49. *Studies in the Polyene Series. Part XIII. Acetylenyl Glycols from Polyene Aldehydes and their Rearrangement with Acids.*

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Acetylenyl glycols (II; $n = 2$ and 3) are prepared from sorbaldehyde (I; $n = 2$) and octatrienal (I; $n = 3$) in 42 and 20% yields respectively. On treatment with acids these glycols undergo dual anionotropic rearrangements giving conjugated polyenyne glycols (III; $n = 2$ and 3), the constitutions of which are proved by complete hydrogenation, followed by hypobromite oxidation of the saturated glycols to known C_{12} and C_{16} dicarboxylic acids. The rearranged glycols, which are both yellow, closely resemble corresponding members of the polyene series in their light-absorption properties.

We have already described the preparation of the acetylenyl glycol from crotonaldehyde and certain of its properties (J., 1943, 268). The Grignard method has now been found to be applicable to the synthesis of acetylenyl glycols from the polyene aldehydes, sorbaldehyde (I; $n = 2$) and octatrienal (I; $n = 3$). Condensation of the former with acetylenyldimagnesium bromide gave the acetylenyl glycol, *tetradeca*-2 : 4 : 10 : 12-*tetraen*-7-*yn*-6 : 9-*diol* (II; $n = 2$) in 42% yield as a colourless crystalline solid, m. p. 95—102°. The wide melting-point range probably indicates that the product is a mixture of isomers, a number of which (stereo and geometrical) are obviously possible. Its light absorption (Fig. 1 and Table I) may be compared with that of a simple diene system, the intensity being considerably accentuated by the presence of two such systems in one and the same molecule. With maleic anhydride it readily formed a solid adduct which, however, was too sparingly soluble to be purified. Zerewitinoff determinations on this and all other glycols described in this paper gave the expected values of two active hydrogen atoms.

Fig. 1.

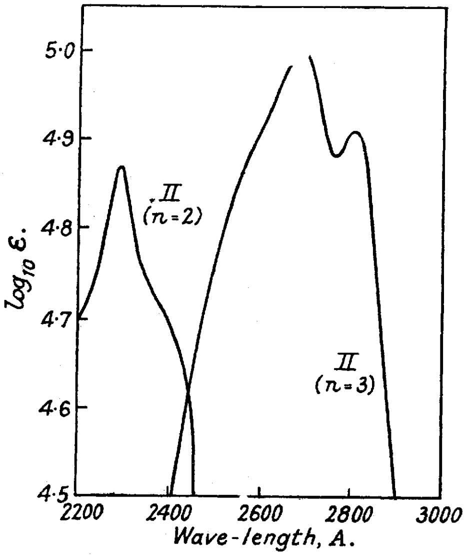
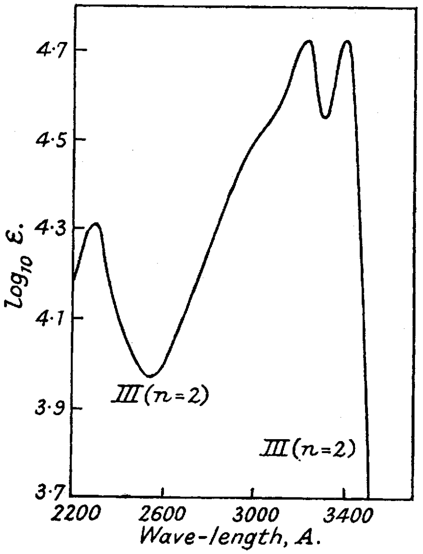


Fig. 2.



$$CH_3\cdot[CH{:}CH]_n\cdot CHO \quad (I.)$$

$$CH_3\cdot[CH{:}CH]_n\cdot CH(OH)\cdot C{\vdots}C\cdot CH(OH)\cdot[CH{:}CH]_n\cdot CH_3 \quad (II.)$$

$$\downarrow \text{acids}$$

$$CH_3\cdot CH(OH)\cdot[CH{:}CH]_n\cdot C{\vdots}C\cdot[CH{:}CH]_n\cdot CH(OH)\cdot CH_3 \quad (III.)$$

In the same manner octatrienal (I; $n = 3$) gave *octadeca*-2 : 4 : 6 : 12 : 14 : 16-*hexaen*-9-*yn*-8 : 11-*diol* (II; $n = 3$), m. p. 154°, in 20% yield, accompanied by a considerable quantity of tarry material, presumably containing some stereoisomers. The locations of the absorption maxima (Fig. 1 and Table I) are similar to those of carbinols containing the conjugated triene chromophore but their intensities are, of course, considerably higher.

