48. Studies in the Polyene Series. Part XII. Ethynylcarbinols from Sorbaldehyde and Octatrienal. Poly-carbon Anionotropic Rearrangements.

By I. M. Heilbron, E. R. H. Jones, and J. T. McCombie

Ethynylcarbinols (I and II) are prepared from sorbaldehyde and octatrienal by reaction with sodium acetylide in liquid ammonia. On treatment with dilute sulphuric acid five- and seven-carbon anionotropic rearrangements yield conjugated *dienyne-* (IV) and *trienyne-carbinols* (V) which after complete hydrogenation, and oxidation of the saturated carbinols, give methyl hexyl and methyl octyl ketones respectively. Insofar as the location of the absorption maximum is concerned, replacement of an ethenoid linkage in a conjugated polyene by an acetylenic bond has a negligible effect.

It has already been demonstrated (Jones and McCombie, J , 1942, 733) that ethynylcarbinols can be prepared from αβ-unsaturated aldehydes by condensation with sodium acetylide in liquid ammonia solution, and this method has now been extended to condensations with polyene aldehydes. From sorbaldehyde there is obtained a 50% yield of *octa*-4 : 6-*dien*-1-*yn*-3-*ol* (I), the light absorption of which (Fig. 1 and table) is typical, both in location and intensity of the maximum, of the conjugated diene system. Similarly, octatrienal gives the crystalline *deca*-4 : 6 : 8-*trien*-1-*yn*-3-*ol* (II) (m. p. 73·5—74·5°) in 30% yield, the carbinol exhibiting an absorption spectrum (Fig. 2 and table) practically identical with that of octatrienol (III).

$\mathrm{CH_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}C{\vdots}CH}$ (I.)
$\mathrm{CH_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}C{\vdots}CH}$ (II.)
$\mathrm{CH_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OH}$ (III.)

In the presence of acids both (I) and (II) undergo facile anionotropic rearrangements analogous to those already described (Jones and McCombie, J., **1943**, 261) with propenylethynyl and similar carbinols from αβ-unsaturated aldehydes. Thus, *octa*-3 : 5-*dien*-1-*yn*-7-*ol* (IV) is produced in good yield when the ethynylcarbinol (I) from sorbaldehyde is shaken with 5% sulphuric acid, its constitution being readily established by complete hydrogenation and oxidation of the saturated carbinol to methyl hexyl ketone. The ethynylcarbinol (II) is converted on shaking in ethereal solution with 2·5% sulphuric acid into *deca*-3 : 5 : 7-*trien*-1-*yn*-9-*ol* (V) (m. p. 82—83°), which on hydrogenation and subsequent oxidation yields methyl octyl ketone.

FIG. 1.

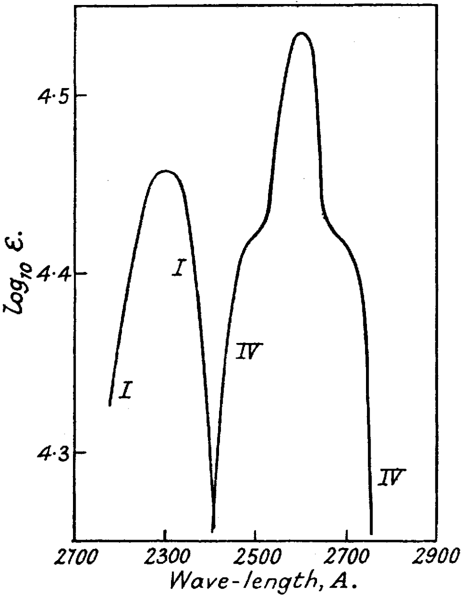
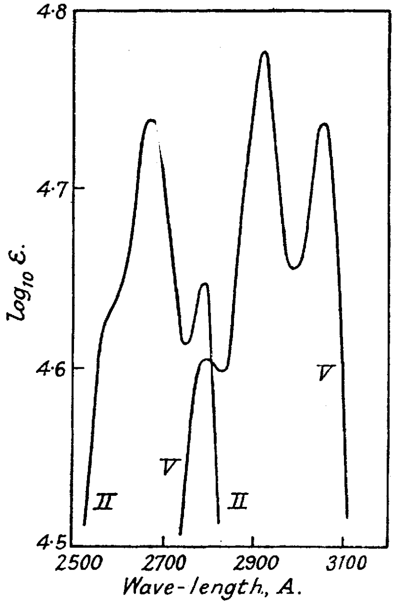


FIG. 2.



