

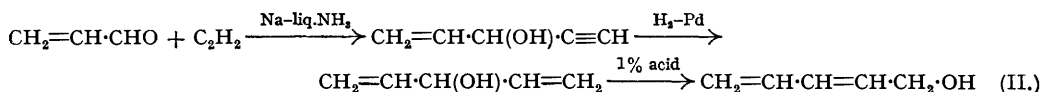
315. *Researches on Acetylenic Compounds. Part XIV. A Study of the Reactions of the Readily Available Ethynyl-ethylenic Alcohol, Pent-2-en-4-yn-1-ol.*

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A variety of reactions of pentenynol, illustrated in the accompanying diagram, has been studied. These include partial hydrogenation, carboxylation, hydration to methylfuran, condensation with formaldehyde to the C₆ glycol, oxidative coupling to the C₁₀ glycol, and oxidation to the corresponding carboxylic acid with chromic acid. Light-absorption data for the diacetylene system in extended chromophores are quoted and discussed.

THE route hitherto available (Heilbron, Jones, Lacey, McCombie, and Raphael, *J.*, 1945, 77) to the ethynylethylenic alcohol, pent-2-en-4-yn-1-ol (I), was extremely unsatisfactory, only about a 4% yield based on acraldehyde being achieved. Now that this interesting substance can be obtained in quantity in a single-stage preparation from easily available starting materials, as described in the preceding paper, a study of some of its many reaction possibilities became worth while.

In the first place its partial hydrogenation to pentadienol (II) was investigated. This substance, which had been found to give an elastic polymer, had previously been prepared (Heilbron, Jones, McCombie, and Weedon, *J.*, 1945, 84) in only very poor yield (*ca.* 5% based on acraldehyde) by the route indicated in the accompanying formulæ. A direct preparation from pentenynol (I) offered the possibility of obtaining reasonable samples of this material



for more detailed polymerisation studies. Partial hydrogenation using a palladium-calcium carbonate catalyst proceeded in a manner similar to that already observed (Heilbron, Jones, McCombie, and Weedon, *loc. cit.*) with the homologous hexenynol, and after careful fractionation a 50% yield of the dienol (II) was obtained.

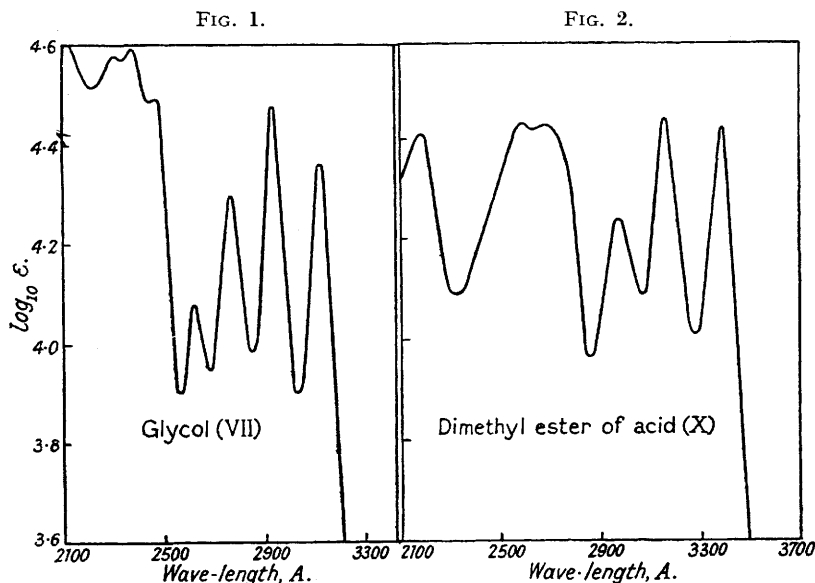
Carboxylation of the Grignard complex (*cf.* Haynes and Jones, *J.*, 1946, 503) gave the *hydroxy-acid* (III), exhibiting the expected light-absorption properties and converted into ϵ -hydroxyhexoic acid on complete hydrogenation. Hydration of pentenynol with sulphuric acid and mercuric sulphate proceeded analogously to that of the homologous hexenynol (Heilbron, Jones, Smith, and Weedon, *J.*, 1946, 54) and yielded 35% of 2-methylfuran (IV); the yield of this highly volatile material could almost certainly be improved by more detailed attention to the reaction conditions, etc.

