). The semicarbazones of 6-*cyclo*hexylhexan-2-one

(Heilbron, Jones, Lewis, Richardson, and Weedon, *loc. cit.*) and 2-*n*-hexyl*cyclo*hexanone (Braude, Bruun, Weedon, and Woods, *loc. cit.*) have m. p. 154° and 129° respectively.

1-cyclo*Hex-1'-enyl-3-methylocta-1 : 4 : 6-trien-3-ol* (VII*a*).—1-*cyclo*Hex-1'-enyl-3-methylocta-4 : 6-dien-1-yn-3-ol (4·0 g.) (Heilbron, Jones, and Richardson, *J.*, 1949, 287) (Unsaturation, equiv. to 4·8 double bonds) in ether (50 c.c.) was reduced with lithium aluminium hydride (0·88 g.) in ether (200 c.c.). Distillation of the crude product gave the *alcohol* (3·4 g.), b. p. 80—90° (bath-temp.)/10^{-4} mm., n_D^{18} 1·5458 (Found: C, 82·75; H, 10·35. $C_{15}H_{22}O$ requires C, 82·5; H, 10·15%) (Unsaturation, equiv. to 3·8 double bonds). Light absorption: max. 227 and 236 mμ; ε = 41,500 and 34,000 respectively.

Unless great care was taken to exclude, and prevent the formation of, minute traces of acid, a partly or fully rearranged product was obtained. In one experiment using half the amount of hydride given above, the product consisted almost entirely of the unchanged acetylenic alcohol.

Rearrangement of 1-cyclo*Hex-1'-enyl-3-methylocta-1 : 4 : 6-trien-3-ol.*—A solution of the unrearranged alcohol (4·9 g.) in a 0·001N-solution of sulphuric acid in acetone (370 c.c.) and water (120 c.c.) was kept at 20° for ½ hour. The solution was neutralised by the addition of aqueous sodium hydrogen carbonate, and the bulk of the acetone was removed under reduced pressure. Isolation with ether gave an oil (4·6 g.), n_D^{19} 1·6055. Light absorption (main band only): max., 304 mμ; $E^{1\%}_{1\,\text{cm.}} = 1670$. Distillation (accompanied by extensive polymerisation) of a small portion gave a mixture of fully conjugated alcohols, b. p. 110—115° (bath-temp.)/10^{-4} mm., n_D^{19} 1·612 (Found: C, 82·2; H, 10·3. $C_{15}H_{22}O$ requires C, 82·5; H, 10·15%). Light absorption: max., 302 and 313 mμ; $E^{1\%}_{1\,\text{cm.}} = 2140$ and 1760 respectively, equiv. to ε = 46,500 and 38,500. Inflexion, 289 mμ; $E^{1\%}_{1\,\text{cm.}} = 1550$.

Rearrangement with a 0·01M-solution of sulphuric acid in aqueous acetone for 1½ hours at 20° gave a similar mixture.

A solution of the mixed rearranged alcohols (1·85 g.; undistilled) in ethyl acetate (15 c.c.) was shaken in hydrogen in the presence first of 6% palladium–calcium carbonate and finally of Adams's catalyst. When absorption was complete, the catalyst and solvent were removed and the residue (1·8 g.), n_D^{20} 1·4701, in glacial acetic acid (10 c.c.) was oxidised by chromium trioxide (0·6 g.) in water (2 c.c.) and acetic acid (2 c.c.). The solution was kept overnight and the product was then isolated in the usual way, giving a mixture of saturated ketones (1·1 g.), n_D^{21} 1·4670. The mixture of 2 : 4-dinitrophenylsemicarbazones after several crystallisations from methanol had m. p. 157—161° (Found: C, 59·3; H, 7·75. Calc. for $C_{22}H_{33}O_5N_5$: C, 59·05; H, 7·45%). The 2 : 4-*dinitrophenylsemicarbazone* prepared from an authentic specimen of 8-*cyclo*hexyl-6-methyloctan-2-one (Heilbron, Jones, and Richardson, *loc. cit.*) crystallised from methanol and had m. p. 173° (Found: C, 59·3; H, 7·35. $C_{22}H_{33}O_5N_5$ requires C, 59·05; H, 7·45%). The derivative of 2-3'-methyloctyl*cyclo*hexanone had m. p. 179° (see below) which was depressed to 151—156° on admixture with the isomeric derivative.