$\mathrm{CH_3{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}C{\vdots}CH}$ (IV.)
$\mathrm{CH_3{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}C{\vdots}CH}$ (V.)
$\mathrm{CH_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OH}$ (VI.)

The absorption spectra of the two isomerised carbinols (IV) and (V) (Figs. 1 and 2 and table), are in accord with previous observations on conjugated polyenyne systems (Parts VIII—XI, J., **1943**, 261—270). The unsymmetrical dienyne system present in the carbinol (IV), the symmetrical dienyne systems of 7-methylnona-3 : 7-dien-5-yn-2-ol (VII) and deca-3 : 7-dien-5-yn-2 : 9-diol (VIII) and

$\mathrm{CH_3{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}C{\vdots}C{\cdot}CMe{:}CH{\cdot}CH_3}$ (VII.)
$\mathrm{CH_3{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}C{\vdots}C{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CH_3}$ (VIII.)

the triene system of octatrienol all exhibit maximal intensities in the region 2600—2675 A. Again, the carbinol (V), containing the conjugated trienyne system, and decatetraenol (VI) both absorb most strongly at about 2950 A. From the evidence now available it is possible to make the generalisation that, insofar as the location of the absorption maximum is concerned, the replacement of an ethenoid linkage of a conjugated polyene system by an acetylenic bond has a negligible effect. As has previously been pointed out, however, and as is further illustrated in the examples given in the table, marked effects on the intensity of absorption are observed although these become less obvious as the size of the polyene system increases.

The literature furnishes but little information concerning anionotropic rearrangements other than those involving the familiar three-carbon system and there are no instances recorded of five- and seven-carbon migrations of hydroxyl groups. The closest approach to analogy with the isomerisations now described is the rearrangement of 1 : 2-dibromohexa-3 : 5-diene to the 1 : 6-isomer in the presence of hydrogen bromide or merely on heating (Farmer, Laroia, Switz, and Thorpe, J., 1927, 2937). It is somewhat surprising that, in spite of the known lability of compounds such as phenylpropenylcarbinol, no attempts have been made to

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
Octa-4 : 6-dien-1-yn-3-ol (I) (Fig. 1)	2300	28,500
Octa-3 : 5-dien-1-yn-7-ol (IV) (Fig. 1)	2600 2470 * 2730 *	34,000 24,500 24,500
7-Methylnona-3 : 7-dien-5-yn-2-ol [1] (VII)	2640	16,500
Deca-3 : 7-dien-5-yn-2 : 9-diol [2] (VIII)	2650 2800	21,500 19,000
Deca-4 : 6 : 8-trien-1-yn-3-ol (II) (Fig. 2)	2675 2780 2580 *	55,000 44,500 43,000
Octatrienol [1] (III)	2645 2760 2560	53,000 46,500 42,500
Deca-3 : 5 : 7-trien-1-yn-9-ol (V) (Fig. 2)	2920 3050 2790	60,000 54,000 40,000
Decatetraenol [3] (VI)	2985 3110	64,000 64,000

* Inflexion.

[1] Heilbron, Johnson, Jones, and Raphael, J., 1943, 265.
[2] Heilbron, Jones, and Raphael, J., 1943, 268.
[3] Reichstein and Trivelli, *Helv. Chim. Acta*, 1932, **15**, 1074.

examine the possible extension of anionotropic systems of this type to include the condensation products of sorbaldehyde and octatrienal with phenylmagnesium bromide.

EXPERIMENTAL.

(Absorption spectra were determined in alcoholic solutions.)

Octa-4 : 6-*dien*-1-*yn*-3-*ol* (I).—Sodium (8·4 g.) was gradually added with stirring to liquid ammonia (500 c.c.) through which a rapid stream of acetylene was passing, and when addition was complete a solution of sorbaldehyde (35 g.) in ether (125 c.c.) was dropped in during an hour. Stirring was continued for a further 4 hours, the acetylene replaced by nitrogen, the mixture treated with ammonium chloride (19·5 g.), and the ammonia allowed to evaporate off overnight. The product was isolated by means of ether and two distillations gave *octa*-4 : 6-*dien*-1-*yn*-3-*ol* (24 g.), as a colourless oil which rapidly darkens on standing; b. p. 71—74°/0·5 mm., $n_D^{20^\circ}$ 1·5126 (Found : C, 78·5; H, 8·1. $C_8H_{10}O$ requires C, 78·7; H, 8·2%). A naphthylurethane or other derivative could not be prepared, probably owing to the instability of the carbinol.

