

*Researches on Acetylenic Compounds. Part XLIII.\* Reductions with Lithium Aluminium Hydride.*

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Lithium aluminium hydride acts as a highly selective reducing agent toward acetylenic alcohols and glycols of various types. The steric configurations of the ethylenic products are discussed; *trans*-forms appear to be produced invariably. A number of spectrographic correlations are described.

THE reduction of cinnamic acid and of cinnamaldehyde either to 3-phenylpropyl alcohol or, under milder conditions, to cinnamyl alcohol (Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 1197, 2548; Hochstein and Brown, *J. Amer. Chem. Soc.*, 1948, **70**, 3484) suggested that acetylenic compounds might similarly undergo partial or complete reduction at the triple bond when treated with lithium aluminium hydride. Such reductions have now been found to occur.

With an excess of the reagent at 20°, phenylpropionic ester was converted essentially into cinnamyl alcohol; when the reactants were mixed at -70°, the product consisted essentially of phenylpropargyl alcohol. Benedict and Russell (*J. Amer. Chem. Soc.*, 1951, **73**, 5444) have described similar reactions with acetylenedicarboxylic and propiolic acids; see also Micovic and Mikhailovic (*Glasnik Chem. Drushty*, 1951, **16**, 19).

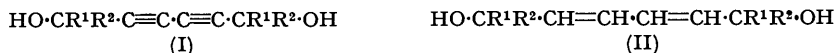
1-Ethynylcyclohexene was unaffected by the reagent in boiling ether, but gave a mixture of unsaturated hydrocarbons in dioxan at the boiling point. Similarly vigorous conditions gave the vinyl compound from 1-ethynylcyclohexanol, while a larger excess of reagent and

\* Part XLI, *J.*, 1954, 147.

a longer reaction period gave 1-ethylcyclohexanol. 1-Phenylprop-2-yn-1-ol, on the other hand, gave the vinyl compound in 94% yield at 34°.

These reactions lack preparative interest, and hence were not studied intensively; they did, however, suggest that hydroxyl groups adjacent to the acetylenic linkage might facilitate reduction.

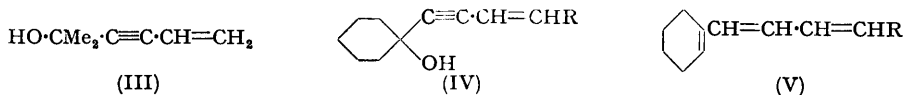
When the reaction was applied to diacetylenic glycols (I) the corresponding dienediols were formed. Material of ca. 87% purity was obtained only when 4 mols. of the hydride



were used, and then with quite short reaction periods. It was also noted that the ultra-violet light-absorption curves of the products resulting from the action of smaller quantities of the reagent, and/or shorter reaction times, were consistent with the presence of (I) and (II) only; if the corresponding vinylacetylenic glycol had been present in appreciable quantity some deviation from additivity would have been expected. Under the optimal conditions a 40% yield of the pure diene glycol was obtained after further crystallisation.

By use of these optimal conditions, a number of other diacetylenic glycols (I) were reduced to the corresponding dienediols. Thus, where  $\text{R}^1\text{R}^2 = [\text{CH}_2]_5$ ,  $\text{R}^1 = \text{R}^2 = \text{Ph}$ , and  $\text{R}^1 = \text{C}_9\text{H}_{19}$ ,  $\text{R}^2 = \text{Me}$ , pure diene glycols were obtained in yields of 40%, 50%, and 25%, respectively. The simplest diacetylenic glycol (I;  $\text{R}^1 = \text{R}^2 = \text{H}$ ) gave the expected diene in 26% yield. The glycol (I;  $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{Me}$ ) gave a liquid diene of about 88% purity (by ultra-violet spectroscopic assay); this compound has since been obtained pure as a low-melting solid by Ahmad, Sondheimer, Weedon, and Woods using our method. The glycol (I;  $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{Ph}$ ) (*J.*, 1952, 4089) gave a reduction product separable by chromatography into the expected diene-glycol and a hydrocarbon fraction. The former melted unsharply even after repeated crystallisation and was probably a mixture of *meso*- and racemic forms. The latter gave on repeated crystallisation all-*trans*-diphenylhexatriene; other hydrocarbons were probably present in the crude non-polar fraction.

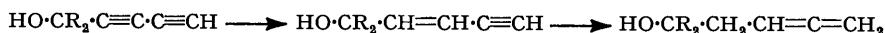
Meanwhile, Chanley and Sobotka (*J. Amer. Chem. Soc.*, 1949, 71, 4140) had described the reduction of 4-cyclohex-1'-enylbut-3-yn-2-ol to the corresponding diene alcohol in good yield, only 0.63 mol. of lithium aluminium hydride being used. Such a method of reducing vinylacetylenic alcohols would be of great value, since inhomogeneous products are usually obtained by catalytic hydrogenation, while success in reductions with a zinc-copper couple (Nazarov and Fisher, *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk*, 1944, 341) apparently depends upon the quality of the zinc used, difficulty having been experienced with this reaction in these laboratories. Accordingly the alcohols (III) and (IV;  $\text{R} = \text{H}$  and  $\text{Me}$ )



were treated with lithium aluminium hydride under the conditions Chanley and Sobotka had used. In each case a good yield of the corresponding diene-alcohol was obtained; that from (IV;  $\text{R} = \text{Me}$ ) was stable, but those derived from (III) and (IV;  $\text{R} = \text{H}$ ), like hexa-3:5-dien-2-ol (Heilbron, Jones, McCombie, and Weedon, *J.*, 1945, 84) and other 1-monomethylbutadienes, were unstable and easily polymerised. These substances proved very susceptible to dehydration in presence of acids (whereas the vinylacetylenic alcohols are remarkably resistant—see Hamlet, Henbest, and Jones, *J.*, 1951, 2652), giving the unstable trienes (V;  $\text{R} = \text{Me}$  and  $\text{H}$ ).

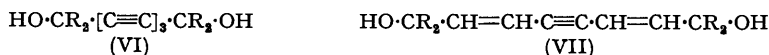
In view of these results with the vinylacetylenic alcohols  $\text{HO}\cdot\text{CR}_2\cdot\text{C}\equiv\text{C}\cdot\text{CH}=\text{CHR}^1$ , two alcohols  $\text{HO}\cdot\text{CR}^1\text{R}^2\cdot\text{CH}=\text{CH}\cdot\text{C}\equiv\text{CH}$  ( $\text{R}^1 = \text{R}^2 = \text{H}$ ;  $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{Me}$ ) were investigated, a small excess (0.6 mol.) of the reagent being employed. That the products were the allenic alcohols,  $\text{HO}\cdot\text{CR}^1\text{R}^2\cdot\text{CH}_2\cdot\text{CH}=\text{C}=\text{CH}_2$ , was proved by ozonolysis, hydrogenation, the absence of intense ultra-violet light absorption, and by infra-red spectroscopy, a strong band at  $1970\text{ cm}^{-1}$  indicating an allene grouping. The very convenient preparation of these alcohols should facilitate introduction of terminal allene systems into a wide variety of structures.

The reduction of the diacetylenic alcohol  $\text{HO}\cdot\text{CMe}_2\cdot\text{C}\equiv\text{C}\cdot\text{C}\equiv\text{CH}$  gave the vinyl-acetylenic analogue  $\text{HO}\cdot\text{CMe}_2\cdot\text{CH}=\text{CH}\cdot\text{C}\equiv\text{CH}$ , previously prepared by anionotropic rearrangement (Jones and McCombie, *J.*, 1943, 261); similarly penta-2 : 4-diyne-1-ol gave pent-2-en-4-yn-1-ol. It is thus evident that the transformation :



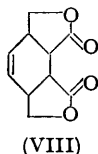
can be effected by two successive lithium aluminium hydride reductions, the same conditions being used in each. The product of the first reduction must be a complex incapable of further reaction since 4 mols. (possibly an unnecessary excess) of the reagent were employed in the reduction of the diacetylenic alcohol.

The method employed for the diacetylenic glycols was next applied to the higher polyacetylenic glycols recently described by Armitage, Cook, Jones, and Whiting (*J.*, 1952, 2010, 2014). When 5 mols. of the reagent were used, the glycols (VI;  $\text{R} = \text{Me}$  and  $\text{Ph}$ )



gave the corresponding divinyl acetylenic glycols (VII) in *ca.* 50% yield—a good example of the specificity of this reaction. The tetra-acetylenic glycol  $\text{HO}\cdot\text{CMe}_2\cdot[\text{C}\equiv\text{C}]_4\cdot\text{CMe}_2\cdot\text{OH}$ , similarly gave  $\text{HO}\cdot\text{CMe}_2\cdot\text{CH}=\text{CH}\cdot[\text{C}\equiv\text{C}]_2\cdot\text{CH}=\text{CH}\cdot\text{CMe}_2\cdot\text{OH}$ , easily recognised by the very characteristic ultra-violet absorption properties of its unsaturated system.