3-Methyloctan-1-ol and 3-Methyloctyl Bromide.—Ethyl 2-methylheptane-1-carboxylate (12·0 g.) (Weedon and Woods, *J.*, 1951, 2687) in ether (50 c.c.) was added during ½ hour to lithium aluminium hydride (6·5 g.) in ether (200 c.c.). The mixture, which boiled gently during the addition, was stirred for 45 minutes and then cooled. Dilute sulphuric acid was added and the product was isolated with ether in the usual manner, giving 3-methyloctan-1-ol (7·8 g.), b. p. 93°/10 mm., n_D^{24} 1·4328 [Levene and Marker, *J. Biol. Chem.*, 1931, **91**, 77, give b. p. 110°/25 mm., n_D^{25} 1·4328 for the (−)-isomer].

Bromination of the alcohol (7·5 g.) with hydrobromic acid (11·0 g.; *d* 1·45) and concentrated sulphuric acid (3·4 c.c.) (cf. *Org. Synth.*, Coll. Vol. I, 2nd Edn., p. 30) gave 3-methyloctyl bromide (7·8 g.), b. p. 87°/12 mm., n_D^{21} 1·4541 (Levene and Marker, *loc. cit.*, give b. p. 104°/25 mm., n_D^{25} 1·4536, for the (+)-isomer).

*2-3'-Methyloctyl*cyclo*hexanone.*—*cyclo*Hexanone (3·5 g.) and 3-methyloctyl bromide (7·5 g.) were added rapidly to a boiling solution of potassium *tert.*-butoxide (from 1·45 g. of potassium) in *tert.*-butanol (25 c.c.). The mixture was heated under reflux for 20 minutes, then cooled and treated with excess of cold (0°) 2N-hydrochloric acid. This gave the *ketone* (2·25 g.), b. p. 84—86°/0·06 mm., n_D^{20} 1·4631 (Found: C, 80·0; H, 12·75. $C_{15}H_{28}O$ requires C, 80·3; H, 12·6%). The 2 : 4-*dinitrophenylsemicarbazone* crystallised from ethyl acetate in needles, m. p. 179° (Found: C, 59·05; H, 7·45. $C_{22}H_{33}O_5N_5$ requires C, 59·05; H, 7·45%). The *semicarbazone*, which was formed in poor yield, crystallised from aqueous methanol in plates, m. p. 124° (Found: N, 14·9. $C_{16}H_{31}ON_3$ requires N, 14·95%).

8-cyclo*Hex-1'-enyl-6-methylocta-3 : 5 : 7-trien-2-one* (XI*a*).—A solution in benzene (1800 c.c.) of aluminium *tert.*-butoxide (75 g.) and the mixture of alcohols (33 g.; undistilled) formed by rearrangement of 1-*cyclo*hex-1'-enyl-3-methylocta-1 : 4 : 6-trien-3-ol was boiled under reflux for

24 hours. Decomposition of the complex with dilute sulphuric acid and isolation of the product gave an oil which, in benzene (200 c.c.), was poured on alumina (700 g.). The chromatogram was developed with light petroleum (b. p. 40—60°) until the eluate no longer gave a positive test with Brady's reagent. The eluate (3 l.) was concentrated (to 172 c.c.) and the resulting solution (estimated to contain *ca.* 9—10 g. of conjugated tetraene C_{15} ketones by evaporation of an aliquot, and determination of the intensity at 361 mμ after dissolution of the residue in alcohol) was poured on a column of alumina (700 g.). The chromatogram was developed with the same solvent and the eluate was collected in 7 fractions. Small portions of each fraction were evaporated and the residues converted into the 2 : 4-dinitrophenylsemicarbazones. The derivative of the required ketone was readily obtained from the most strongly adsorbed fractions (4—7) which were combined (2 l.) and evaporated. Distillation of the residue (3·7 g.), n_D^{20} 1·635, gave the crude ketone (2·5 g.), b. p. 80—90° (bath-temp.)/10^{-4} mm., n_D^{25} 1·66. Light absorption : max. 350 and 363 mμ; $E_{1\,cm.}^{1\%}$ = 1340 and 1340, indicating a purity of *ca.* 70%. The 2 : 4-dinitrophenylsemicarbazone (from aqueous pyridine) had m. p. 215° (decomp.), undepressed on admixture with the derivative of 8-*cyclo*hex-1′-enyl-6-methylocta-3 : 5 : 7-trien-2-one (preceding paper). (Fractions 1—3 gave mixtures of derivatives which could not be separated.)

The ketone (0·416 g.; distilled) in ethyl acetate (20 c.c.) was shaken in hydrogen in the presence of Adams's catalyst (50 mg.) until absorption was complete (176 c.c. at 20°/765 mm., equiv. to 3·8 double bonds). Removal of catalyst and solvent gave the saturated ketone (0·385 g.) which was converted into the 2 : 4-dinitrophenylsemicarbazone. This crystallised from ethyl acetate in needles (0·23 g.), m. p. 173°, undepressed on admixture with the derivative of 8-*cyclo*hexyl-6-methyloctan-2-one but depressed by that of 2-3′-methyloctyl*cyclo*hexanone. Attempts to oxidise the mixture of tetraene alcohols by manganese dioxide were unsuccessful.

6-*Methylundeca*-2 : 4 : 9-*trien*-7-*yn*-6-*ol* (VI*b*).—Pent-2-en-4-yne (12 g.) (Eglinton and Whiting, *J.*, 1950, 3650) was added to ethylmagnesium bromide (from 3·6 g. of magnesium) in ether (300 c.c.), and the mixture was boiled under reflux for 3 hours and then cooled to 0°. Hepta-3 : 5-dien-2-one (16·5 g.) in ether (150 c.c.) was added during 3 hours and the mixture was stirred overnight at 20°. Aqueous ammonium chloride was added and the ethereal layer was separated, washed with water, dried (Na_2SO_4 + trace of K_2CO_3), and evaporated. Distillation of the residue gave the *alcohol* (18·6 g.), b. p. 55—65° (bath-temp.)/10^{-4} mm., n_D^{22} 1·5281 (Found : C, 81·35; H, 9·15. $C_{12}H_{16}O$ requires C, 81·75; H, 9·15%) (Unsaturation, equiv. to 5·3 double bonds). Light absorption : max. 227 mμ; ε = 38,500.

6-*Methylundecan*-6-*ol*.—The preceding alcohol (0·736 g.) in ethyl acetate (15 c.c.) was hydrogenated in the presence of Adams's catalyst (50 mg.) (total hydrogen absorbed, 492 c.c. at 18°/754 mm., equiv. to 4·9 double bonds). Removal of catalyst and distillation gave 6-*methylundecan*-6-*ol* (0·646 g.), b. p. 80—90° (bath-temp.)/0·5 mm., n_D^{18} 1·4403 (Found : C, 77·5; H, 14·05. $C_{12}H_{26}O$ requires C, 77·35; H, 14·05%).

6-*Methylundeca*-2 : 4 : 7 : 9-*tetraen*-6-*ol* (VII*b*).—6-Methylundeca-2 : 4 : 9-trien-7-yn-6-ol (12·0 g.) in ether (100 c.c.) was reduced with lithium aluminium hydride (3·2 g.) in ether (500 c.c.), giving the *alcohol* (9·5 g.), b. p. 79—80°/0·3 mm., n_D^{21} 1·5281 (Found : C, 80·95; H, 10·4. $C_{12}H_{18}O$ requires C, 80·85; H, 10·15%) (Unsaturation, equiv. to 3·8 double bonds. Light absorption : max. 227 mμ; ε = 44,000.