Octa-3 : 5-*dien*-1-*yn*-7-*ol* (IV).—A mixture of the above carbinol (10 g.) and sulphuric acid (50 c.c., 5% w/v), together with a trace of quinol, was shaken under nitrogen for 12 hours at 20°. Isolation by means of ether gave *octa*-3 : 5-*dien*-1-*yn*-7-*ol* (6 g.) as a colourless oil which darkens rapidly on standing; b. p. 62—65°/0·5 mm., $n_D^{16^\circ}$ 1·5468. With a solution of antimony trichloride in chloroform, both this carbinol and its isomeride give transient blue colorations which quickly change to black (Found : C, 78·8; H, 8·0. $C_8H_{10}O$ requires C, 78·7; H, 8·2%).

Methyl Hexyl Ketone.—A solution of (IV) (1·4 g.) in ethyl acetate (30 c.c.) was shaken with hydrogen in the presence of platinic oxide (100 mg.) until absorption was complete. The catalyst and solvent were removed, the latter through a column, and the residual carbinol was oxidised with chromic acid to methyl hexyl ketone; semicarbazone, m. p. 121—122° (Bouveault and Locquin, *Bull Soc. chim.*, 1904, **31**, 1157, give m. p. 122°); 2 : 4-dinitrophenylhydrazone, m. p. 58—59° (Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2957, gives m. p. 58°). Neither of these derivatives depressed the m. p. of an authentic specimen.

Deca-4 : 6 : 8-*trien*-1-*yn*-3-*ol* (II).—This was prepared by the method described above [sodium (2·7 g.) and octatrienal (14 g.)] with the difference that, after the addition of ammonium chloride, the ammonia was evaporated off during 2 hours. Distillation of the product isolated by means of ether gave a pale yellow oil, b. p. 94—96°/1 mm., which readily solidified, and on crystallisation from light petroleum (b. p. 60—80°), *deca*-4 : 6 : 8-*trien*-1-*yn*-3-*ol* (5 g.) was obtained as long colourless needles, m. p. 73·5—74·5° (Found : C, 81·0; H, 8·35. $C_{10}H_{12}O$ requires C, 81·1; H, 8·1%). *Active hydrogen* (Zerewitinoff) : the carbinol (101 mg.) evolved 33·1 c.c. of methane at 23°/754 mm., equivalent to 2·0 active hydrogen atoms per mol. The carbinol is very sensitive to atmospheric oxidation, a brown resin being formed. With a solution of antimony trichloride in chloroform it gives a transient purple coloration rapidly changing to green.

Deca-3 : 5 : 7-*trien*-1-*yn*-9-*ol* (V).—A solution of (II) (1 g.) in ether (10 c.c.) containing a trace of quinol was shaken with sulphuric acid (20 c.c.; 2·5% w/v) in the dark in an atmosphere of nitrogen at 20° for 22 hours. Isolation in the usual manner gave a crystalline product from which *deca*-3 : 5 : 7-*trien*-1-*yn*-9-*ol* (0·5 g.) was obtained from light petroleum (b. p. 60—80°) as colourless needles, m. p. 82—83° (Found : C, 81·15; H, 8·2. $C_{10}H_{12}O$ requires C, 81·1; H, 8·1%). The carbinol is unstable in air. With a solution of antimony trichloride in chloroform it gives a transient purple coloration rapidly becoming green.

Methyl Octyl Ketone.—A solution of (V) (0·4 g.) in ethyl acetate (35 c.c.) was shaken with hydrogen in the presence of platinic oxide (100 mg.) until absorption was complete. Oxidation of the resulting saturated carbinol with chromic acid yielded methyl octyl ketone, which gave a semicarbazone, m. p. 121—122° (Pickard and Kenyon, J., 1911, **99**, 57, give m. p. 121°), undepressed on admixture with an authentic specimen.

The authors are indebted to the Rockefeller Foundation and to Imperial Chemical Industries (Dyestuffs), Ltd. for grants.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W.7.
[*Received, November 3rd*, 1943.]