69. *Studies in the Polyene Series. Part XI. The Anionotropic Rearrangement of the Acetylenic Glycol from Crotonaldehyde.*

By I. M. HEILBRON, E. R. H. JONES, and R. A. RAPHAEL.

Treatment of an ethereal solution of the acetylenic glycol (I) from crotonaldehyde with 10% sulphuric acid brings about a dual anionotropic rearrangement resulting in the formation of the isomeric *glycol* (II). The constitution of the latter is established by hydrogenation to *decane*-2 : 9-*diol* and subsequent oxidation to suberic acid. The light absorption of (II) is consistent with the presence of the conjugation dienyne chromophore in the molecule.

THE preparation and properties of the symmetrical acetylenic glycols derived from saturated aldehydes and ketones have been extensively investigated, particularly by Dupont (*Ann. Chim.*, 1913, **30**, 485), following Iotsitch (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 239; 1903, **35**, 430, 1269; 1906, **38**, 252, 656). Both investigators utilised acetylenedimagnesium bromide, and this remains the most convenient laboratory method (see *inter alia*, Zalkind and Labuzov, *J. Gen. Chem. Russia*, 1939, **9**, 1525; Marvel and Dunlap, *J. Amer. Chem. Soc.*, 1939, **61**, 2716; Schokina, Kildischeva, and Preobashenski, *J. Gen. Chem. Russia*, 1941, **11**, 425). Glycol formation can also be effected by direct interaction of acetylene and carbonyl compounds, catalysts such as potassium hydroxide (Babajan, *ibid.*, 1940, **10**, 480, 1177) or heavy-metal acetylides (I.G. Farbenind., B.P. 508,062; General Aniline and Film Corp., U.S.P. 2,238,471) being used. Both symmetrical and unsymmetrical glycols can be made by condensing ethynylcarbinols with carbonyl compounds, and although the Grignard method has been mainly employed for this purpose (see *inter alia*, Marvel, Mozingo, and Kirkpatrick, *J. Amer. Chem. Soc.*, 1939, **61**, 2006; Marvel and Walton, *J. Org. Chem.*, 1942, **7**, 93; Zalkind and Gverdtsiteli, *J. Gen. Chem. Russia*, 1939, **9**, 855), condensing agents such as sodamide (Henecka, *Chem. Abstracts*, 1937, **31**, 2592; Burkhardt and Hindley, J., 1938, 987), potassium *tert.*-butoxide (*idem, ibid.*), and potassium hydroxide (Babajan, *loc. cit.*, p. 1177) are also effective. A process is also described (McCallum, U.S.P. 2,162,676) whereby an alkali- or alkaline-earth-metal compound of an ethynylcarbinol is heated to 60°, whereupon the metal compound of the corresponding acetylenic glycol is produced in good yield.

The acetylenic glycol from crotonaldehyde (deca-2 : 8-dien-5-yn-4 : 7-diol) (I) was prepared originally by Dupont (*loc. cit.*) by the Grignard method; the only other mention in the literature is its formation, in unstated yield, by the interaction of crotonaldehyde with acetylene in the presence of copper acetylide at 120—130° (I.G. Farbenind., *loc. cit.*). We have found Dupont's method satisfactory, although the yield of the pure crystalline product is not above 50%. The glycol can also be obtained, in somewhat poorer yield, by condensation of the Grignard complex from propenylethynylcarbinol with crotonaldehyde (unpublished work), but all attempts to prepare it by condensation of crotonaldehyde either with acetylene itself or with propenylethynylcarbinol by means of sodium in liquid ammonia have proved fruitless. The use of the other condensing agents described above is ruled out because of their powerful catalytic effect on the self-condensation of crotonaldehyde.

An investigation of the behaviour of the glycol (I) in the presence of acidic reagents has now been undertaken, since the corresponding ethynylcarbinol undergoes a facile anionotropic rearrangement under these conditions (Jones and McCombie, Part VIII, this vol., p. 261). On shaking an ethereal solution of the glycol (I) with 10% sulphuric acid, an isomeric glycol, produced almost quantitatively, was isolated as a viscous liquid (*bisphenylurethane*, m. p. 181°). Proof of its constitution as *deca*-3 : 7-*dien*-5-*yn*-2 : 9-*diol* (II) was readily obtained by hydrogenation to *decane*-2 : 9-*diol*, m. p. 33° (*bisphenylurethane*) which was oxidised to the known decane-2 : 9-dione (*dioxime*), which in turn was oxidised to suberic acid with hypobromite.