When pentenynol was originally obtained (*J.*, 1945, 77) one of the few reactions carried out with it involved the condensation of its Grignard complex with butaldehyde to give an ethylenic-acetylenic glycol. Attempts to condense formaldehyde with pentenynol in the same manner were not successful, but by using a copper hydroxide catalyst (General Aniline and Film Corp., U.S.P. 2,238,471) and an aqueous solution of formaldehyde, the *diol* (V) was obtained in 40% yield. Its light-absorption properties were as expected for the structure (V) and this was conclusively proved by hydrogenation to hexane-1:6-diol. The Mannich condensation of pentenynol with formaldehyde and diethylamine, to give the amino-alcohol (VI), has already been described in Part XI (p. 1578).

In Part XII of this series (p. 1580), in which the scope of the oxidative coupling of ethynyl-carbinols to diacetylenic glycols in the presence of cuprous ammonium chloride has been considerably extended, the employment of the ethynyl-ethylenic alcohol, hex-3-en-5-yn-2-ol, in such reactions was described. Pentenynol also can readily be oxidised by air in cuprous salt solution giving a good yield of the *glycol* (VII), hydrogenated to decane-1:10-diol. The light-absorption curve for this glycol is given in Fig. 1, and in the Table the data are compared with those for its homologue, the preparation of which from hexenynol is described in Part XII. It will be noted that the locations of the longer wave-length bands (2930 and 3120 Å.) of both glycols approximate very closely to those recorded for decatetraenol, containing four conjugated ethylenic linkages. Therefore, although conjugated diacetylenes, unlike the vinyl-acetylenes and dienes, fail to show high intensity absorption in the ultra-violet (see Part XII), when the diacetylene grouping becomes part of a larger chromophore, as in glycols such as (VII), it appears to be capable of transmitting electronic vibrations, giving rise to absorption

corresponding to fully conjugated systems. As in all other cases where acetylenic bonds are involved in chromophoric systems, considerable intensity reductions are observed. The multiplicity of shorter wave-length bands indicates a marked tendency of the diacetylene grouping to participate in partial chromophores, probably of the en-yne and ene-diyne types.

Oxidation of pentenynol in acetone solution with chromic acid (cf. Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39) gives a 60% yield of the corresponding acid (VIII) which,



	$\gamma_{\max.}, \text{A.}$	$\epsilon_{\max.}$		$\gamma_{\max.}, \text{A.}$	$\epsilon_{\max.}$	
Deca-2 : 8-diene-4 : 6-diyne-1 : 10-diol (VII)	2300	38,000	Pent-3-en-1-yn-5-ol-1-carboxylic acid (III)	2450	13,000	
	2370	39,000				
	2470	30,000		But-1-en-3-yne-1-carboxylic acid (VIII)	2420	12,500
	2620	12,000				
	2765	20,000				
	2930	30,000				
Dodeca-3 : 9-diene-5 : 7-diyne-2 : 11-diol ¹	3120	23,000	Methyl ester of (VIII)	2440	18,000	
				* 2510	15,500	
	2350	42,000	Hex-3-en-1-yn-5-ol-1-carboxylic acid ²	2455	12,000	
	2470	30,500			* 2560	9,500
	2640	10,500		Sorbic acid	2540	25,000
	2770	18,000				
Decatetraenol ²	2930	30,500	Dimethyl ester of (X)	2190	26,000	
	3120	24,500			2580	27,500
					2680	27,500
				2970	17,500	
				3160	28,500	
				3390	27,500	

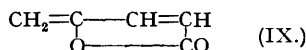
* Inflection.

¹ For preparation see Part XII, p. 1579.

² Reichstein and Trivelli, *Helv. Chim. Acta*, 1932, **15**, 1074.

³ Haynes and Jones, *J.*, 1946, 503.