6-*Methylundeca*-3 : 5 : 7 : 9-*tetraen*-2-*ol* (XII*b*).—The preceding alcohol (1·25 g.) in a 0·01M-solution of sulphuric acid in water (32 c.c.) and acetone (91 c.c.) was kept at 20° for 90 minutes. 2N-Sodium carbonate was added to raise the pH to 7—8, the bulk of the acetone was removed under reduced pressure, and the product isolated with ether. Distillation, which was accompanied by extensive polymerisation, gave the *alcohol* (0·3 g.), b. p. 75—85° (bath-temp.)/10^{-4} mm., n_D^{20} 1·6105 (Found : C, 81·1; H, 10·15. $C_{12}H_{18}O$ requires C, 80·85; H, 10·15%). Light absorption : max. 302 and 316 mμ; ε = 48,000 and 42,000 respectively. The alcohol solidified partly at 0°.

6-*Methylundecan*-2-*ol and* 6-*Methylundecan*-2-*one*.—The preceding alcohol (1·522 g., undistilled) was hydrogenated in ethyl acetate (25 c.c.) in the presence of 7% palladium–calcium carbonate (0·3 g.), giving 6-*methylundecan*-2-*ol* (1·1 g.), b. p. 90—100° (bath-temp.)/0·3 mm., n_D^{20} 1·4386 (Found : C, 77·0; H, 13·7. $C_{12}H_{26}O$ requires C, 77·35; H, 14·05%).

The alcohol (0·9 g.) in glacial acetic acid (5 c.c.) was treated with chromium trioxide (0·4 g.) in water (1 c.c.) and acetic acid (2 c.c.), and the mixture was kept overnight. The ketonic product (0·8 g.) gave the 2 : 4-dinitrophenylsemicarbazone in good yield as needles (from alcohol), m. p. 185°, undepressed on admixture with an authentic specimen (Bharucha and Weedon, *J.*, 1953, 1571).

6-*Methylundeca*-3 : 5 : 7 : 9-*tetraen*-2-*one* (XI*b*).—A solution of 6-methylundeca-3 : 5 : 7 : 9-tetraen-2-ol (4·5 g., undistilled) and aluminium *tert.*-butoxide (10·8 g.) in benzene (300 c.c.) and acetone (140 c.c.) was heated under reflux for 24 hours. Working up in the usual way gave the crude ketone (4·3 g.), n_D^{20} 1·64—1·65. Light absorption: max., 353 mμ; $E_{1\,\text{cm.}}^{1\%} = 1480$. Inflexion, 358 mμ; $E_{1\,\text{cm.}}^{1\%} = 1340$. In *n*-hexane at 0° it deposited a solid which crystallised from the same solvent, giving 6-methylundeca-3 : 5 : 7 : 9-tetraen-2-one (0·2 g.), m. p. 85° (*idem, loc. cit.*, give m. p. 85—87°).

6-cyclo*Hex*-1′-*enylhexa*-4 : 5-*dien*-2-*ol* (XIV).—6-*cyclo*Hex-1′-enylhex-3-en-5-yn-2-ol (5·0 g.) (Heilbron, Jones, Lewis, Richardson, and Weedon, *loc. cit.*) in ether (40 c.c.) with lithium aluminium hydride (1·35 g.) in ether (125 c.c.) gave an oil (5·0 g.), n_D^{28} 1·5351. Light absorption: max., 229 and 270 mμ; $E_{1\,\text{cm.}}^{1\%} = 1000$ and 100 respectively. Distillation of a portion (0·5 g.) gave the *alcohol* (0·4 g.), b. p. 70—80° (bath-temp.)/10^{-4} mm., n_D^{23} 1·5358 (Found: C, 80·65; H, 10·15. $C_{12}H_{18}O$ requires C, 80·85; H, 10·15%). Light absorption: max. 228 mμ; $\varepsilon = 23{,}000$.