*Stereochemistry of the Reduction Products.*—In the catalytic hydrogenation of acetylenic compounds *cis*-ethylenes are usually obtained, but chemical reduction usually gives products of *trans*-configuration (see Greenlee and Fernelius, *J. Amer. Chem. Soc.*, 1942, 64, 2505; Crombie, *Quart. Reviews*, 1952, 6, 101). In the present work *trans*-ethylenes were apparently formed in every case. The glycol obtained from  $\text{HO}\cdot\text{CPh}_2\cdot[\text{C}\equiv\text{C}]_2\cdot\text{CPh}_2\cdot\text{OH}$  differs from the previously-described material resulting from catalytic hydrogenation, and more direct evidence is provided by the occurrence of strong absorption in the infra-red near  $960\text{ cm.}^{-1}$  in six reaction products containing diene, vinyl-acetylene, and vinyl ethynylvinyl groupings. In no case was a strong band observed in the  $680\text{--}730\text{ cm.}^{-1}$  region typical of simple *cis*-ethylenes. The ultra-violet absorption spectra of the glycols (II) confirm this conclusion. Braude and Coles (*J.*, 1951, 2085) showed that allylic hydroxyl groups increased the intensity of absorption of *trans*- but not of *cis*-1-substituted butadienes; and the even greater absorption intensity of these glycols, relative to hexa-2 : 4-diene, implies that both ethylenic linkages are probably *trans*. Final proof of the *trans-trans*-configuration of the glycol (II;  $\text{R} = \text{H}$ ) was obtained by means of a Diels–Alder reaction with maleic anhydride, which gave the dilactone (VIII). This reaction was complicated by the simultaneous occurrence of polymer formation, and gave a yield of only 20%; however, Diels–Alder reactions even with *cis*-piperylene are known to proceed with such difficulty (see *inter al.*, Craig, *J. Amer. Chem. Soc.*, 1950, 72, 1678) that this reaction can be considered good evidence of a *trans-trans*-configuration.



In earlier attempts to obtain chemical confirmation of the double-bond configuration in the glycols (II), the three isomeric methyl muconates were prepared by the method of Elvidge, Linstead, Orkin, Sims, Baer, and Pattison (*J.*, 1950, 2228, 2235). All, however, gave little or none of the expected primary glycols on treatment with lithium aluminium hydride under varied conditions, and the *trans-trans*-ester also failed to react normally with methylmagnesium iodide.

The ultra-violet absorption spectra of certain of the compounds obtained have been discussed above inasmuch as they assist in identification; but in the case of the diene alcohols and glycols, constitution and purity may be assured independently, and some interesting correlations may be deduced. The results are tabulated.

The data for a range of diene glycols (II) add to the evidence in favour of small but definite hyperchromic and bathochromic effects resulting from the introduction of a hydroxyl group on a carbon atom adjacent to a diene system, as was first observed by Braude and Coles (*loc. cit.*). However, it appears that a marked increase in the intensity of absorption of a 1 : 4-disubstituted diene also results when the length of the existing

alkyl group is considerably increased—indeed it has been suggested, in view of the higher  $\epsilon$  values obtained with long-chain dienes that the value for  $\epsilon_{\max}$ , quoted for hexa-2 : 4-diene is too low (Bolland and Koch, *J.*, 1945, 445), although considerable care was taken by Gillam *et al.* (*loc. cit.*) to avoid errors due to the polymerisation of the simple hydrocarbon.

TABLE 1. *Light absorption of trans-trans-dienes, CHR=CH·CH=CHR.*

R	R <sup>1</sup>	$\lambda_{\max}$ . (Å)	$10^{-3} \epsilon$	Ref.	R	R <sup>1</sup>	$\lambda_{\max}$ . (Å)	$10^{-3} \epsilon$
Me ...	Me	2270	22·5	<sup>1</sup>	CH <sub>2</sub> ·OH .....	CH <sub>2</sub> ·OH	2290	31
C <sub>6</sub> H <sub>13</sub>	[CH <sub>2</sub> ] <sub>7</sub> ·CO <sub>2</sub> H	2310	29	<sup>2</sup>	CMe <sub>2</sub> ·OH .....	CMe <sub>2</sub> ·OH	2290	32
Me ...	C<[CH <sub>2</sub> ] <sub>5</sub> ·OH	2305	27·5		CMe(C <sub>9</sub> H <sub>19</sub> )·OH	CMe(C <sub>9</sub> H <sub>19</sub> )·OH	2305	39
					C<[CH <sub>2</sub> ] <sub>5</sub> ·OH	C<[CH <sub>2</sub> ] <sub>5</sub> ·OH	2330	33

TABLE 2. *Light absorption of trans-dienes, CHR=CH·CH=CH<sub>2</sub>.*

R	$\lambda_{\max}$ . (Å)	$10^{-3} \epsilon$	Ref.	R	$\lambda_{\max}$ . (Å)	$10^{-3} \epsilon$
Me .....	2230	23·0	<sup>1</sup>	CMe <sub>2</sub> ·OH .....	2240	24·5 *
CHMe·OH .....	2230	28·0	<sup>3</sup>	C<[CH <sub>2</sub> ] <sub>5</sub> ·OH .....	2260	22 *

\* Intensity values may be low.

<sup>1</sup> Booker, Evans, and Gillam, *J.*, 1940, 1453; configuration probable from method of formation.

<sup>2</sup> Nichols, Herb, and Riemenschneider, *J. Amer. Chem. Soc.*, 1951, **73**, 247. <sup>3</sup> Heilbron, Jones, McCombie, and Weedon, *loc. cit.*

If the effect is real, the remarkably high intensity observed (and verified by replicate determinations) for (II; R<sup>1</sup> = Me, R<sup>2</sup> = C<sub>9</sub>H<sub>19</sub>) is at once explicable, as both of these hyperchromic effects would be simultaneously operative. Much scattered evidence supports the postulated weight effect (cf. Koch, *J.*, 1948, 1123, for an example involving the  $\beta$ -alkylstyrene chromophore); it evidently involves also a small bathochromic shift (*ca.* +10 Å for each substitution of C<sub>6</sub>H<sub>13</sub> for Me).

Another, and quite distinct, small effect discernible in the figures quoted is the bathochromic effect resulting from the substitution of 1-hydroxycyclohexyl for 1-hydroxy-1-methylethyl or hydroxymethyl. This implies that the effect of an exocyclic environment observed by Woodward (*J. Amer. Chem. Soc.*, 1942, **64**, 72) as responsible for a shift of +50 Å in the absorption maximum of a conjugated diene, is paralleled by a similar but smaller shift (+20 Å) when the exocyclic bond is that joining a  $\geq$ C·OH group to the diene system. The double operation of this effect brings  $\lambda_{\max}$  for (II; R<sup>1</sup>R<sup>2</sup> = [CH<sub>2</sub>]<sub>5</sub>) to 2330 Å, perhaps the first instance of a simple disubstituted diene found to absorb maximally at or above the wave-length given by Woodward (*loc. cit.*) for trisubstituted dienes (2320 Å).

The glycols (II; R<sup>1</sup> = R<sup>2</sup> = Ph) and (II; R<sup>1</sup> = Ph, R = H) showed maxima displaced by +120 Å and +135 Å, respectively, and intensified when compared with the aliphatic glycols. Similar displacements were observed in the cases of (X; R = Ph), where the system ·CH=CH·C≡C·CH=CH· is involved, and the diacetylenic glycols (I; R<sup>1</sup> = R<sup>2</sup> = Ph) and (I; R<sup>1</sup> = Ph, R<sup>2</sup> = H) discussed earlier (Armitage, Cook, Entwistle, Jones, and Whiting, *J.*, 1952, 1998). Evidently interaction through >CR·OH groupings between aryl or alkenyl groups and unsaturated systems of varied types is a general phenomenon.

### EXPERIMENTAL

"Lithium aluminium hydride" refers to a commercial grade estimated to contain about 85% of the actual reagent, melting-points were determined on the Kofler block, and ultraviolet absorption spectra were determined in absolute ethanol with a Unicam SP 500 spectrophotometer.

*Reduction of Methyl Phenylpropiolate.*—(a) A solution of lithium aluminium hydride (0·5M; 62·5 c.c.) in ether was cooled to -78° while methyl phenylpropiolate (10·0 g.) was added dropwise. After 5 min., water (5 c.c.) was added, and the mixture was allowed to reach room temperature. Isolation of the product and distillation of the neutral fraction gave fairly pure phenylpropargyl alcohol (7·9 g., 96%), b. p. 103—105°/1·5 mm.,  $n_D^{25}$  1·5820,  $\lambda_{\max}$  2420 and 2510 Å ( $\epsilon$  = 14,600 and 13,600, respectively). Its 3 : 5-dinitrobenzoate had m. p. 131—132°. An authentic specimen,  $n_D^{25}$  1·5834,  $\lambda_{\max}$  2410 and 2500 Å ( $\epsilon$  = 16,900 and 14,000, respectively) (Lai, *Bull. Soc. chim.*, 1933, **53**, 682), gave an identical 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 131—132° (Found: N, 8·4. C<sub>16</sub>H<sub>10</sub>O<sub>6</sub>N<sub>2</sub> requires N, 8·6%).

(b) When, in the above experiment, 94 c.c. of the standard solution of the hydride and a reaction-time of 15 min. at room temperature were employed, the distillate (6.9 g., 83%) had b. p.  $78^{\circ}/0.5$  mm.,  $n_D^{15}$  1.5852,  $\lambda_{\max}$ , 2500,  $\lambda_{\text{infl}}$ , 2485 Å ( $\epsilon = 17,400$  and 17,200, respectively). Recrystallisation of the partly solidified product from light petroleum gave *trans*-cinnamyl alcohol (2.0 g.), m. p.  $33^{\circ}$  undepressed on admixture with an authentic specimen, which had  $\lambda_{\max}$ , 2510,  $\lambda_{\text{infl}}$ , 2485 Å,  $\epsilon = 19,600$  and 19,400, respectively.

*1-Vinylcyclohexanol*.—A mixture of 1-ethynylcyclohexanol (4.0 g.) and lithium aluminium hydride (2.0 g.) in dioxan (100 c.c.) was refluxed for 1 hr. Addition of water and distillation of the product gave 1-vinylcyclohexanol (3.0 g.), b. p.  $62-64^{\circ}/11$  mm.,  $n_D^{14}$  1.4758 (Nazarov *et al.*, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1946, 305, give b. p.  $67.5-68^{\circ}/15$  mm.,  $n_D^{20}$  1.4740). No precipitate was obtained with ammoniacal silver nitrate solution. The 3 : 5-dinitrobenzoate melted at  $103.5-104^{\circ}$  (Cook and Lawrence, *J.*, 1938, 61, give m. p.  $101-102^{\circ}$ ).

*1-Ethylcyclohexanol*.—A mixture of 1-ethynylcyclohexanol (6.2 g.) and lithium aluminium hydride (5.0 g.) in dioxan (250 c.c.) was heated under reflux for 18 hr. Isolation of the product as above gave 1-ethylcyclohexanol (4.5 g., 71%), b. p.  $67^{\circ}/16$  mm.,  $n_D^{15}$  1.4678 (Williams and Edwards, *J. Amer. Chem. Soc.*, 1947, 69, 336, give b. p.  $77^{\circ}/20$  mm.,  $n_D^{20}$  1.4618). No hydrogen was absorbed over reduced platonic oxide; the 3 : 5 dinitrobenzoate had m. p.  $127.5-128.5^{\circ}$  (Cook and Lawrence, *loc. cit.*, give m. p.  $127-127.5^{\circ}$ ).

*1-Phenylprop-2-en-1-ol*.—1-Phenylprop-2-yn-1-ol (5.0 g.) was added to an ethereal suspension of lithium aluminium hydride (3.6 g.), and the mixture was heated under reflux for 4 hr. Decomposition of the complex and distillation of the neutral fraction yielded the alcohol (4.75 g., 94%), b. p.  $56^{\circ}/0.05$  mm.,  $n_D^{16}$  1.5410 (Braude, Jones, and Stern, *J.*, 1946, 396, give b. p.  $53-54^{\circ}/0.15$  mm.,  $n_D^{15}$  1.5464). The *p*-nitrobenzoate formed plates, m. p.  $45.5-46^{\circ}$ , from methanol (Burton and Ingold, *J.*, 1928, 904, give m. p.  $45-46^{\circ}$ ).

*2-Methylhexa-3 : 5-dien-2-ol*.—To a stirred suspension of lithium aluminium hydride (1.08 g.) in ether (300 c.c.), 2-methylhex-5-en-3-yn-2-ol (Nazarov and Torgov, *Zhur. Obshchey Khim. S.S.S.R.*, 1948, 18, 1332) was added, and the mixture was heated under reflux for 3 hr. Distillation of the product gave the diene-alcohol (4.48 g., 88%), b. p.  $55^{\circ}/12.5$  mm.,  $n_D^{20}$  1.4758 (Found : C, 74.6; H, 10.35. Calc. for  $C_7H_{12}O$  : C, 74.9; H, 10.7%). Nazarov and Fisher, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1942, 135, record b. p.  $42-43^{\circ}/9$  mm.,  $n_D^{20}$  1.4693.

*1-1'-Hydroxycyclohexylbuta-1 : 3-diene*.—Reduction of 1-1'-hydroxycyclohexylbut-3-en-1-yne (2.0 g.) (Hamlet, Henbest, and Jones, *loc. cit.*) with lithium aluminium hydride (0.32 g.) for 3 hr. at  $35^{\circ}$  gave, after distillation, the *diene-alcohol* (1.38 g.), b. p.  $100^{\circ}/13$  mm.,  $n_D^{24}$  1.5075, m. p.  $23^{\circ}$  (Found : C, 79.1; H, 10.75.  $C_{10}H_{16}O$  requires C, 78.9; H, 10.6%).

*1-1'-Hydroxycyclohexylpenta-1 : 3-diene*.—Similar reduction of the higher homologue (*ibid.*, *loc. cit.*; mixture of *cis*- and *trans*-isomers) (5.0 g.) gave the corresponding *diene* (3.95 g.), b. p.  $87^{\circ}/0.7$  mm.,  $n_D^{19}$  1.5192 (Found : C, 79.2; H, 10.9.  $C_{11}H_{18}O$  requires C, 79.4; H, 10.9%).

*1-cycloHex-1'-enylbuta-1 : 3-diene*.—This was prepared by distilling the corresponding tertiary alcohol from a little potassium hydrogen sulphate. The product, dissolved in light petroleum, was passed through alumina. The very unstable *hydrocarbon* had b. p.  $145^{\circ}$  (bath temp.)/14 mm.,  $n_D^{21}$  1.5594,  $\lambda_{\max}$ , 2555, 2650, and 2750 Å ( $\epsilon = 32,300$ , 43,400, and 34,500, respectively) (Found : C, 89.3; H, 10.65.  $C_{10}H_{14}$  requires C, 89.5; H, 10.5%).

*1-cycloHex-1'-enylpenta-1 : 3-diene*.—Prepared similarly, this had b. p.  $70^{\circ}$  (bath temp.)/0.1 mm.,  $n_D^{20}$  1.5605,  $\lambda_{\text{infl}}$ , 2600,  $\lambda_{\max}$ , 2670 and 2770 Å ( $\epsilon = 27,500$ , 36,800, and 29,100, respectively) (Found : C, 88.75; H, 10.95.  $C_{11}H_{16}$  requires C, 89.1; H, 10.9%).

*Penta-3 : 4-dien-1-ol*.—Reduction of pent-2-en-4-yn-1-ol (6.0 g.; Haynes, Heilbron, Jones, and Sondheimer, *J.*, 1947, 1583) with lithium aluminium hydride (1.7 g.) at  $35^{\circ}$  for 3 hr. gave the allenic *alcohol* (5.1 g.), b. p.  $57-58^{\circ}/16$  mm.,  $n_D^{23}$  1.4760 (Found : C, 69.1, 69.9; H, 8.7, 9.1.  $C_5H_8O$  requires C, 71.4; H, 9.6%). Catalytic hydrogenation over reduced platonic oxide resulted in an uptake of 2.2 mol. A 3 : 5-dinitrobenzoate, m. p.  $39-40.5^{\circ}$ , was obtained (Found : C, 51.9; H, 3.7; N, 10.0.  $C_{12}H_{10}O_6N_2$  requires C, 51.8; H, 3.65; N, 9.9%).

*Hexa-4 : 5-dien-2-ol*.—Reduction of hex-3-en-5-yn-2-ol (8.0 g.; Heilbron, Jones, Smith, and Weedon, *J.*, 1946, 54) with lithium aluminium hydride (2.05 g.) as above gave the allenic *alcohol* (5.4 g.), b. p.  $54-55^{\circ}/14$  mm.,  $n_D^{18}$  1.4718 (Found : C, 73.1; H, 10.5.  $C_6H_{10}O$  requires C, 73.4; H, 10.25%). Hydrogenation over reduced platonic oxide (absorption 2.05 mol.) and oxidation with chromic acid gave hexan-2-one, isolated as its 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p.  $108-109^{\circ}$ . On ozonolysis in acetic acid solution, formaldehyde was obtained, isolated in 59% yield as the dimedone derivative, m. p. and mixed m. p.  $188-189^{\circ}$ .

*Pent-2-en-4-yn-1-ol*.—Penta-2 : 4-diyn-1-ol (3.0 g.; Armitage, Jones, and Whiting, *J.*, 1952,

1993) was added to an ethereal suspension of lithium aluminium hydride (2.85 g.), and the mixture was heated under reflux for 4 hr. Isolation of the product gave pent-2-en-4-yn-1-ol (1.7 g.), b. p. 61°/10 mm.,  $n_D^{20}$  1.4970 (Haynes *et al.*, *loc. cit.*, give b. p. 71—73°/19 mm.,  $n_D^{20}$  1.4972).

*2-Methylhex-3-en-5-yn-2-ol.*—Treatment of 2-methylhexa-3:5-diyne-2-ol (4.9 g.; Armitage, Jones, and Whiting, *loc. cit.*) with lithium aluminium hydride (7.7 g.) as above gave the vinylacetylenic alcohol (3.45 g.), b. p. 69—73°/22 mm.,  $n_D^{20}$  1.4764 (Jones and McCombie, *loc. cit.*, give b. p. 91—93°/50 mm.,  $n_D^{20}$  1.4711). Light absorption: maximum, 2230 Å, inflexion, 2310 Å;  $\epsilon = 12,200$  and 9100, respectively.

*Diacetylenic Glycols.*—In preliminary experiments with (I;  $R^1 = R^2 = Me$ ) reaction time and reagent proportions were varied independently, the total glycol fraction (insoluble in cold benzene) being analysed spectroscopically. All products gave the diene-glycol (II) on repeated crystallisation, in low yield when smaller quantities of the hydride were employed. The use of more than 4 mol. of reagent did not increase the purity of crude (II), but did reduce the total glycol fraction.

*General Method for Diacetylenic Glycols.*—To a stirred mixture of lithium aluminium hydride (4.5 mol.) and ether (100 c.c./g.) the diacetylenic glycol (Armitage, Jones, and Whiting, *J.*, 1951, 44) was added, and the mixture was heated under reflux for 4—18 hr.; the reaction period was not critical. Addition of ethyl acetate, then sulphuric acid, and isolation of the neutral fraction gave a syrup which was dissolved in warm benzene. The solid which separated on cooling was recrystallised to constant melting point and ultra-violet absorption intensity. The following were thus obtained:

trans-trans-2:7-Dimethylocta-3:5-diene-2:7-diol (2.0 g.) [from the corresponding diacetylenic glycol (5.0 g.)] as needles, m. p. 107—108° (from benzene) (Found: C, 70.3; H, 10.6.  $C_{10}H_{18}O_2$  requires C, 70.55; H, 10.7%). Unlike the starting material, the diene-glycol decomposed partly in a few weeks in air at room temperature.

10:15-Dimethyltetracos-11:13-diene-10:15-diol, m. p. 104—105°, in 25% yield (Found: C, 79.05; H, 12.55.  $C_{26}H_{50}O_2$  requires C, 79.1; H, 12.75%).

1:4-Bis-1'-hydroxycyclohexylbuta-1:3-diene, obtained in 40% yield, had m. p. 115—116° after crystallisation from light petroleum (b. p. 60—80°) (Found: C, 76.5; H, 10.5.  $C_{16}H_{26}O_2$  requires C, 76.75; H, 10.5%).

1:1:6:6-Tetraphenylhexa-2:4-diene-1:6-diol, m. p. 177°, was obtained in 50% yield (Found: C, 86.35; H, 6.25.  $C_{30}H_{26}O_2$  requires C, 86.1; H, 6.25%).

*Hexa-2:4-diene-1:6-diol.*—The corresponding diacetylenic glycol (8.0 g.) was reduced with lithium aluminium hydride (13.8 g.; crude), and the product was isolated by continuous extraction with ether. Sublimation of the resultant semi-solid material at  $10^{-4}$  mm. followed by four recrystallisations from benzene gave the diene-glycol (2.2 g., 27%), m. p. 105.5—106.5° (Found: C, 63.35; H, 6.65. Calc. for  $C_8H_{10}O_2$ : C, 63.15; H, 6.85%) (Prévost, *Ann. Chim.*, 1928, 10, 398, gives m. p. 105°).

3:6-Bishydroxymethylcyclohex-4-ene-1:2-dicarboxylic Dilactone.—The above glycol (350 mg.), maleic anhydride (300 mg.), and benzene (40 c.c.) were heated under reflux for 30 min., set aside at 20° for 18 hr., and then evaporated to dryness. Crystallisation of the product from ethanol gave the dilactone (120 mg., 20%) as needles, m. p. 167.5—168.5° (Found: C, 62.0; H, 5.25.  $C_{10}H_8O_4$  requires C, 61.85; H, 5.2%).

1:6-Diphenylhexa-1:3:5-triene and trans-trans-1:6-Diphenylhexa-2:4-diene-1:6-diol.—Reduction of 1:6-diphenylhexa-2:4-diyne-1:6-diol (6.6 g.) by the general method for 4 hr. gave a neutral fraction which was separated into (a) a portion soluble in cold benzene (3.9 g.), and (b) an insoluble residue. The former was passed through alumina (deactivated) in benzene solution, then crystallised three times from light petroleum, giving diphenylhexatriene (1.7 g., 30%), m. p. 197—200° (Found: C, 93.1; H, 6.8. Calc. for  $C_{18}H_{16}$ : C, 93.1; H, 6.9%). Light absorption: maximum, 3525 Å, inflexions, 3360 and 3685 Å ( $\epsilon = 66,000$ , 53,500, and 49,000, respectively). Kuhn *et al.* (*Z. physikal. Chem.*, 1935, 29, B, 384) give m. p. 200° and ultra-violet maxima at 3350, 3490, and 3700 Å ( $\epsilon = 54,000$ , 67,000, and 55,000, respectively).

The residue (a) was recrystallised from hot benzene to give the trans-trans-glycol (1.8 g., 27%), m. p. 108.5—111° not altered on recrystallisation (Found: C, 80.85; H, 6.95.  $C_{18}H_{18}O_2$  requires C, 81.2; H, 6.8%). Kuhn *et al.* (*Ber.*, 1938, 71, 1889) give m. p. 103—104° for the glycol (*cis-cis*?) obtained by catalytic semihydrogenation.

2:9-Dimethyldeca-3:7-dien-5-yne-2:9-diol.—Reduction, by the general method used for diacetylenic glycols, of 2:9-dimethyldeca-3:5:7-triyne-2:9-diol (2.0 g.; Armitage, Cook, Jones, and Whiting, *J.*, 1952, 2010) gave the divinylacetylenic glycol (0.9 g., 44%), which

formed needles, m. p. 120.5—121.5, after recrystallisation from benzene (Found: C, 74.1; H, 9.15.  $C_{13}H_{18}O_2$  requires C, 74.15; H, 9.35%). Light absorption: maxima, 2635 and 2780 Å ( $\epsilon = 22,800$  and 18,400); inflexion, 2150 Å ( $\epsilon = 9200$ ) (cf. Heilbron, Jones, *et al.*, *J.*, 1945, 77).

1 : 1 : 8 : 8-Tetraphenylocta-2 : 6-dien-4-yne-1 : 8-diol.—The triacetylenic glycol from benzophenone (3.0 g.) was reduced as described above, giving after 4 hr. the tetraphenyloctadienyndiol (1.75 g., 58%) as irregular plates, m. p. 161—162°, from benzene (Found: C, 86.5; H, 6.05.  $C_{32}H_{26}O_2$  requires C, 86.8; H, 5.9%). Light absorption: maxima, 2755 and 2860 Å ( $\epsilon = 28,400$  and 22,700, respectively).

2 : 11-Dimethyldodeca-3 : 9-diene-5 : 7-diyne-2 : 11-diol.—Reduction of the corresponding tetrayne-glycol (Armitage, Jones, and Whiting, *J.*, 1952, 2014) at the boiling-point gave a crude product the ultra-violet absorption spectrum of which suggested over-reduction. When, however, the glycol was stirred with 5 mols. of the hydride at room temperature for 18 hr., the characteristic bands of the expected chromophore were prominent in the crude neutral product. This, a red syrup (2.0 g. from 2.0 g. of the starting material) was dissolved in warm benzene (10 c.c.) and treated with animal charcoal. When the solution cooled, crystals (0.4 g.; m. p. 92—105°) separated, and were purified by chromatography on deactivated alumina. Recrystallisation of the product (0.3 g.; m. p. 104—114°) from aqueous methanol gave needles, m. p. 123—125° (Found: C, 77.1; H, 8.45.  $C_{14}H_{18}O_2$  requires C, 77.0; H, 8.3%). Light absorption: maxima, 2290, 2360, 2480, 2620, 2760, 2930, and 3120 Å ( $\epsilon = 33,100, 33,700, 25,700, 9400, 17,600, 27,300, \text{ and } 22,300$ , respectively) (cf. Bowden, Heilbron, Jones, and Sargent, *J.*, 1947, 1579).

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