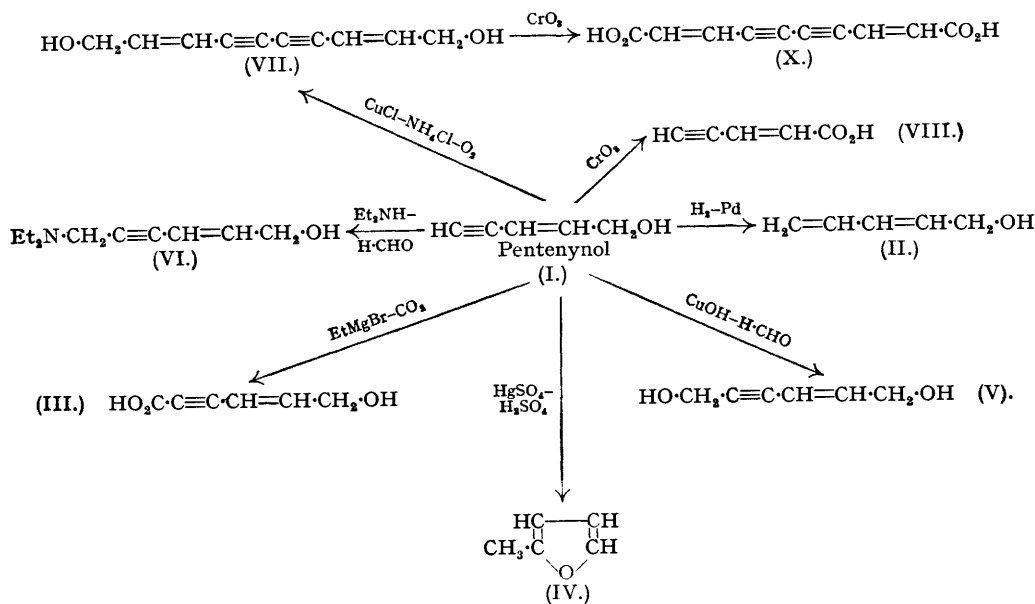
though stable in ether solution, rapidly polymerises when pure even in a vacuum in the dark. This instability may be due to the facile occurrence of an intramolecular hydration, leading to



the formation of the unsaturated lactone (IX), which would be expected to polymerise easily. Such a hypothesis is all the more convincing, since the *methyl* ester is comparatively stable. The structure of the acid is confirmed by hydrogenation to valeric acid and by the light-absorption data for the acid and its ester (Table) which are somewhat similar (although, of

course, lower in intensity) to that of sorbic acid. The glycol (VII) when oxidised under similar conditions with chromic acid gives the amorphous *di-acid* (X) purified through its crystalline *dimethyl* ester, proof of structure being obtained by hydrogenation to sebacic acid. Light-absorption data for the ester (see Fig. 2 and Table) again indicate the participation of the diacetylene group in an extended conjugated system.

Reactions of Pent-2-en-4-yn-1-ol.



EXPERIMENTAL.

(Light-absorption data determined in alcohol solutions.)

Penta-2 : 4-dien-1-ol (II).—A solution of pent-2-en-4-yn-1-ol (160 g.) in ethyl acetate (400 c.c.) was hydrogenated using a palladium-calcium carbonate catalyst (20 g.; 0.3% Pd) until 46.7 l. of gas had been absorbed. The product obtained after removal of catalyst and solvent was carefully fractionated through a column containing a 50×1.5 cm. section packed with single turn glass helices. The numerous fractions collected were divided into two portions: (i) B. p. $32\text{--}34^\circ/1.5$ mm. (34 g.), n_D^{18} 1.4620—1.4730. (ii) *Penta-2 : 4-dien-1-ol* (82.5 g.), b. p. $34\text{--}40^\circ/1.5$ mm., n_D^{18} 1.4770—1.4893. There was a considerable resinous residue. Light absorption: Maximum, 2230 Å., $\epsilon = 26,000$. (Heilbron *et al.*, *J.*, 1945, 87, give b. p. $95\text{--}97^\circ/100$ mm., n_D^{18} 1.4902. Maximum, 2230 Å., $\epsilon = 25,000$.) The various fractions composing portion (ii) differed but slightly in their light-absorption intensities; the refractive index variations are doubtless due to the presence of geometrical isomerides.

