129. *Researches on Acetylenic Compounds. Part XV. The Oxidation of Primary Acetylenic Carbinols and Glycols.*

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By employing the method previously devised (Part I, Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39) for the oxidation of secondary carbinols and glycols of the acetylenic series, acids have now been obtained from the corresponding primary compounds in yields of up to 40%.

In Part I of this series (*loc. cit.*) it was shown that secondary acetylenic carbinols and glycols could be oxidised to the corresponding ketones by means of chromic acid in acetone, excellent yields being obtainable in many cases. A study of similar oxidations of primary acetylenic carbinols and glycols to the corresponding acids represents a desirable sequel to this work.

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Two isolated examples have already been described in another connexion (Heilbron, Jones, and Sondheimer, *J.*, **1947**, 1586), the carbinol (I) being oxidised to the acid (II), and the glycol (III)

$$\underset{\text{(I.)}}{\mathrm{HC{\equiv}C{\cdot}CH{=}CH{\cdot}CH_2{\cdot}OH}} \longrightarrow \underset{\text{(II.)}}{\mathrm{HC{\equiv}C{\cdot}CH{=}CH{\cdot}CO_2H}}$$

$$\underset{\text{(III.)}}{\mathrm{HO{\cdot}CH_2{\cdot}CH{=}CH{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CH_2{\cdot}OH}} \longrightarrow \underset{\text{(IV.)}}{\mathrm{HO_2C{\cdot}CH{=}CH{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CO_2H}}$$

$$\underset{\text{(V.)}}{\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CH_2{\cdot}OH}} \longrightarrow \underset{\text{(VI.)}}{\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CO_2H}}$$

$$\underset{\text{(VII.)}}{\mathrm{HC{\equiv}C{\cdot}CH_2{\cdot}CH_2{\cdot}OH}} \longrightarrow \underset{\text{(VIII.)}}{\mathrm{HC{\equiv}C{\cdot}CH_2{\cdot}CO_2H}}$$

giving the dibasic acid (IV). A more extensive study of this kind of oxidation has now been made with various types of carbinols and glycols, and the reaction appears to be of general applicability, although the yields (20—40%) are not as satisfactory as those observed with the secondary carbinols.

When non-2-en-4-yn-1-ol (V) (Haynes, Heilbron, Jones, and Sondheimer, *J.*, **1947**, 1583) was treated with chromic acid in acetone, it was found that oxidation did not proceed as readily as with the lower homologue (I), and only by using a 50% excess of the oxidising agent, and re-oxidising the recovered neutral material, could a 21% yield of the *acid* (VI) be obtained. This, unlike the acid (II) containing a free ethynyl group, is quite stable; its structure was confirmed by its light-absorption properties (see table), which are very similar to those of sorbic acid. The β-acetylenic alcohol, but-3-yn-1-ol (VII), could be oxidised similarly to give a 28% yield of the interesting *prop-2-yne-1-carboxylic acid* (*ethynylacetic acid*) (VIII), the structure of which was confirmed by hydrogenation to butyric acid.

When the glycol (IX) (Heilbron, Jones, Lacey, McCombie, and Raphael, *J.*, **1945**, 77) was oxidised in the usual way with excess of chromic acid, a 23% yield of the unstable *keto-acid* (X) could be isolated, the structure of which was confirmed by the formation of a 2 : 4-*dinitrophenylhydrazone* and by its light-absorption properties (see table).

	$\lambda_{\text{max.}}$, A.	$\varepsilon_{\text{max.}}$		$\lambda_{\text{max.}}$, A.	$\varepsilon_{\text{max.}}$
(II) [1]	2420	12,500	Dimethyl ester of (XII)	2500	15,000
(VI)	2560	17,000		2550	15,000
Sorbic acid	2540	25,000		2650	12,000
			Muconic acid [2]	2650	25,000
(X)	2600	12,000			
	2720	11,000			

[1] Heilbron, Jones, and Sondheimer, *J.*, 1947, 1586.

[2] Hausser, Smakula, Kuhn, and Hoffer, *Z. physikal. Chem.*, 1935, *B*, **29**, 371.

The glycol (XI) (Heilbron, Jones, and Sondheimer, *J.*, **1947**, 1586) was similarly oxidised in 40% yield to the dibasic acid (XII), which could not readily be purified and gave erratic analytical results. It was, however, readily converted into the crystalline *dimethyl* ester, the structure of which was confirmed by its light-absorption data; these are very similar to those of the closely related muconic acid ($\mathrm{HO_2C{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}CO_2H}$), though as usual the presence of the acetylenic bond causes a marked decrease in the intensity of maximal absorption.

$$\underset{\text{(IX.)}}{\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CH_2{\cdot}OH}} \longrightarrow \underset{\text{(X.)}}{\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CO_2H}}$$

$$\underset{\text{(XI.)}}{\mathrm{HO{\cdot}CH_2{\cdot}CH{=}CH{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}OH}} \longrightarrow \underset{\text{(XII.)}}{\mathrm{HO_2C{\cdot}CH{=}CH{\cdot}C{\equiv}C{\cdot}CO_2H}}$$

