370. *Researches on Acetylenic Compounds. Part XXXIV.* Further Studies on the Synthesis of Diacetylenic Glycols.*

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A study has been made of the effects of changes in the several variable factors which influence the copper-catalysed oxidative coupling of acetylenic alcohols to give conjugated diacetylenic glycols, leading to improvements in the convenience and range of application of this reaction. The ultra-violet light-absorption properties of a large number of diacetylenic compounds have been examined.

THE oxidative coupling of acetylenic alcohols (Zalkind *et al.*, *J. Gen. Chem. U.S.S.R.*, (*a*) 1937, **7**, 227; 1939, **9**, (*b*) 971, (*c*) 1725; *Ber.*, 1936, **69**, 128), *e.g.*:

$$2HO{\cdot}CMe_2{\cdot}C{\equiv}CH + O_2 \xrightarrow{CuCl-NH_4Cl} HO{\cdot}CMe_2{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CMe_2{\cdot}OH$$

is one of a relatively small class of reactions in which two molecules are linked together directly to give a symmetrical product. Since it takes place under milder conditions than

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* Part XXXIII, preceding paper.

most of the alternative coupling processes (*e.g.* the Wurtz and the Kolbe reaction and the acyloin condensation) and frequently gives very high (>90%) yields, improvements in its range of application are of considerable potential value. As originally described it gave satisfactory yields only with tertiary ethynyl-alcohols, and the first method adopted (Part XII; Bowden, Heilbron, Jones, and Sargent, *J.*, 1947, 1579) to achieve such an improvement, *i.e.*, the use of a higher reaction temperature, *ca.* 55°, is in one respect a retrograde step, inasmuch as many acetylenic compounds are unstable under these conditions. Accordingly, the various factors influencing the reaction have now been examined separately in order to find a method of effecting the reaction at room temperature which would nevertheless be applicable to secondary ethynyl-alcohols.

Zalkind and Aizikovich [*loc. cit.* (*a*)] stated that the substitution of oxygen for air increased the rate of coupling of ethynyldimethylcarbinol about sixfold, but they apparently did not examine the use of oxygen with those (secondary) ethynyl-alcohols which gave very low yields by their standard procedure. When oxygen is used, and intimate contact between the two phases is ensured by using an atmospheric-pressure hydrogenation apparatus of the usual type, such alcohols couple quite rapidly at room temperature and give excellent yields of the expected glycols. Although it had been shown (Part XII, *loc. cit.*) that in many cases small (~0·2 mol.) quantities of cuprous salts were effective in promoting coupling, *i.e.* that their action is catalytic, it was found that better yields of diol were obtained from ethynylmethylcarbinol when the original larger proportions (4—6 mols.) were employed. In all probability this is merely the result of the fact that cuprous salts accelerate the coupling reaction, increasing its importance relative to side-reactions.

In earlier work strongly acid conditions were used for the coupling of acetylenic alcohols, whereas hydrocarbons have usually been coupled in ammoniacal solution (see *inter al.*, Glaser, *Ber.*, 1869, **2**, 422; Schlubach and Wolf, *Annalen*, 1950, **568**, 141). To clarify this matter experiments on the coupling of ethynylmethylcarbinol were carried out at varied pH values. The cuprous chloride–ammonium chloride solution normally used has a pH value of about 3 before the acetylenic compound is added. This can be varied by addition of hydrochloric acid or ammonia; above about pH 5 the copper derivative usually precipitates. Despite this, the coupling reaction proceeds slowly, giving fair yields, though some of the copper derivative is unchanged at the end of the reaction. As Zalkind *et al.* (*locc. cit.*) observed, the reaction also takes place in strongly ammoniacal solution, but the alkaline solution (cuprammonium hydroxide is a strong base) clearly decomposes some of the product and yields are low. On the other hand addition of acid is also possible without having marked effects on the reaction period or yield. These results are tabulated in the experimental section.