A warm solution of the pentadienol (0.4 g.) and maleic anhydride (0.5 g.) in benzene (4 c.c.) was set aside at 20° overnight. Recrystallisation of the separated solid from water gave the lactonic acid (0.48 g.), m. p. 176° (Heilbron *et al.*, *loc. cit.*, give m. p. $175\text{--}176^\circ$) undepressed on admixture with an authentic specimen.

Pent-3-en-1-yn-5-ol-1-carboxylic Acid (III).—Benzene (200 c.c.) was gradually added to a solution of ethylmagnesium bromide (from 12.5 g. magnesium) in ether (250 c.c.) at the same time as the latter was distilled off. When the temperature of the issuing vapours reached 70° , the mixture was cooled (ice) and pent-2-en-4-yn-1-ol (20.5 g.) was added during $\frac{1}{2}$ hour. After refluxing for $1\frac{1}{2}$ hours, the suspension of a fine white powder was shaken in an autoclave with solid carbon dioxide (500 g.) for 22 hours at 20° . The complex was decomposed with ice and dilute sulphuric acid and the aqueous layer was continuously extracted with ether during 24 hours. The combined extracts were washed with sodium bicarbonate solution, and from the ether layer pent-2-en-4-yn-1-ol (12.8 g.) was recovered. The bicarbonate extract was acidified and continuously extracted with ether for 48 hours. The product so obtained was crystallised from benzene-ethyl acetate (4:1) giving the *acid* (6.2 g.) as a micro-crystalline powder, m. p. $135\text{--}136^\circ$, which after subliming at 90° (bath temp.)/ 10^{-4} mm. and crystallisation from the same solvents formed plates, m. p. 137° (Found: C, 57.3; H, 5.05. $\text{C}_6\text{H}_6\text{O}_3$ requires C, 57.15; H, 4.8%). The *S-benzylisothiuronium* salt separated from ethyl acetate-ethanol (4:1) in plates, m. p. $155\text{--}156^\circ$ (decomp.) (Found: N, 9.55. $\text{C}_{14}\text{H}_{16}\text{O}_3\text{N}_2\text{S}$ requires N, 9.6%).

A solution of the acid (1.9 g.) in methanol (30 c.c.) was hydrogenated using platinum oxide (10 mg.) as catalyst. The crude ϵ -hydroxyhexoic acid (1.8 g.) was converted into the lactone by heating it at 160° for 5 minutes, and the lactone was then heated for 3 hours with hydrazine hydrate on the steam-

bath. The hydrazide of ϵ -hydroxyhexoic acid crystallised from ethyl acetate-methanol (6 : 1) in plates, m. p. 115° (Natta, Hill, and Carothers, *J. Amer. Chem. Soc.*, 1934, **56**, 456, give m. p. 114–115°).

2-Methylfuran (IV).—A mixture of pent-2-en-4-yn-1-ol (8 g.), sulphuric acid (40 c.c., 0.5% w/v), and mercuric sulphate (0.2 g.) was distilled in steam until the distillate was no longer cloudy (about 50 c.c. in $\frac{1}{2}$ hour). The distillate was saturated with salt, the upper layer separated and dried (CaCl₂), and distillation gave 2-methylfuran (2.6 g.), b. p. 64°/769 mm., n_D^{20} 1.4342 (Kizhner, *J. Gen. Chem. Russia*, 1931, **1**, 1212, gives b. p. 64°/749 mm., n_D^{18} 1.4365).

The furan (0.25 g.) was added to a warm solution of maleic anhydride (0.3 g.) in benzene (1 c.c.). After $\frac{1}{2}$ hour, the solvent was evaporated, and the residue was recrystallised from ether to give the adduct (0.4 g.) as needles, m. p. 81° (Rinckes, *Rec. Trav. chim.*, 1931, **50**, 1127, gives m. p. 80°).

Hex-2-en-4-yne-1 : 6-diol (V).—A copper hydroxide catalyst was made by precipitating a solution of cuprous chloride (3 g.) in hydrochloric acid (45 c.c., 12%) with potassium hydroxide solution (45 c.c., 40%); it was filtered off and washed well with water. The wet catalyst was then stirred with pent-2-en-4-yn-1-ol (15 g.), formaldehyde solution (20 g.; 40% w/v), water (6 c.c.), and calcium carbonate (0.2 g.) under reflux for 42 hours at 90° in nitrogen. The catalyst was filtered off, and distillation gave some starting material (2 g.) and a viscous liquid (7.9 g.), b. p. 120–130°/10⁻³ mm., n_D^{18} 1.5442. This rapidly solidified and after crystallisation from benzene-ethyl acetate (6 : 1) furnished the glycol (6.8 g.) as needles, m. p. 58–59° (Found: C, 64.1; H, 6.9. C₈H₁₀O₂ requires C, 64.25; H, 7.2%). Light absorption: Maximum, 2270 Å.; ϵ = 15,000. Inflexion, 2370 Å.; ϵ = 12,000. The *bisphenylurethane* crystallised from ethanol in needles, m. p. 157° (Found: N, 8.0. C₂₀H₁₈O₄N₂ requires N, 8.0%).

Hexane-1 : 6-diol.—A solution of the above glycol (1 g.) in methanol (40 c.c.) was hydrogenated using platinum oxide catalyst (10 mg.). The product distilled at 147–148°/18 mm. as a viscous oil which rapidly solidified, and crystallisation from ether gave hexane-1 : 6-diol (0.6 g.), m. p. 41–42° (Hamonet, *Bull. Soc. chim.*, 1905, **33**, 539, gives b. p. 152°/17 mm., m. p. 42°). The bisphenylurethane formed needles, m. p. 170°, from ethanol (Hamonet, *loc. cit.*, gives m. p. 171–172°).

Deca-2 : 8-diene-4 : 6-diyne-1 : 10-diol (VII).—Pent-2-en-4-yn-1-ol (34 g.) was added during 10 minutes to a stirred solution of ammonium chloride (240 g.) and cuprous chloride (150 g.) in water (600 c.c.) at 55°. Air was then bubbled through the red solution (at 55°) for 2½ hours, and the product was isolated by repeated ethereal extraction. Crystallisation from water gave the diol (22 g.) as yellow plates, sintering at 130°, m. p. 153–155° (decomp.) which, on further crystallisation from the same solvent or from benzene (in an atmosphere of nitrogen), formed colourless plates, m. p. 155–156° (decomp.) (Found: C, 74.25; H, 6.05. C₁₀H₁₀O₂ requires C, 74.05; H, 6.2%). The glycol develops a brown colour in air or light. The *dibenzoate*, prepared with benzoyl chloride in pyridine at 20° overnight, separated from light petroleum (b. p. 80–100°) in needles, m. p. 96° (Found: C, 77.4; H, 5.0. C₂₄H₁₈O₄ requires C, 77.8; H, 4.9%). Light absorption: Maxima, 2340, 2640, 2810, 2950, 3150 Å.; ϵ = 63,000, 12,000, 22,000, 26,000, and 23,500 respectively.

In smaller scale experiments, in which the proportion of copper salt to carbinol was increased still further, yields up to 72% were obtained.

Hydrogenation of the glycol (0.49 g.) in methanol (40 c.c.) with platinum oxide (5 mg.) and crystallisation of the product from benzene gave decane-1 : 10-diol (0.31 g.) as a microcrystalline powder, m. p. 71–71.5° (Folkers and Adkins, *J. Amer. Chem. Soc.*, 1932, **54**, 1146, give m. p. 70.8–71.8°; Manske, *Org. Synth.*, Coll. Vol. II, 154, gives m. p. 72–74°).

But-1-en-3-yne-1-carboxylic Acid (VIII).—A mixture of chromium trioxide (35 g.) and concentrated sulphuric acid (56 g.) was made up to 175 c.c. with water, and this solution was added, with constant shaking during 30 minutes, to a cooled solution of pent-2-en-4-yn-1-ol (20.5 g.) in acetone (150 c.c.), the temperature being kept at 15°. After being shaken for a further 1½ hours, the mixture was poured into water and repeatedly extracted with ether. The acidic material was removed by extraction with sodium bicarbonate solution, which after acidification and ether extraction furnished *but-1-en-3-yne-1-carboxylic acid* (14.1 g.) as a light yellow crystalline mass, m. p. 92–93°; crystallisation from light petroleum (b. p. 80–100°) gave long colourless needles, m. p. 94°. The acid soon forms an acetone insoluble polymer, even when sealed up in a vacuum in the dark (Found: C, 62.55; H, 4.5. C₅H₄O₂ requires C, 62.5; H, 4.2%). The *S-benzylisothiuronium* salt separated from ethyl acetate in plates, m. p. 172–173° (Found: N, 10.9. C₁₃H₁₄O₂N₂S requires N, 10.7%). The acid (10 g.) was refluxed for 16 hours with methyl-alcoholic sulphuric acid (2% ; 200 c.c.); isolation by the usual procedure gave, besides some high boiling material, *methyl but-1-en-3-yne-1-carboxylate* (5.35 g.) as a pleasant smelling oil, b. p. 59°/34 mm., n_D^{21} 1.4820. On ice cooling it solidified to plates, m. p. 19–20° (Found: C, 65.7; H, 5.85. C₆H₆O₂ requires C, 65.45; H, 5.5%). A solution of the acid (0.65 g.) in ethyl acetate (30 c.c.) was shaken with hydrogen in the presence of platinum oxide until absorption was complete. The crude valeric acid (0.6 g.) was converted into the amide in the usual way, to give the latter as leaflets, m. p. 104–105° (Robertson, *J.*, 1919, 1220, gives m. p. 106°).

Octa-1 : 7-diene-3 : 5-diyne-1 : 8-dicarboxylic Acid (X).—A mixture of chromium trioxide (13 g.) and concentrated sulphuric acid (20.8 g.) was made up to 65 c.c. with water, and this solution was added, with constant shaking, to a cooled solution of deca-2 : 8-dien-4 : 6-diyne-1 : 10-diol (4 g.) in acetone (75 c.c.) at such a rate as to keep the temperature at 25°. The solution was shaken for a further hour, then poured into water and repeatedly extracted with ether. The acidic material was removed by shaking with sodium bicarbonate solution, which after acidification and ether extraction gave *octa-1 : 7-dien-3 : 5-diyne-1 : 8-dicarboxylic acid* (1.7 g.) as a yellow amorphous powder, charring at ca. 300°, which after several precipitations from aqueous methyl alcohol was pale yellow but still non-crystalline.

The diacid (1.6 g.) was refluxed with methyl-alcoholic sulphuric acid (1.5% ; 70 c.c.) for 14 hours. On cooling, a mass of straw-coloured plates separated, and were filtered off; the filtrate was poured into water, and excess of sodium bicarbonate solution was added. Ether extraction and crystallisation of the resulting solid from methyl alcohol gave, when mixed with the solid obtained before, *dimethyl octa-1 : 7-dien-3 : 5-diyne-1 : 8-dicarboxylate* (1.35 g.) as straw-coloured plates, m. p. 103–104°. On

further recrystallisation from the same solvent, it was obtained as light yellow plates, m. p. 106° , which gradually develop a brown colour (Found : C, 66.3; H, 4.7. $C_{12}H_{10}O_4$ requires C, 66.05; H, 4.65%).

The diacid was regenerated by keeping a solution of the ester (0.3 g.) in methyl alcohol (125 c.c.) containing potassium hydroxide (4 g.) for 48 hours at room temperature. Most of the solvent was evaporated, water was added, and the acid product, isolated from the acidified reaction mixture with ether, gave the diacid (0.21 g.) having the same properties as before (Found : C, 63.85, 63.6; H, 3.9, 4.05. $C_{10}H_8O_4$ requires C, 63.15; H, 3.2%). Light absorption : Maxima, 2580, 2650, 2955, 3155, 3375 μ . ; $\epsilon = 28,500, 28,500, 17,500, 28,500$, and 28,500 respectively.

Sebacic Acid.—The di-ester (130 mg.) in methyl alcohol (75 c.c.) was shaken with hydrogen in the presence of platonic oxide (10 mg.) until absorption was complete. The solution was refluxed for $1\frac{1}{2}$ hours with potassium hydroxide (2 g.), and working up in the usual way gave sebacic acid (70 mg.), m. p. 132° , undepressed on admixture with an authentic specimen (m. p. $131-132^{\circ}$).

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