It was reported by Johnson (*J.*, **1946**, 1009) that attempts to oxidise butyne-1 : 4-diol to acetylenedicarboxylic acid both with chromic acid and under Oppenauer conditions resulted in failure. We have found that oxidation of the diol with a 25% excess of chromic acid in acetone gave, after continuous extraction of the product, a 23% yield of the dicarboxylic acid, identical with an authentic sample. In this connexion it was of interest to investigate the behaviour of a primary acetylenic carbinol in an Oppenauer-type oxidation (cf. Heilbron, Jones, and Richardson, *J.*, **1949**, 287). When pent-2-en-4-yn-1-ol (I) was heated under reflux with aluminium *tert.*-butoxide in benzene and acetone, only polymeric material could be isolated. This is probably because of the presence of a free ethynyl group in the molecule, as the carbinol (XIII)

$$\underset{\text{(XIII.)}}{\mathrm{Ph{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CH_2{\cdot}OH}} \longrightarrow \underset{\text{(XIV.)}}{\mathrm{Ph{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}CO{\cdot}CH_3}}$$

(Haynes, Heilbron, Jones, and Sondheimer, *J.*, 1947, 1583) behaved normally under these conditions, and the *ketone* (XIV) arising from condensation of the intermediate aldehyde with acetone (cf. Batty, Burawoy, Harper, Heilbron, and Jones, *J.*, 1938, 175) could be isolated.

EXPERIMENTAL.

Light-absorption data were determined in alcoholic solutions, unless stated otherwise.

The chromic acid solution used for the oxidations described below was made by diluting a mixture of chromium trioxide (100 g.) and concentrated sulphuric acid (160 g.) to 500 c.c. with water.

Oct-1-*en*-3-*yne*-1-*carboxylic Acid* (VI).—The chromic acid solution (36 c.c.) was added to a stirred and cooled solution of non-2-en-4-yn-1-ol (5·0 g.; Haynes, Heilbron, Jones, and Sondheimer, *loc. cit.*) in acetone (30 c.c.) during 20 minutes, the temperature being kept at 10°. After a further 16 hours' stirring, water was added, and the acidic material was extracted to give a syrup (2·5 g.). By re-oxidising the neutral portion, another 0·7 g. of acidic material was obtained. The combined acidic fractions were distilled; the fraction, b. p. 116—118°/10^{-3} mm., partly solidified, and on crystallisation from pentane gave *oct*-1-*en*-3-*yne*-1-*carboxylic acid* (1·16 g.; 21%) as plates, m. p. 43—44°, which on recrystallisation from the same solvent was increased to 45° (Found: C, 70·35; H, 7·75. $C_9H_{12}O_2$ requires C, 71·0; H, 7·95%). In an experiment in which only a 10% excess of chromic acid was used (and the neutral fraction was not re-oxidised), only a 9% yield of the acid was obtained.

Prop-2-*yne*-1-*carboxylic Acid* (*Ethynylacetic Acid*) (VIII).—The chromic acid solution (350 c.c.) was added to a stirred and cooled solution of but-3-yn-1-ol (38 g.; Macallum, U.S.P. 2,125,384) in acetone (350 c.c.) during 105 minutes, the temperature being kept at about 20°. After another 45 minutes' stirring, water was added, and the solution was saturated with salt and continuously extracted with ether for 16 hours. Evaporation of the dried extract and crystallisation of the residue from light petroleum (b. p. 40—60°) gave the *acid* (12·6 g.) as plates, m. p. 80—82°, which on further crystallisation from the same solvent was increased to 83—83·5° (Found: C, 56·85; H, 4·9. $C_4H_4O_2$ requires C, 57·15; H, 4·8%). The S-*benzyl*iso*thiouronium* salt crystallised from ethanol in plates, m. p. 153° (Found: N, 11·0. $C_{12}H_{14}O_2N_2S$ requires N, 11·15%).

A solution of the acid (0·8 g.) in methyl acetate (40 c.c.) was shaken in hydrogen with platinic oxide (20 mg.) (434 c.c. of hydrogen absorbed at 21°/772 mm. equivalent to $\overline{\overline{|}}$1·95). The crude butyric acid (0·8 g.) was converted into the *p*-bromophenacyl ester which formed leaflets, m. p. 61—62°, undepressed on admixture with an authentic specimen (m. p. 62°).

Oct-1-*en*-3-*yn*-5-*one*-1-*carboxylic Acid* (X).—The chromic acid solution (10·3 c.c.) was added to a stirred and cooled solution of non-2-en-4-yne-1 : 6-diol (1·21 g.; Heilbron, Jones, Lacey, McCombie, and Raphael, *loc. cit.*) in acetone (10 c.c.) during 15 minutes, the temperature being kept below 25°. After a further 15 minutes' stirring, water was added and the acidic material was extracted. Evaporation of the ethereal extract and crystallisation of the residue from light petroleum (b. p. 40—60°) gave the *keto-acid* (0·30 g.) as plates, m. p. 58—59°, which on further crystallisation from the same solvent was raised to 62° (Found: C, 65·65; H, 6·1. $C_9H_{10}O_3$ requires C, 65·05; H, 6·05%). The 2 : 4-*dinitrophenylhydrazone* crystallised from aqueous methanol in orange plates, m. p. 151—152° (Found: N, 16·1. $C_{15}H_{14}O_6N_4$ requires N, 16·2%). Light absorption: Main band, maximum, 3770 A.; ε = 26,500.

But-1-*en*-3-*yne*-1 : 4-*dicarboxlic Acid* (XII).—Chromic acid solution (63 c.c.) was added to a stirred and cooled solution of hex-2-en-4-yne-1 : 6-diol (4·0 g.; Heilbron, Jones, and Sondheimer, *loc. cit.*) in acetone (50 c.c.) during 30 minutes, the temperature being kept below 30°. After another hour's stirring at room temperature, water was added and the mixture was thoroughly extracted with ether. The acidic material was removed by washing with sodium hydrogen carbonate solution, which after acidification and another thorough extraction with ether gave the crude di-acid (2·05 g.) as a pale yellow powder, charring at *ca.* 160° and decomposing vigorously at *ca.* 240°. It could be sublimed at 130° (bath temp.)/10^{-5} mm., and after recrystallisation from nitroethane it was obtained as a white microcrystalline powder, decomposing on heating as before. It gave erratic analytical results.

The di-acid (0·5 g.) was refluxed with methanolic sulphuric acid (2·5%; 25 c.c.) for 20 hours. Working up in the usual way gave *dimethyl but*-1-*en*-3-*yne*-1 : 4-*dicarboxylate* (0·45 g.), which after crystallisation from light petroleum (b. p. 40—60°) or aqueous methanol formed plates, m. p. 53° (Found: C, 56·9; H, 4·95. $C_8H_8O_4$ requires C, 57·15; H, 4·8%).

Acetylenedicarboxylic Acid.—The chromic acid solution (58 c.c.) was added to a stirred and cooled solution of butyne-1 : 4-diol (3·0 g.) in acetone (60 c.c.) during 30 minutes, the temperature being kept at *ca.* 10°. Stirring was continued at room temperature for a further 16 hours; water was then added, and the organic material was removed by continuous ether extraction for 12 hours. Evaporation of the dried ether extract, followed by drying in a vacuum desiccator for 36 hours and finally crystallisation from nitroethane, gave acetylenedicarboxylic acid (0·92 g.; 23%) as prisms, m. p. 176—177° (decomp.), undepressed on admixture with an authentic specimen, m. p. 178° (decomp.).

8-*Phenylocta*-3 : 5-*dien*-7-*yn*-2-*one* (XIV).—A mixture of 5-phenylpent-2-en-4-yn-1-ol (4 g.; Haynes, Heilbron, Jones, and Sondheimer, *loc. cit.*), aluminium *tert.*-butoxide (8 g.), benzene (200 c.c.), and acetone (80 c.c.) was refluxed in nitrogen for 42 hours. Dilute acid was added, and the dried organic layer was evaporated. The red syrup which remained was dissolved in ethanol (90 c.c.) and acetic acid (9 g.), and Girard reagent T (7 g.) was added. The solution was refluxed for 1 hour, cooled, and poured into ice and water (800 g.) containing enough sodium hydrogen carbonate to neutralise 90% of the acetic acid. The solution was thoroughly extracted with ether; ether (300 c.c.) and sulphuric acid (100 c.c.; 25%) were then added to the aqueous layer, and the mixture was left for 2 hours with occasional shaking. The ether layer was separated, dried, and evaporated. The liquid residue was distilled at 110° (bath temp.)/10^{-4} mm., to give a yellow viscous oil (1·2 g.), which after 24 hours at 0° partly solidified. Crystallisation from light petroleum (b. p. 40—60°) gave 8-*phenylocta*-3 : 5-*dien*-7-*yn*-2-*one* (0·75 g.) as light yellow plates, m. p. 67° (Found: C, 85·85; H, 6·3. $C_{14}H_{12}O$ requires C, 85·65; H, 6·15%). Light absorption: Maxima, 2280, 2380, 3270 A.; ε = 10,000, 10,000, and 35,000, respectively. Inflexion, 3380 A.; ε = 35,000. The 2 : 4-*dinitrophenylhydrazone* crystallised from methanol–ethyl acetate as dark red prisms, m. p. 207—209° (Found : N, 15·2. $C_{20}H_{16}O_4N_4$ requires N, 14·9%). Light absorption (in chloroform) : Main band, maximum, 4110 A.; ε = 36,500.

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