Table I.

(Solutions in alcohol.)

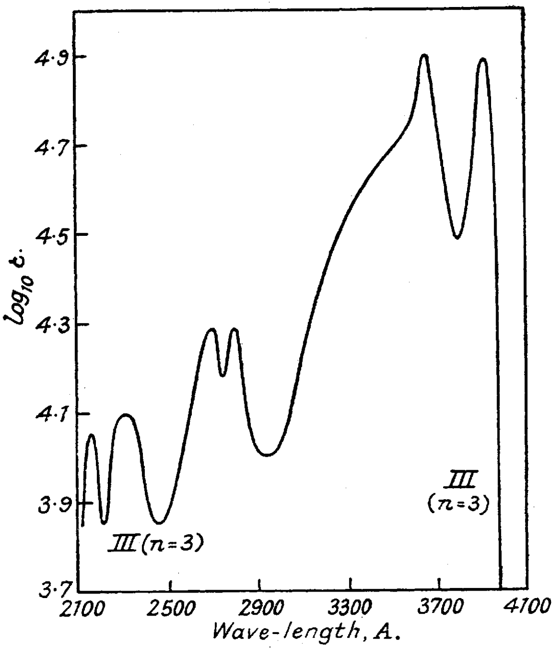
	$\lambda_{max.}$, A.	$\varepsilon_{max.}$		$\lambda_{max.}$, A.	$\varepsilon_{max.}$
Tetradeca-2 : 4 : 10 : 12-tetraen-7-yn-6 : 9-diol (II; $n = 2$) (Fig. 1)	2290	74,000	Deca-4 : 6 : 8-trien-1-yn-3-ol[1]	2580 *	43,000
	2370 *	54,000		2675	55,000
Octa-4 : 6-dien-1-yn-3-ol[1]	2300	28,500		2780	44,500
1 : 6-Diacetoxyhexa-2 : 4-diene[2]	2280	27,500	Octatrienol[3]	2560	42,500
Octadeca-2 : 4 : 6 : 12 : 14 : 16-hexaen-9-yn-8 : 11-diol (II; $n = 3$) (Fig. 1)	2690	100,000		2645	53,000
	2810	81,000		2780	46,500

* Inflexions.

[1] Heilbron, Jones, and McCombie, preceding paper.
[2] Booker, Evans, and Gillam, J., 1940, 1453.
[3] Heilbron, Johnson, Jones, and Raphael, J., 1943, 265.

The rearrangements of the ethynylcarbinols from sorbaldehyde and octatrienal, yielding conjugated polyenyne carbinols have already been reported (previous paper); by similar but dual anionotropic rearrangements of the above glycols (II; $n = 2$ and 3) in the presence of acids, symmetrical conjugated polyenyne glycols (III; $n = 2$ and 3) should be produced, substances of considerable interest because of their approach to carotenoid structures. When an ethereal solution of the glycol (II; $n = 2$) from sorbaldehyde was shaken with 5% sulphuric acid, the isomeric glycol, *tetradeca*-3 : 5 : 9 : 11-*tetraen*-7-*yn*-2 : 13-*diol* (III; $n = 2$), containing the symmetrical conjugated tetraenyne system, was isolated in 25% yield. The comparatively low yield is probably due to the fact that the product appears to be a single stereoisomer. It was obtained as crystals, m. p. 115—116°, which were colourless when viewed by transmitted light, but pale yellow in reflected light. Previous work in this field (preceding paper) indicates that the polyene and polyenyne series are closely allied as far as light-absorption properties are concerned. Consequently, the appearance of colour in the glycol (III; $n = 2$) is to be expected, since the closely related tetradecapentaenol (IV) is described by Kuhn and Grundmann (*Ber.*, 1938, **71**, 442) as crystallising in straw-yellow leaflets, and pure crystalline vitamin A (Baxter and Robeson, *J. Amer. Chem. Soc.*, 1942, **64**, 2411) and the crystalline farnesinol (V) (Fischer and Hultzsch, *Ber.*, 1935, **68**, 1733), all containing the conjugated pentadienol system, are pale yellow.