By using the conditions found to be optimal for ethynylmethylcarbinol, a number of other alcohols have been submitted to the reaction, with the results shown in Table 1. The yields listed refer to purified products.

TABLE 1. *Coupling of various acetylenic alcohols.*

		Previous methods				Previous methods	
Compound	Yield, %		Yield, %	Compound	Yield, %		Yield, %
$HC{\equiv}C{\cdot}CH_2{\cdot}OH$	88[1]	a	—	$HC{\equiv}C{\cdot}CH_2{\cdot}CHMe{\cdot}OH$...	98[2]	b	80
$HC{\equiv}C{\cdot}CHMe{\cdot}OH$ ...	94[2]	b	82	$HC{\equiv}C{\cdot}CHPh{\cdot}OH$	88[3]	b	48[4]
$HC{\equiv}C{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	82[2]	b	42	$HC{\equiv}C{\cdot}CH{=}CH{\cdot}CH_2{\cdot}OH$	84[3]	c	70

[1] Product extracted continuously and recrystallised. [2] Product extracted continuously and distilled at 10^{-4} mm. [3] Product isolated by filtration and ether-extraction of filtrate. [4] Several attempts to repeat this original experiment gave yields of only 0—25%.

a. For unpublished German work, see Copenhaver and Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold, 1949, p. 121. b. Bowden, Heilbron, Jones, and Sargent, *loc. cit.* c. Heilbron, Jones, and Sondheimer, *J.*, 1947, 1586.

The control over the acidity of the solution which may be exercised without preventing the coupling reaction has permitted the oxidative coupling of the acid-labile ethynylpropenylcarbinol, either to the glycol (I), or to the corresponding rearranged glycol (III). The results of carrying out this reaction at various acidities are tabulated in the experimental section. The presence of (II) was inferred from the absorption band at 2840 Å shown by the product, analogous to the highest wave-length band of propenyldiacetylene, referred to below.

$$\begin{tikzcd}
CH_3{\cdot}CH{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CH \arrow[r, "pH\ 6{\cdot}5;\ 93\%"] \arrow[d, "pH\ 1;\ 81\%"] & {[CH_3{\cdot}CH{=}CH{\cdot}CH(OH){\cdot}C{\equiv}C]_2}\ (I) \\
{[CH_3{\cdot}CH(OH){\cdot}CH{=}CH{\cdot}C{\equiv}C]_2}\ (III) & CH_3{\cdot}CH{=}CH{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CH(OH){\cdot}CH_3\ (II) \arrow[l]
\end{tikzcd}$$

It was found, rather unexpectedly, that hex-3-en-5-yn-2-ol was converted at pH 3 into an uncrystallisable syrup, although this alcohol had given a 25% yield of crystalline (III) in the earlier work (Bowden, Heilbron, Jones, and Sargent, *loc. cit.*). This syrup had light-absorption properties very similar to those of crystalline (III), and probably consisted of a mixture of isomers of this glycol (both *cis–trans* and *meso–rac.* isomerism are possible).

The acid-catalysed rearrangement of (I) proved more difficult to effect than might have been expected. It did, however, take place to completion in a 10% (wt./vol.) solution of sulphuric acid in 95% ethanol at room temperature. In order to verify the two-stage nature of the reaction ($I \xrightarrow{k_1} II \xrightarrow{k_2} III$) and to determine approximately the ratio of k_1 to k_2 the reaction mixture was examined spectroscopically. A typical light-absorption curve for the acid solution when rich in (II) is compared with the spectra of (III) and propenyldiacetylene in Fig. 1. The glycol (III) has an absorption maximum (cf. Bowden, Heilbron, Jones, and Sargent, *loc. cit.*) at 3130 Å ($\varepsilon = 22{,}800$) where neither (I) nor propenyldiacetylene shows appreciable absorption (the latter has $\varepsilon = 70$ at 3100 Å). The glycol (II) shows a maximum at 2840 Å, agreeing well with that of propenyldiacetylene at 2800 Å ($\varepsilon = 11{,}000$) at a wave-length corresponding to a minimum in the spectrum of (III) with $\varepsilon_{\text{min.}} = 6850$. Since (I) is practically transparent at 2840 Å it is possible to determine (III) directly from the intensity of absorption at 3130 Å, and to estimate (II) by measuring ε_{2840}, subtracting the contribution which can be ascribed to (III), and assuming $\varepsilon_{2840} = 11{,}000$ for (II). Residual (I) can then be found by difference. The results so obtained and tabulated below are in practice accurate only so long as the proportion of (III) is fairly low.

TABLE 2. *Rearrangement of dodeca-2 : 10-diene-5 : 7-diyne-4 : 9-diol.*

Time, mins.	Amount of (I) $(1 - x)$		Amount of (II) $(x - y)$		Amount of (III) y		10^3k_1
(t)	Found	Calc.*	Found	Calc.†	Found	Calc.‡	from (ii)
5	0·979	0·980	0·021	0·019	0·0008	0·0006	4·05
20	0·924	0·923	0·073	0·075	0·002	0·002	3·94
35	0·871	0·869	0·120	0·123	0·009	0·008	3·98
65	0·781	0·771	0·195	0·207	0·024	0·022	3·92
95	0·671	0·684	0·288	0·272	0·041	0·044	4·20
125	0·615	0·607	0·315	0·323	0·070	0·070	3·83
185	0·436	0·477	0·432	0·388	0·132	0·135	4·44
245	0·410	0·375	0·408	0·417	0·182	0·208	3·64

* From equation (i). † From equations (i) and (ii). ‡ From equation (iii).

By assuming that each of the stages is pseudounimolecular and irreversible (Braude and Jones, *J.*, 1944, 436), and by denoting the weights of (I), (II), and (III) in grams per 100 c.c. of solution after t minutes as $(1 - x)$, $(x - y)$, and y, respectively, one may write the equations :

$$1 - x = e^{-k_1t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

or

$$k_1 = \frac{2{\cdot}303}{t} \log_{10} \frac{1}{1 - x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

and

$$y = \{k_2(1 - e^{-k_1t}) - k_1(1 - e^{-k_2t}\}/(k_2 - k_1) \quad . \quad . \quad . \quad . \quad . \quad (iii)$$

In the special case where $k_2 = k_1$ the integrated equation is

$$y = 1 - e^{-k_1 t}(1 + k_1 t) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (iv)$$

From the experimental values of $(1 - x)$, values were calculated for k_1, the mean being $4{\cdot}0 \times 10^{-3}$ with a standard error of $0{\cdot}1 \times 10^{-3}$. By assuming the mean value, k_2 was determined approximately by substituting various values in (iii) and comparing calculated values of y with the experimental results at $t = 125$; poor agreement was obtained except with $k_2 = 2{\cdot}5$—$3{\cdot}5 \times 10^{-3}$. Equation (iv) also gave results in poor agreement with those found. With $k_2 = 3{\cdot}0 \times 10^{-3}$, however, agreement was good over a wide range of reaction times, a consequence which confirms the validity of the original hypotheses.

Irreversibility and the absence of side-reactions, apart from partial etherification (cf. Heilbron, Jones, and Weedon, *J.*, 1945, 81; Braude, Jones, and Stern, *J.*, 1946, 396), were confirmed by the identity, within experimental error, of the final extinction coefficients, over the whole spectrum, with those of recrystallised (III). While much more precise data would be needed to make possible comparison of k_1 and k_2 for the rearrangement of (I) with corresponding constants for other similar reactions, the values obtained are of the same order of magnitude as those found for ethynylpropenylcarbinol itself (Braude and Jones, *loc. cit.*).

Light Absorption of Conjugated Diacetylenes

The absorption spectrum of gaseous diacetylene in the near ultra-violet was examined by Woo and Chu (*J. Chem. Phys.*, 1935, **3**, 541; 1937, **5**, 786). Their observations were extended to the vacuum ultra-violet by Price and Walsh (*Trans. