313. *Researches on Acetylenic Compounds. Part XII. The Preparation of Conjugated Diacetylenic Glycols by the Oxidative Coupling of Various Types of Ethynylcarbinols.*

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Contrary to the experiences of earlier workers it has now been found that the coupling of ethynylcarbinols to diacetylenic glycols, by aerial oxidation in the presence of cuprous ammonium chloride, is a general reaction applicable to carbinols of various types. The scope of synthetic reactions with acetylenic compounds is thereby considerably extended, and these interesting glycols become readily available for more detailed study. Moreover, the function of the cuprous salt appears to be largely catalytic, and coupling can be effected with the use of much less than one equivalent of cuprous ammonium chloride. Light-absorption data for the conjugated diacetylene chromophore are recorded and compared with those of conjugated diene and vinylacetylene systems.

THE formation of diacetylenes by the oxidative coupling of metallic derivatives of mono-substituted acetylenes was first observed as early as 1869, and several alternative procedures have since been described. These mainly involve oxidation of either the cuprous or the

$$2\mathrm{R{-}C{\equiv}C{-}M} \longrightarrow \mathrm{R{-}C{\equiv}C{-}C{\equiv}C{-}R}$$

halogenomagnesium acetylides with agents such as oxygen, ferricyanide, cupric salts, etc. (For summary and references see "The Chemistry of Acetylene," Nieuwland and Vogt, Rheinhold, New York, 1945.) Cupric acetylides are apparently unstable, and, in all reactions in which they should be produced, coupling to diacetylenes occurs.

The oxidation of the readily available ethynylcarbinols (*e.g.*, I) is of particular importance and interest since it provides facile synthetic routes to bifunctional compounds difficult to prepare by other means. This is especially true since the only alternative route to the

$$\begin{array}{rl} \text{(I.)}\ \mathrm{R_1R_2C(OH){\cdot}C{\equiv}CH} \searrow & \\ & \mathrm{R_1R_2C(OH){\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}C(OH)R_1R_2}\quad \text{(II.)} \\ \mathrm{HC{\equiv}C{\cdot}C{\equiv}CH + 2R_1R_2CO} \nearrow & \end{array}$$

diacetylenic glycols (II), *i.e.*, *via* diacetylene, is ruled out because of the practical difficulties involved in preparing this hydrocarbon in quantity. It should be noted, however, that diacetylene has become available in Germany in recent years as a by-product (7%) in the Huels arc process for the production of acetylene from gaseous hydrocarbons.

Zal'kind and his collaborators (*J. Gen. Chem. Russia*, 1937, **7**, 227; 1939, **9**, 971, 1725; *Ber.*, 1936, **69**, 128) reported that aerial oxidation of the cuprous acetylides of tertiary ethynyl-carbinols at room temperature gave good yields of the corresponding diacetylenic glycols, but that only very indifferent yields could be obtained with secondary ethynylcarbinols. These authors sought a theoretical explanation of this lack of reactivity of the secondary carbinols in terms of the opposing inductive effects of the hydroxyl and alkyl groups involved.

It has now been ascertained that by carrying out the aerial oxidation at somewhat higher temperatures, *e.g.* in the range 50—70°, coupling of a wide variety of ethynylcarbinols can be achieved, in most cases to give excellent yields. Methyl-, propyl-, and phenyl-ethynylcarbinols give the secondary glycols (III; R = Me, Pr, and Ph respectively) as mixtures of the *dl*- and *meso*-forms. The reaction can be extended to carbinols made from alkylene oxides giving the *glycols* (IV; R = H and Me), the latter again probably as a mixture of stereoisomerides. The

$$\text{(III.)}\ \mathrm{R{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH(OH){\cdot}R} \qquad \mathrm{R{\cdot}CH(OH){\cdot}CH_2{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}CH(OH){\cdot}R}\ \text{(IV.)}$$

$$\mathrm{CH_3{\cdot}CH(OH){\cdot}CH{=}CH{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CH(OH){\cdot}CH_3}\quad \text{(V.)}$$

glycol derived from ethylene oxide (*i.e.*, IV; R = H), the structure of which has been proved by hydrogenation to octane-1 : 8-diol, is remarkably unstable, being very readily converted into a scarlet insoluble pigment by what appears to be a photo-catalysed oxidation.