FIG. 3.



$CH_3\cdot[CH{:}CH]_5\cdot CH(OH)\cdot CH_2\cdot CH_3$ (IV.)
$CMe_2{:}CH\cdot CH{:}CH\cdot CMe{:}CH\cdot CH{:}CH\cdot CMe{:}CH\cdot CH_2\cdot OH$ (V.)

Also, Kuhn and Grundmann (*loc. cit.*) observed that in the series of dimethylpolyenes, $CH_3\cdot[CH{:}CH]_n\cdot CH_3$, whereas 1 : 8-dimethyloctatetraene ($n = 4$) is colourless, 1 : 12-dimethyldodecahexaene ($n = 6$) is yellow.

The glycol (II; $n = 3$) from octatrienal could not be isomerised completely in a heterogeneous medium, but a solution in alcohol or acetone containing some 10% sulphuric acid gradually became yellow, and after 24 hours the rearranged glycol, *octadeca*-3 : 5 : 7 : 11 : 13 : 15-*hexaen*-9-*yn*-2 : 17-*diol* (III; $n = 3$) was isolated in 80% yield as lemon-yellow needles, m. p. 149°.

The structures of both glycols (III; $n = 2$ and 3) were proved by complete hydrogenation by means of Adams's catalyst, followed by oxidation of the saturated 2 : 13- and 2 : 17-glycols with hypobromite to decane-1 : 10-dicarboxylic and tetradecane-1 : 14-dicarboxylic (thapsic) acids, respectively.

The similarity in colour between the isomerised glycols and corresponding polyenes has already been discussed and, as would be expected, the complete absorption spectra are closely analogous (Figs. 2 and 3; Table II).

TABLE II.

(Solutions in alcohol.)

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$		$\lambda_{max.}$, A.	$\varepsilon_{max.}$
Tetradeca-3 : 5 : 9 : 11-tetraen-7-yn-2 : 13-diol (III; $n = 2$) (Fig. 2)	2280	20,000	1 : 12-Dimethyldodecahexaene[5] (in $CHCl_3$ *)	3280	25,000
	3230	54,000		3400	46,000
	3410	54,000		3600	69,500
Vitamin A[4]	3280	51,000		3750	49,500
Octadeca-3 : 5 : 7 : 11 : 13 : 15-hexaen-9-yn-2 : 17-diol (III; $n = 3$) (Fig. 3)	2150	11,000	Dihydro-α-crocetin[6] (VI)	3470	59,000
	2310	13,000		3650	74,000
	2700	19,500		3860	64,500
	2800	19,500	Dihydrobixin methyl ester[6] (VII)	3870	56,000
	3650	79,500		4070	79,000
	3920	78,500		4310	67,500

* Main max. probably at about 3550 A. in alcohol.

[4] Baxter and Robeson, *J. Amer. Chem. Soc.*, 1942, **64**, 2411.
[5] Kuhn, *Angew. Chem.*, 1937, **50**, 703.
[6] Euler, Karrer, Klussman, and Morf, *Helv. Chim. Acta*, 1932, **15**, 504.

No absorption data for a conjugated heptaene system are available, and consequently the spectrum (Fig. 3) of the rearranged glycol (III; $n = 3$) from octatrienal has to be compared with those of dihydro-α-crocetin (VI) and the methyl ester of dihydrobixin (VII), containing six and eight conjugations, respectively. Such a comparison is not strictly justified, for Kuhn and Grundmann (*Ber.*, 1937, **70**, 1318) have observed that in the case of carotenoid polyenes the presence of a substituent methyl group on the polyene chain causes displacement

$CO_2H\cdot CHMe\cdot CH{:}CH\cdot CH{:}CMe\cdot CH{:}CH\cdot CH{:}CH\cdot CMe{:}CH\cdot CH{:}CH\cdot CHMe\cdot CO_2H$ (VI.)
$CO_2Me\cdot CH_2\cdot[CH{:}CMe\cdot CH{:}CH]_2\cdot[CH{:}CH\cdot CMe{:}CH]_2\cdot CH_2\cdot CO_2Me$ (VII.)

of the absorption maxima to longer wave-lengths, the increase being of the order of 50 A. for each such group. If this " correction " be applied to the main absorption maxima of (VI) and (VII) (containing two and four side-chain methyl groups respectively), the values 3550 A. and 3870 A. respectively are obtained. In the preceding paper it was observed that, as far as the locations of the maxima are concerned, the absorption spectra of polyenes are but little affected by replacing one of the ethylenic linkages by an acetylenic linkage and it is again apparent that the intensity differences, so marked in the simple conjugated vinyl- and divinyl-acetylenes, become much less significant as the number of ethylenic bonds increases.

Another similarity between the conjugated polyenynes and the corresponding polyenes is observed in the straight line obtained when the squares of the wave-lengths of the main maxima of all of the polyenynes so far examined are plotted against the number of conjugations, the linearity of this relationship in the case of polyenes having already been established by Lewis and Calvin (*Chem. Reviews*, 1939, **25**, 273).

The subsidiary maxima at shorter wave-lengths observed with the polyenyne glycols (Figs. 2 and 3) are characteristic of polyenes, although these so-called " vorbanden " are not always recorded in the literature. Lewis and Calvin (*loc. cit.*) postulate that the ratio (*R*) of the wave-length of the subsidiary maximum to that of the main maximum should increase with increasing conjugation towards a maximum of 2. This was observed by them to be the case for all polyenes for which figures were available, and it also holds good for the polyenyne glycols ($R = 1{\cdot}2$, 1·45, and 1·7 when $n = 3$, 5, and 7, respectively).

EXPERIMENTAL.

Tetradeca-2 : 4 : 10 : 12-*tetraen*-7-*yn*-6 : 9-*diol* (II; $n = 2$).—Pure dry acetylene was passed into an ethereal solution of ethylmagnesium bromide (from magnesium, 6 g.) at 20° during 24 hours, dry ether being added at intervals to maintain a constant volume of about 750 c.c. The acetylene was then replaced by nitrogen, and a solution of freshly distilled sorbaldehyde (22 g.) in dry ether (30 c.c.) was added during 30 minutes, accompanied by vigorous stirring which was continued for a further 2 hours. The Grignard complex was decomposed by treatment with a solution of ammonium nitrate (80 g.) in water, the aqueous phase was extracted several times with ether and, after the combined ethereal extracts had been washed consecutively with very dilute sulphuric acid and sodium bicarbonate solution and dried, the solvent was removed under diminished pressure. The residual pale brown viscous liquid was treated with dry benzene (15 c.c.), and, on standing at 0° for 24 hours, the glycol crystallised. The solid was repeatedly washed on the filter with small quantities of cold benzene, and crystallisation from benzene–light petroleum (b. p. 40—60°) and finally from *cyclo*hexane gave the *diol* (II; $n = 2$) (12 g.) as colourless prismatic needles, m. p. 95—102° (Found : C, 76·8; H, 8·15. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%). *Active hydrogen* (Zerewitinoff) : The glycol (128 mg.) gave 27·9 c.c. of methane at 21°/743 mm., equivalent to 1·95 active hydrogen atoms per mol. With a solution of antimony trichloride in chloroform the glycol gave a black precipitate.

Octadeca-2 : 4 : 6 : 12 : 14 : 16-*hexaen*-9-*yn*-8 : 11-*diol* (II; $n = 3$).—To a vigorously stirred suspension of acetylenyldimagnesium bromide (from magnesium, 6 g.) in ether, a solution of freshly distilled octatrienal (31 g.) in dry ether (40 c.c.) was added during ½ hour. Stirring, decomposition, and isolation were then carried out as previously described. In this case much ether had to be employed owing to the low solubility of the glycol in this solvent. The black syrup obtained after removal of the solvent was kept in contact with dry ether (50 c.c.) at 0° for 24 hours, and the crystalline glycol so obtained was filtered off and washed with several small portions of cold ether. A further quantity was obtained by repeating the treatment on the mother-liquors. Crystallisation from chloroform gave the *diol* (II; $n = 3$) (7 g.) as a mat of colourless needles, m. p. 154° (Found : C, 79·5, 79·7; H, 8·2, 8·15. $C_{18}H_{22}O_2$ requires C, 79·95; H, 8·2%). *Active hydrogen* (Zerewitinoff) : The glycol (75 mg.) gave 13·1 c.c. of methane at 21°/763 mm. (1·95 active hydrogen atoms per mol.) With a solution of antimony trichloride in chloroform the glycol gave an immediate blue-green colour.

Tetradeca-3 : 5 : 9 : 11-*tetraen*-7-*yn*-2 : 13-*diol* (III; $n = 2$).—A solution of the diol (II; $n = 2$) (2 g.) in ether (10 c.c.) was shaken for 24 hours with sulphuric acid (20 c.c.; 5% w/v) at 20° under nitrogen. A yellow solid remained on evaporation of the washed and dried ethereal solution, and after being washed with small quantities of benzene and recrystallised under nitrogen from carbon tetrachloride, this yielded the *diol* (III; $n = 2$) (500 mg.) as plates, m. p. 115—116° (sealed tube) to an orange liquid (Found : C, 77·2; H, 8·1. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%). *Active hydrogen* (Zerewitinoff) : The glycol (81 mg.) evolved 17·4 c.c. of methane at 22°/777 mm. (1·95 active hydrogen atoms per mol.). With a solution of antimony trichloride in chloroform, the glycol gave an immediate deep blue-violet colour, and a black precipitate slowly appeared; with anhydrous formic acid it slowly gave a greenish-blue coloration.

Decane-1 : 10-*dicarboxylic Acid*.—A solution of the above glycol (200 mg.) in methyl alcohol (15 c.c.) was shaken with hydrogen in the presence of platinic oxide (10 mg.) until absorption was complete. The crude tetradecane-2 : 13-diol obtained on removal of catalyst and solvent was shaken for 48 hours at 20° with sodium hypobromite solution (10 c.c.; 1·5%). The solid precipitated on acidification of the reaction mixture was crystallised from water, yielding decane-1 : 10-dicarboxylic acid, m. p. 126°, undepressed on admixture with an authentic specimen.

Octadeca-3 : 5 : 7 : 11 : 13 : 15-*hexaen*-9-*yn*-2 : 17-*diol* (III; $n = 3$).—A solution of the diol (II; $n = 3$) (4 g.) in alcohol or acetone was treated with sulphuric acid (10 c.c.; 10% w/v) and sufficient solvent was added to give a clear solution which was then set aside at 20° for 24 hours, by which time it had become deep yellow. After addition of an equal volume of water, the precipitated glycol was isolated by means of ether. Crystallisation of the product from benzene, under nitrogen, gave the *diol* (III; $n = 3$) (3·2 g.) as lemon-yellow needles, sinters 145°, m. p. 149° (sealed tube) to an orange liquid (Found : C, 80·0; H, 8·55. $C_{18}H_{22}O_2$ requires C, 79·95; H, 8·2%). *Active hydrogen* (Zerewitinoff) : The glycol (102 mg.) evolved 17·3 c.c. of methane at 18°/768 mm. (1·95 active hydrogen atoms per mol.). With a solution of antimony trichloride in chloroform the glycol gave an immediate deep blue-violet colour. With anhydrous formic acid it gave an immediate brilliant green colour.

Tetradecane-1 : 14-*dicarboxylic Acid* (*Thapsic Acid*).—A solution of the above glycol (200 mg.) in methyl alcohol (15 c.c.) was shaken with hydrogen and platinic oxide (10 mg.) until absorption ceased. After removal of the catalyst and solvent, the crude octadecane-2 : 17-diol was finely powdered, and shaken with sodium hypobromite solution (10 c.c.; 15%) for 48 hours at 20°. Acidification with concentrated hydrochloric acid gave a solid which, after crystallisation from ethyl acetate, had m. p. 125—126° (Schmid and Kemeny, *Monatsh.*, 1935, **66**, 4, give m. p. 126° for thapsic acid).

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