6-cyclo*Hexylhexan*-2-*ol and* 6-cyclo*Hexylhexan*-2-*one*.—The preceding alcohol (1·234 g.) in ethyl acetate (30 c.c.) was shaken in hydrogen in the presence of Adams's catalyst until absorption was complete (453 c.c. at 20°/761 mm., equiv. to 2·7 double bonds). Filtration and distillation gave the saturated alcohol (0·84 g.), b. p. 100—110° (bath-temp.)/1 mm., n_D^{23} 1·4680, which was oxidised in glacial acetic acid (3·5 c.c.) by the addition of a solution of chromium trioxide (0·3 g.) in acetic acid (1·5 c.c.) and water (1 c.c.). Next morning the crude ketone (0·7 g.) was isolated and converted into the semicarbazone which crystallised from methanol in plates (0·35 g.), m. p. 154°, undepressed on admixture with an authentic specimen (*idem, loc. cit.*, give m. p. 154°).

1-1′-*Hydroxy*cyclo*hexylhex*-4-*en*-1-*yn*-3-*ol* (XVI).—Ethynyl*cyclo*hexanol (62 g.) in benzene (100 c.c.) was added during 1½ hours to a stirred solution of ethylmagnesium bromide (from magnesium, 24 g.) in benzene (250 c.c.), and the resulting solution was warmed to 40° for 2 hours. The mixture was cooled to 0°, a solution of crotonaldehyde (45 g.) in benzene (70 c.c.) was added during ½ hour, and stirring was continued overnight at room temperature. Decomposition of the complex with ammonium chloride and isolation of the product with benzene gave the *glycol* (35 g.) as a very viscous oil, b. p. 120—130° (bath-temp.)/10^{-5} mm., n_D^{22} 1·5135 (Found: C, 74·15; H, 9·6. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·35%). The glycol exhibited no light absorption of intensity $E_{1\,\text{cm.}}^{1\%} > 20$ at 220—400 mμ.

When the reaction was carried out in ether solution the glycol was obtained in 12% yield.

1-1′-*Hydroxy*cyclo*hexylhexan*-3-*ol and* 1-1′-*Hydroxy*cyclo*hexylhexan*-3-*one*.—The preceding glycol (2·89 g.) in ethyl acetate (50 c.c.), and Adams's catalyst (0·15 g.), were shaken in hydrogen until absorption was complete (925 c.c. at 17°/760 mm., equiv. to 2·6 double bonds). After removal of catalyst and solvent, distillation of the residue gave the saturated *glycol* (2·23 g.), b. p. 90—100° (bath-temp.)/10^{-4} mm., n_D^{23} 1·4830 (Found: C, 71·95; H, 11·6. $C_{12}H_{24}O_2$ requires C, 71·95; H, 12·05%). The *bis*-3 : 5-*dinitrobenzoate* crystallised from aqueous acetone in prisms, m. p. 169° (Found: C, 53·55; H, 5·0. $C_{26}H_{28}O_{12}N_4$ requires C, 53·05; H, 4·8%).

The glycol (1·69 g.) in glacial acetic acid (5 c.c.) was treated with chromium trioxide (0·56 g.) in water (2 c.c.) and acetic acid (2 c.c.). The mixture was kept overnight, then poured into cold 10% (w/v) sodium hydroxide solution (20 c.c.). The product was isolated by extraction with ether. Distillation yielded 1-1′-*hydroxy*cyclo*hexylhexan*-3-*one* (0·8 g.), b. p. 90—100° (bath-temp.)/10^{-5} mm., n_D^{20} 1·4782 (Found: C, 72·85; H, 11·5. $C_{12}H_{22}O_2$ requires C, 72·65; H, 11·2%).

1-1′-*Hydroxy*cyclo*hexylhex*-4-*en*-1-*yn*-3-*one* (XVII).—1-1′-Hydroxy*cyclo*hexylhex-4-en-1-yn-3-ol (5·7 g.) in acetone (300 c.c.) was shaken with manganese dioxide (75 g.) at 20° for 6 hours. The mixture was filtered and the solution evaporated under reduced pressure to a viscous oil (5·7 g.), n_D^{20} 1·5264. Light absorption: max. 228, 236, and 242 mμ; $E_{1\,\text{cm.}}^{1\%} = 620$, 575, and 450 respectively.

Chromatography of the crude product on alumina (*ca.* 250 g.) from benzene solution and distillation gave the *hydroxy-ketone* (3·73 g.), b. p. 100° (bath-temp.)/10^{-5} mm., n_D^{22} 1·5268 (Found: C, 74·9; H, 8·45. $C_{12}H_{16}O_2$ requires C, 74·95; H, 8·4%). Light absorption: max. 227 mμ; $E_{1\,\text{cm.}}^{1\%} = 620$; $\varepsilon = 12{,}000$. Inflexion, 236 mμ; $E_{1\,\text{cm.}}^{1\%} = 580$; $\varepsilon = 11{,}000$. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in bright prisms, m. p. 166° (Found: N, 14·9. $C_{18}H_{20}O_5N_4$ requires N, 15·05%). Light absorption in $CHCl_3$ (main band only): max., 386 mμ; $\varepsilon = 35{,}000$.

1-cyclo*Hex*-1′-*enylhex*-4-*en*-1-*yn*-3-*one* (XIX).—Phosphorus oxychloride (1·0 g.) in toluene (4 c.c.) and pyridine (4 c.c.) was added dropwise at 0° to a solution of the preceding hydroxy-ketone (1·0 g.) in toluene (4 c.c.). The mixture was warmed at 70—80° for 1 hour, then cooled, and ice was added. Isolation in the usual manner and distillation of the product gave the *ketone* (0·5 g.) as an unstable oil, b. p. 55—65° (bath-temp.)/10^{-4} mm., n_D^{17} 1·5683 (Found: C, 82·3; H, 8·3. $C_{12}H_{14}O$ requires C, 82·7; H, 8·1%). Light absorption: max., 280 and 304 mμ; ε = 12,000 and 15,000 respectively. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in orange prisms, m. p. 176°, undepressed on admixture with a specimen prepared from the product of manganese dioxide oxidation of 1-*cyclo*hex-1′-enylhex-4-en-1-yn-3-ol (Heilbron, Jones, Lewis, Richardson, and Weedon, *loc. cit.*) (Found: N, 15·85. $C_{18}H_{18}O_4N_4$ requires N, 15·8%). Light absorption in $CHCl_3$ (main band only): max. 397 mμ; ε = 31,500.

The hydroxy-ketone was recovered after being heated for 1 hour in benzene solution containing a trace of toluene-*p*-sulphonic acid.

6-1′-*Hydroxy*cyclo*hexylhex*-3-*en*-5-*yn*-2-*ol* (XV; R = H).—(*a*) 1-1′-Hydroxy*cyclo*hexylhex-4-en-1-yn-3-ol (3·0 g.) was shaken with a trace of quinol and 5% (w/v) sulphuric acid (30 c.c.) at room temperature for 36 hours. Isolation of the product with ether and distillation gave the *glycol* (1·8 g.), b. p. 120—130° (bath-temp.)/10^{-4} mm., n_D^{20} 1·5321 (Found: C, 73·95; H, 9·5. $C_{12}H_{18}O_2$ requires C, 74·15; H, 9·35%). Light absorption: max., 227 mμ; ε = 17,500; inflexion, 233 mμ; ε = 16,000.

(*b*) A solution of the di-Grignard complex of hex-3-en-5-yn-2-ol (40 g.) (Heilbron, Jones, Smith, and Weedon, *J.*, 1946, 57) in benzene (300 c.c.) was prepared in the usual manner, then cooled to 0°. *cyclo*Hexanone (45 g.) in benzene (75 c.c.) was added dropwise during ½ hour. Stirring was continued overnight at 20° and the solution poured into a saturated solution of ammonium chloride (200 g.) in water. Isolation in the usual manner gave the glycol (40 g.), b. p. 120—130° (bath-temp.)/10^{-4} mm., n_D^{15} 1·529. Light absorption: max. 227 mμ; ε = 12,000. Inflexion 234 mμ; ε = 10,000. Active hydrogen (Zerewitinoff): the glycol (50·6 mg.) yielded 13·2 c.c. of methane at 15°/747 mm., equiv. to 2·1 atoms of active hydrogen per mol.

6-1′-*Hydroxy*cyclo*hexyl-hexan*-2-*ol and -hexan*-2-*one*—The preceding glycol (4·324 g.) in ethyl acetate (50 c.c.) was shaken in hydrogen in the presence of Adams's catalyst (0·15 g.) until absorption was complete (1454 c.c. at 18°/760 mm., equiv. to 2·8 double bonds). The solvent and catalyst were removed and the residue was distilled, giving the saturated *glycol* (3·6 g.), b. p. 100—110° (bath-temp.)/10^{-5} mm., n_D^{18} 1·4870 (Found: C, 72·25; H, 11·9. $C_{12}H_{24}O_2$ requires C, 71·95; H, 12·05%). The *bis*-3 : 5-*dinitrobenzoate*, crystallised from acetone, had m. p. 133—135° (Found: C, 53·45; H, 5·1. $C_{26}H_{28}O_{12}N_4$ requires C, 53·05; H, 4·8%).

The saturated glycol (1·37 g.) in glacial acetic acid (5 c.c.) was treated with chromium trioxide (0·46 g.) in water (2 c.c.) and glacial acetic acid (2 c.c.). The mixture was kept at 20° overnight, then poured into aqueous sodium hydroxide (20 c.c.; 10% w/v). Isolation of the product with ether and distillation gave the *hydroxy-ketone* (0·85 g.), b. p. 90—100° (bath-temp.)/10^{-5} mm., n_D^{21} 1·4801 (Found: C, 72·55; H, 11·15. $C_{12}H_{22}O_2$ requires C, 72·65; H, 11·2%). The 2 : 4-*dinitrophenylsemicarbazone*, crystallised from alcohol, had m. p. 184° (decomp.) (Found: N, 16·2. $C_{19}H_{27}O_6N_5$ requires N, 16·6%).

6-1′-*Hydroxy*cyclo*hexylhex*-3-*en*-5-*yn*-2-*one* (XVIII).—6-1′-Hydroxy*cyclo*hexylhex-3-en-5-yn-2-ol (8·0 g.) in acetone (300 c.c.) was shaken with magnanese dioxide (75 g.) at 20° for 6 hours. Removal of oxide and solvent gave an oil (8·0 g.), n_D^{19} 1·5285. The ketonic product was separated by means of the Girard reagent P (cf. Girard and Sandulesco, *Helv. Chim. Acta*, 1936, **19**, 1095) and distilled, giving the *hydroxy-ketone* (1·3 g.), b. p. 100—110° (bath-temp.)/10^{-5} mm., n_D^{19} 1·5390 (Found: C, 74·9; H, 8·6. $C_{12}H_{16}O_2$ requires C, 74·95; H, 8·4%). Light absorption: max., 268 mμ; ε = 19,000. Inflexions, 258 and 272 mμ; ε = 17,500 and 17,500. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in red prisms, m. p. 184° (Found: C, 57·75; H, 5·55; N, 14·65. $C_{18}H_{20}O_5N_4$ requires C, 58·05; H, 5·4; N, 15·05%). Light absorption in $CHCl_3$ (main band only): max., 382 mμ; ε = 34,500.

The same yield of hydroxy-ketone was obtained by carrying out the above oxidation in a mixture (10 : 1) of light petroleum (b. p. 40—60°) and dioxan.

6-cyclo*Hex*-1′-*enylhex*-3-*en*-5-*yn*-2-*one* (XX).—Phosphorus oxychloride (1·2 g.) in toluene (5 c.c.) and pyridine (4 c.c.) was added dropwise at 0° to a solution of the preceding hydroxy-ketone (1·0 g.) in toluene (4 c.c.). The mixture was warmed at 70—80° for 1½ hours. Isolation of the product in the usual way gave an oil (0·5 g.), b. p. 70—75° (bath-temp.)/10^{-3} mm., n_D^{20} 1·5791, which with alcoholic semicarbazide acetate gave the semicarbazone of 6-*cyclo*hex-1′-enylhex-3-en-5-yn-2-one, yellow plates (0·44 g.) (from methanol), m. p. 186° (Heilbron, Jones, Lewis, Richardson, and Weedon, *loc. cit.*, give m. p. 185°). Light absorption: max., 310 mμ; ε = 43,500. Inflexion, 320 mμ; ε = 37,000. The semicarbazone (0·2 g.) was converted into the 2 : 4-*dinitrophenylhydrazone* which crystallised from ethyl acetate in needles (0·15 g.), m. p. 181—183°, undepressed on admixture with a specimen made from the authentic ketone (Found: N, 16·2. $C_{18}H_{18}O_4N_4$ requires N, 15·8%). Light absorption in $CHCl_3$ (main band only): max., 398 mμ; ε = 37,000.

The hydroxy-ketone was recovered after ½ hour's heating in benzene containing a trace of toluene-*p*-sulphonic acid.

2-(*Tetrahydro-2-pyranyloxy*)*hex*-3-*en*-5-*yne*.—A few drops of concentrated hydrochloric acid were added to a mixture of hex-3-en-5-yn-2-ol (32 g.) and dihydropyran (28 g.), the temperature being kept at 20°. After 3 hours the mixture was diluted with ether, and the solution was washed with aqueous sodium hydroxide (10% w/v), dried, and evaporated. Distillation gave the *tetrahydropyranyl ether* (40 g.), b. p. 99—100°/10 mm., n_D^{23} 1·4771, which gave a white precipitate with ammoniacal silver nitrate (Found : C, 72·9; H, 8·95. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·95%). Light absorption : max., 227 mμ; ε = 16,500.

6-1′-*Hydroxy*cyclo*hexyl*-2-(*tetrahydro*-2-*pyranyloxy*)*hex*-3-*en*-5-*yne*.—The preceding tetrahydropyranyl ether (6·5 g.) in ether (3 c.c.) was added during 15 minutes to a stirred solution of sodamide (prepared from 0·8 g. of sodium; cf. Vaughn, Vogt, and Nieuwland, *J. Amer. Chem. Soc.*, 1934, **56**, 2120) in liquid ammonia (100 c.c.). After 3 hours, *cyclo*hexanone (3·5 g.) in ether (5 c.c.) was added dropwise and stirring was continued for 3½ hours. Ammonium chloride (2 g.) was added and the ammonia was allowed to evaporate overnight. The residue was extracted with ether, and the ethereal solution was washed with water and dried (Na_2SO_4). Distillation gave the *hydroxy-acetal* (4·0 g.), b. p. 105—115° (bath-temp.)/10^{-4} mm., n_D^{23} 1·5155 (Found : C, 73·7; H, 9·1. $C_{17}H_{26}O_3$ requires C, 73·35; H, 9·4%) (Unsaturation, equiv. to 3 double bonds). Light absorption: max., 227 mμ; ε = 20,000. Inflexion, 236 mμ; ε = 14,000. Active hydrogen (Zerewitinoff) : the hydroxy-acetal (0·121 g.) gave 11·5 c.c. of methane at 15°/750 mm., equiv. to 1·1 atoms of active hydrogen per mol.

Reaction in ethereal solution of the tetrahydropyranyl ether with *cyclo*hexanone, by the Grignard method, gave 6-1′-hydroxyl*cyclo*hexylhex-3-en-5-yn-2-ol. The structure of the product was confirmed by Zerewitinoff determination (2·05 atoms of active hydrogen per mol.), and by oxidation (manganese dioxide) to the hydroxy-ketone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 185°).

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