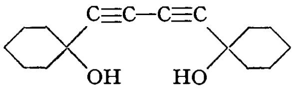
Not only can simple ethynylcarbinols be coupled up by this process, but even conjugated ethynylethylenic carbinols such as hexenynol [$\mathrm{CH_3{\cdot}CH(OH){\cdot}CH{=}CH{\cdot}C{\equiv}CH}$] can be oxidised. The *glycol* (V) obtained from this carbinol is a crystalline solid, presumably stereochemically pure, and its structure is proved by its hydrogenation to *dodecane*-2 : 11-*diol*, which on oxidation gives sebacic acid. Another example of this type is furnished in Part XIV (p. 1586) where the light-absorption data for the chromophore present in glycols such as (V) are discussed.

In addition to demonstrating the general nature of this oxidative coupling reaction, it has also been shown, contrary to earlier work in this field, that it is unnecessary to employ a large excess of cuprous ammonium chloride. While this work was in progress information became available that the I.G. Farb. at Ludwigshafen had effected the oxidation of propargyl alcohol to hexadiynediol using only catalytic quantities of cuprous salt. Three representative glycols (II, $R_1 = Me$, $R_2 = Et$; II, $R_1R_2 = CH_2 < [CH_2]_4 >$; and III, R = Pr) have been prepared in this way, by employing 0·2—0·5 equivalent of cuprous chloride. Although the process is rendered somewhat slower and higher reaction temperatures have to be employed, the yields remain excellent.

The light-absorption properties of the diacetylenic glycols, recorded in the accompanying Table, agree with those previously determined for 2 : 7-dimethylocta-3 : 5-diyne-2 : 7-diol (II; $R_1 = R_2 = Me$) (mentioned by Jones and McCombie, *J.*, 1943, 261). The conjugated diacetylene chromophore exhibits absorption at rather longer wave-lengths than conjugated vinylacetylenes and dienes, but the intensities are only of a very low order. The progressive diminution in intensity and the accompanying appearance of fine structure in the conjugated diene, en-yne, and di-yne systems is of some interest.

Various aspects of the chemistry of these readily accessible diacetylenic glycols are at present being studied in these laboratories.

Light-absorption data of conjugated diacetylenic glycols compared with those of conjugated dienes and vinylacetylenes.

(In alcoholic solutions.)	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
$CH_3{\cdot}CH{=}CH{\cdot}CH{=}CH_2$ [1]	2235	23,000
$CH_3{\cdot}CH(OH){\cdot}CH{=}CH{\cdot}C{\equiv}CH$ [2]	2230	13,500
	2300 *	9,500
$Me_2C(OH){\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}C(OH)Me_2$	2290	310
	2410	300
	2560	180
$HO{\cdot}CH_2{\cdot}CH_2{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	2280	540
	2390	540
	2510	360
$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3$	2260	355
	2410	410
	2640	250
$CH_3{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH(OH){\cdot}CH_3$ (m. p. 67°)	2300	1,930
	2370	1,860
$C_3H_7{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH(OH){\cdot}C_3H_7$	2320	360
	2420	400
	2550	265
	2820 *	90
	2310	294
	2420	347
	2440	332
	2570	160
$C_2H_5{\cdot}CMe(OH){\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CMe(OH){\cdot}C_2H_5$	2300	330
	2420	368
	2550	204
$C_9H_{19}{\cdot}CMe(OH){\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CMe(OH){\cdot}C_9H_{19}$	2400 2420 2520	515
	2660	555
	2820	465
	3080 [3]	135
$Ph{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH(OH){\cdot}Ph$	2460	1,150
	2600	785

* Inflexion.

[1] Booker, Evans and Gillam, *J.*, 1940, 1453.

[2] Jones and McCombie, *J.*, 1943, 261.

[3] This band may arise from the presence of a **small** quantity of dehydrated material.

EXPERIMENTAL.

Octa-3 : 5-*diyne*-2 : 7-*diol* (III; R = Me).—Methylethynylcarbinol (37 g.) in ethanol (20 c.c.) was added to a mixture of cuprous chloride (100 g.), ammonium chloride (160 g.), hydrochloric acid (1 c.c.), and water (425 c.c.) at room temperature. The temperature was raised to 55° and air was passed in for 6½ hours, a condenser containing solid carbon dioxide and alcohol being used to prevent loss of carbinol. Isolation with ether and distillation gave a mixture of stereoisomers of octa-3 : 5-diyne-2 : 7-diol (31 g.), m. p. 84—87° (change of state at 65°), b. p. *ca.* 120°/10^{-4} mm. A single process of chromatography on 2 g. of this product gave one of the stereoisomeric forms (0·3 g.), m. p. 64—67° (Lespieau, *Ann. Chim.*, 1912, **27**, 137, quotes m. p. 67·5—68° for one of the isomeric forms. The other has m. p. 108—109° according to Zal'kind and Gverdtsiteli, *J. Gen. Chem. Russia*, 1939, **9**, 971).

Dodeca-5 : 7-*diyne*-4 : 9-*diol* (III; R = Pr).—(*a*) Propylethynylcarbinol (25 g.; Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 45) in ethanol (25 c.c.) was added dropwise during 15 minutes to a solution of ammonium chloride (160 g.), cuprous chloride (100 g.), and concentrated hydrochloric acid (1·5 c.c.) in water (450 c.c.) at 50—55°. The mixture was stirred for 15 minutes at this temperature; air was then passed in for 2 hours, by which time the mixture had assumed a deep greenish colour. After cooling, the product was isolated with ether and distilled from a Claisen flask with a low, wide side-arm giving the glycol (21·2 g.), b. p. 134°/10^{-2} mm., $n_D^{21°}$ 1·5178 (Zal'kind and Gverdtsiteli, *loc. cit.*, give b. p. 159—162°/7 mm.).

(*b*) Propylethynylcarbinol (5 c.c.) was added to a solution of ammonium chloride (16 g.), cuprous chloride (10 g.), and concentrated hydrochloric acid (0·15 c.c.) in water (45 c.c.) during 5 minutes. With the mixture at a temperature of 50—55°, air was passed in and a further 25 c.c. of the carbinol was added dropwise during 1 hour. After oxidation for 8 hours precipitation of cupric salts commenced. Sufficient dilute hydrochloric acid was added to the cooled mixture to dissolve the solid, and isolation with ether gave the glycol (23 g.), b. p. 138°/10^{-3} mm., $n_D^{19.5°}$ 1·5175. One of the stereoisomeric forms of the *bis-a-naphthylurethane* was isolated from the mixture of isomers by recrystallisation from ethanol. It formed needles, m. p. 158° (Found: N, 5·05. $C_{34}H_{20}O_4N_2$ requires N, 5·25%).

Dodecane-4 : 9-*diol*.—Dodeca-5 : 7-diyne-4 : 9-diol (4·85 g.) in ethyl acetate (100 c.c.) was hydrogenated in the presence of platinic oxide (10 mg.) until absorption ceased. Removal of catalyst and solvent and crystallisation of the residual solid from light petroleum (b. p. 40—60°) gave *dodecane*-4 : 9-*diol* (4·5 g.) as lustrous leaflets, m. p. 53° (Found: C, 71·45; H, 12·75. $C_{12}H_{26}O_2$ requires C, 71·25; H, 12·95%).

1 : 6-*Diphenylhexa*-2 : 4-*diyne*-1 : 6-*diol* (III; R = Ph).—Phenylethynylcarbinol (25 g.; Jones and McCombie, *J.*, 1942, 733) in ethanol (50 c.c.) was added to a mixture of ammonium chloride (160 g.), cuprous chloride (100 g.), concentrated hydrochloric acid (1·5 c.c.), and water (450 c.c.) at 50—55°. Air was passed in for 2 hours; isolation with ether and crystallisation from benzene gave a mixture of stereoisomers as leaflets (12 g.), m. p. 102°. Repeated crystallisations from benzene gave matted needles with m. p. 122° (sintered at 90° and softened at 103°) (Zal'kind and Gverdtsiteli, *loc. cit.*, give m. p. 132—133°).