(I.) $CH_3\cdot CH{:}CH\cdot CH(OH)\cdot C{\vdots}C\cdot CH(OH)\cdot CH{:}CH\cdot CH_3$

(II.) $CH_3\cdot CH(OH)\cdot CH{:}CH\cdot C{\vdots}C\cdot CH{:}CH\cdot CH(OH)\cdot CH_3$

$CH_3\cdot CH(OH)\cdot CH{:}CH\cdot C{\vdots}C\cdot CMe{:}CH\cdot CH_3$ (III.)

Since the unisomerised material (I) is a crystalline solid, m. p. 91°, it is probably stereochemically pure, being either the *meso*- or racemic form, presumably of the *trans-trans*-glycol. The liquid isomer (II) is certainly a mixture of at least two stereoisomeric forms, for on one occasion a small quantity of a solid glycol was isolated after long standing.

Further evidence of the correctness of the structure assigned to (II) is provided by its absorption spectrum (Fig. 1 and table) and that of its *diacetate* (Fig. 2 and table), both of which closely resemble those of 7-methylnona-3 : 7-dien-5-yn-2-ol (III) (Heilbron, Johnson, Jones, and Raphael, preceding paper) and octatrienol in the location of the maxima. As was to be expected from previous observations, the intensity of the absorption of the conjugated dienyne systems is much less than that of the conjugated trienol.

	$\lambda_{max.}$, A.	$\epsilon_{max.}$	$\lambda_{max.}$, A.	$\epsilon_{max.}$	$\lambda_{max.}$, A.	$\epsilon_{max.}$
Deca-3 : 7-dien-5-yn-2 : 9-diol (II) (Fig. 1)	—	—	2650	21,500	2800	19,000
Diacetate of (II) (Fig. 2)	2560	14,000	2650	22,000	2780	18,500
7-Methylnona-3 : 7-dien-5-yn-2-ol (III)	—	—	2640	16,500	—	—
Octatrienol	2560	42,500	2645	53,000	2780	46,500

FIG. 1.

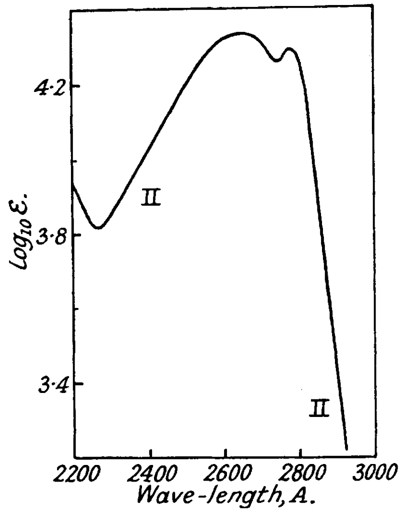
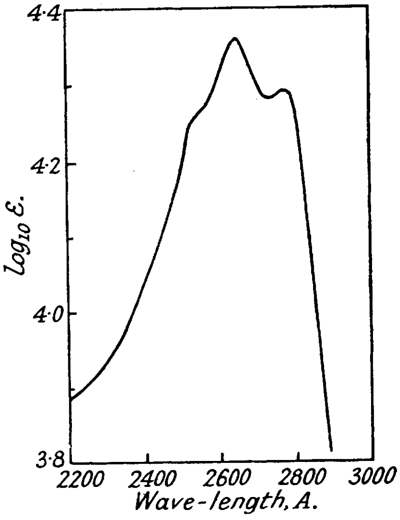


FIG. 2.



Diacetate of II.

We believe the dual anionotropic rearrangement described here to be unique, and we are exploring the scope of this novel reaction.

EXPERIMENTAL.

(Absorption spectra were determined in alcoholic solutions.)

Deca-2 : 8-*dien*-5-*yn*-4 : 7-*diol* (I) (cf. *Dupont, loc. cit.*).—Pure, dry acetylene was passed into a solution of ethylmagnesium bromide (from magnesium, 12 g.) in ether (100 c.c.) during 24 hours, the volume of the solution being maintained constant by continuous addition of ether. Freshly distilled crotonaldehyde (35 g.) was then added during 1 hour with vigorous stirring which was continued for a further 2 hours, after which the Grignard complex was decomposed with a saturated solution of ammonium chloride (60 g.). The aqueous layer was repeatedly extracted with ether and the combined extracts were washed with dilute sulphuric acid and sodium bicarbonate solution and dried. Evaporation of the ether gave a brown, viscous liquid (30 g.), which solidified almost completely on standing at 0°. The crystalline glycol was freed from oily contaminants by trituration with a small quantity of ether at 0°, and then separated from carbon tetrachloride or light petroleum (b. p. 80—100°) in prisms (28 g.), m. p. 91° (Dupont, *loc. cit.*, gives m. p. 90—92°). Small quantities of the crude glycol have been distilled at 70—75° (bath temp.)/10^{-4} mm. but this effects little purification: distillation of large amounts may result in explosive decomposition. The glycol shows no appreciable light absorption in the range 2200—4000 A.

Deca-3 : 7-*dien*-5-*yn*-2 : 9-*diol* (II).—A solution of the above glycol (5 g.) in ether (20 c.c.) was shaken at 20° under nitrogen with sulphuric acid (30 c.c., 10% w/v) for 24 hours, and from the washed and dried ethereal phase there were obtained 4·3 g. of *deca*-3 : 7-*dien*-5-*yn*-2 : 9-*diol*, a viscous liquid, b. p. 65—70° (bath temp.)/10^{-4} mm., $n_D^{21°}$ 1·5511 (Found : C, 72·5; H, 8·5. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·5%). On one occasion, after standing for many weeks at 0°, a small sample was obtained as needles, m. p. 56·5—57°, presumably a pure isomer. *Active hydrogen* (Zerewitinoff) : The glycol (78 mg.) evolved 22·8 c.c. of methane at 22°/762 mm., equivalent to 1·9 active hydrogen atoms per molecule. The *diacetate*, prepared by the action of acetyl chloride on a pyridine solution of the glycol, was obtained as a comparatively mobile liquid, which darkened somewhat on standing; b. p. 131—132°/10^{-3} mm., $n_D^{27°}$ 1·5005 (Found: C, 67·3; H, 7·25. $C_{14}H_{18}O_4$ requires C, 67·15; H, 7·25%). The *bisphenylurethane* crystallised from ethyl acetate in needles, m. p. 181° (Found : N, 7·1. $C_{24}H_{24}O_4N_2$ requires N, 6·9%).

Decane-2 : 9-*diol*.—A solution of deca-3 : 7-dien-5-yn-2 : 9-diol (5 g.) in methyl alcohol (30 c.c.) was shaken with hydrogen in the presence of platinic oxide (10 mg.) until absorption was complete. Removal of the catalyst and solvent gave *decane*-2 : 9-*diol* (4·6 g.) as a viscous liquid, b. p. 114°/5 mm., $n_D^{21·5°}$ 1·4505, which on standing slowly formed large prisms, m. p. 33° (Found : C, 68·85; H, 12·35. $C_{10}H_{22}O_2$ requires C, 68·9; H, 12·7%). *Active hydrogen* (Zerewitinoff) : The glycol (53 mg.) evolved 15·3 c.c. of methane at 24°/756 mm., corresponding to 2·1 active hydrogen atoms per molecule. The *diacetate* was obtained as a mobile liquid, b. p. 108°/4 mm., $n_D^{28°}$ 1·4281 (Found: C, 64·7; H, 10·3. $C_{14}H_{26}O_4$ requires C, 65·1; H, 10·15%). The *bisphenylurethane* crystallised from methyl alcohol in plates, m. p. 134° (Found : C, 69·9; H, 7·8. $C_{24}H_{32}O_4N_2$ requires C, 69·85; H, 7·8%).

Decane-2 : 9-*dione*.—This was obtained in 65% yield by oxidation of the diol (2 g.) with chromic anhydride in sulphuric acid. On crystallisation from light petroleum (b. p. 40—60°), it formed leaflets, m. p. 62° (Blaise and Koehler, *Bull. Soc. chim.*, 1909, **5**, 691 gave m. p. 64°). The *dioxime* separated from benzene as a microcrystalline powder, m. p. 132° (Found : N, 14·3. $C_{10}H_{20}O_2N_2$ requires N, 14·0%).

Suberic acid. Decane-2 : 9-dione (100 mg.) was shaken with sodium hypobromite solution (10 c.c.; 15%) for 48 hours at 20°. The acid product, isolated from the acidified reaction mixture by means of ether, on crystallisation from water gave suberic acid, m. p. 136°, and 138° when mixed with an authentic specimen (m. p. 139°). Oxidation of the dione with nitric acid gave adipic acid.

The authors are indebted to the Rockefeller Foundation for financial assistance.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W.7.

[*Received, March* 18*th*, 1943.]