Octa-3 : 5-*diyne*-1 : 8-*diol* (IV; R = H).—A solution of but-1-yn-4-ol (15 g.) (Macullum, U.S.P. 2,125,384) in ethanol (25 c.c.) was added to ammonium chloride (96 g.), cuprous chloride (60 g.), and concentrated hydrochloric acid (0·9 c.c.) in water (270 c.c.) during 20 minutes. Air was passed in at 50—55° for 2 hours and after the mixture had been cooled and saturated with salt the product was isolated with ether, giving *octa*-3 : 5-*diyne*-1 : 8-*diol* (7·1 g.), m. p. 42—43°, b. p. 135°/10^{-4} mm. The solid became scarlet on exposure to light and air and no satisfactory analytical data could be obtained (Found: C, 68·0; H, 7·1. $C_8H_{10}O_2$ requires C, 69·5; H, 7·3%). The *diacetate* crystallised from petroleum (b. p. 80—100°) in needles, m. p. 63° (Found: C, 64·85; H, 6·3. $C_{12}H_{14}O_4$ requires C, 64·85; H, 6·35%). A solution of the diol (3·3 g.) in ethyl acetate (50 c.c.) was hydrogenated in the presence of platinic oxide (20 mg.) giving octane-1 : 8-diol (3·0 g.), m. p. 60—61° (from ethyl acetate) (Franke and Lieben, *Monatsh.*, 1914, **35**, 1939, give m. p. 60°).

Deca-4 : 6-*diyne*-2 : 9-*diol* (IV; R = Me).—1-Pentyn-4-ol (25 g., Haynes and Jones, *J.*, 1946, 954) in ethanol (50 c.c.) was added to a mixture of ammonium chloride (160 g.), cuprous chloride (100 g.), concentrated hydrochloric acid (1·5 c.c.), and water (450 c.c.) at 50—55° during 30 minutes. Air was then passed in for 135 minutes at 50—55°, and extraction of the cooled mixture with ether and distillation of the dried extract gave *deca*-4 : 6-*diyne*-2 : 9-*diol* (20·35 g.), b. p. 136°/10^{-3} mm., $n_D^{17°}$ 1·5345. This material solidified at 0° but melted at room temperature (Found: C, 72·35; H, 8·7. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·5%). One of the stereoisomeric forms of the *bis*-3 : 5-*dinitrobenzoate*, m. p. 192°, was isolated by fractional precipitation with petrol from an ethyl acetate solution of the mixture of isomers (Found: N, 10·0. $C_{24}H_{18}O_{12}N_4$ requires N, 10·1%).

Di-(1-*hydroxy*cyclo*hexyl*)*butadiyne* (II; $R_1R_2 = C_5H_{10}$).—3 C.c. of a solution of 1-ethynyl*cyclo*hexanol (25·2 g., Hennion and Murray, *J. Amer. Chem. Soc.*, 1942, **64**, 1220) in ethanol (30 c.c.) were added to a solution of ammonium chloride (8 g.), cuprous chloride (2·5 g., 0·2 equivalent), and concentrated hydrochloric acid (0·5 c.c.) in water (25 c.c.) at 30°, and the mixture stirred for 5 minutes. The temperature was raised to 70°, air was passed in, the rest of the carbinol solution was added dropwise during 3½ hours, and oxidation was continued for a further 4½ hours. The mixture was poured into 300 c.c. of ammonium chloride solution and the precipitated solid completely freed from copper salts by washing it with N-hydrochloric acid followed by water. After being dried, this solid was recrystallised twice from benzene to give di-(1-hydroxy*cyclo*hexyl)butadiyne (23·5 g.), m. p. 173° (Zal'kind and Aizikovich, *J. Gen. Chem. Russia*, 1937, **7**, 227, give m. p. 173°) (Found: C, 78·05; H, 8·85. Calc. for $C_{16}H_{22}O_2$: C, 78·0; H, 9·0%).

3 : 8-*Dimethyldeca*-4 : 6-*diyne*-3 : 8-*diol* (II; R_1 = Me; R_2 = Et).—10 C.c. of a solution of methylethylethynylcarbinol (20·8 g.; Campbell, Campbell, and Eby, *J. Amer. Chem. Soc.*, 1938, **60**, 2882) in ethanol (25 c.c.) were added to a solution of ammonium chloride (8 g.), cuprous chloride (2·5 g.), and concentrated hydrochloric acid (0·05 c.c.) in water (25 c.c.), and the mixture stirred for a minute at room temperature. The colour changed from brown to green. The temperature was raised to and maintained at 65—70° whilst air was passed in at a rate of about 2 l. per minute. The remainder of the carbinol solution was added in 5 c.c. portions during the next 8 hours, and the oxidation was continued for a further 5 hours. The cooled mixture was poured into 200 c.c. of ammonium chloride solution and the resultant solid washed with dilute hydrochloric acid to give 14 g. of a solid, m. p. 80—88°. With 6 equivs. of cuprous ammonium chloride solution the yield is slightly better and the reaction takes only 2 hours. Solution of a portion (2 g.) in the minimum volume of ethyl acetate followed by partial precipitation with petroleum (b. p. 80—100°) gave one of the stereoisomeric forms (0·85 g.), m. p. 88° (I.G. Farb. F.P. 765,469 give m. p. 89°) (Found: C, 73·95; H, 9·25. Calc. for $C_{12}H_{18}O_2$: C, 74·2; H, 9·35%).

Dodeca-3 : 9-*diene*-5 : 7-*diyne*-2 : 11-*diol* (V) (with F. SONDHEIMER).—Hex-3-en-5-yn-2-ol (6 g.; Heilbron, Jones, Smith, and Weedon, *J.*, 1946, 57) was slowly dropped into a stirred solution of ammonium chloride (80 g.) and cuprous chloride (50 g.) in water (200 c.c.), maintained at 55°. Air was bubbled through the red solution at this temperature for 2 hours during which time much black gum separated. The product isolated by repeated ether extraction contained much polymeric material from which it was separated by boiling with water. This furnished the *diol* (1·5 g.) as light yellow needles, m. p. 92°, which after recrystallisation from either water or benzene (nitrogen atmosphere) gave colourless needles, m. p. 94—95° (Found: C, 75·5; H, 7·45. $C_{12}H_{14}O_2$ requires C, 75·75; H, 7·4%). The glycol slowly becomes yellow in air. Light absorption: see Part XIV, p. 1587.

Dodecane-2 : 11-*diol* (with F. SONDHEIMER).—A solution of the above glycol (400 mg.) in methanol (20 c.c.) was shaken with hydrogen in the presence of platinic oxide (10 mg.) until absorption was complete. Crystallisation of the product from pentane–ether (3 : 1) gave *dodecane*-2 : 11-*diol* (350 mg.) as plates, m. p. 54—55° (Found: C, 71·1; H, 12·85. $C_{12}H_{26}O_2$ requires C, 71·25; H, 12·95%). Oxidation of the diol with chromic acid in sulphuric acid gave a 75% yield of dodecane-2 : 11-dione, leaflets from light petroleum (b. p. 40—60°), m. p. 67° (Cason and Prout, *J. Amer. Chem. Soc.*, 1944, **66**, 48, give m. p. 67·4—67·8°). Sebacic acid, m. p. 130—131°, undepressed on admixture with an authentic specimen (m. p. 132°), was obtained when the diketone was shaken with sodium hypobromite solution for 48 hours at 20°.

10 : 15-*Dimethyltetracosa*-11 : 13-*diyne*-10 : 15-*diol* (II; $R_1 = Me$; $R_2 = C_9H_{19}$).—Methylnonylethynylcarbinol (10 g.; Locquin and Sung, *Compt. rend.*, 1922, **174**, 1427) in ethanol (10 c.c.) was added to a mixture of ammonium chloride (64 g.), cuprous chloride (40 g.), concentrated hydrochloric acid (0·4 c.c.), and water (200 c.c.), and stirred at 65—67°. Oxygen was passed through at about 3 l. per minute, and after 45 minutes the reaction mixture was cooled, hydrochloric acid was added to dissolve copper salts, and the product was isolated with ether. Distillation gave the *glycol* (2·75 g.), b. p. 210°/10^{-2} mm., m. p. 40—43° (Found: C, 79·9; H, 11·7. $C_{26}H_{46}O_2$ requires C, 79·95; H, 11·85%). 5·4 G. of carbinol were recovered.

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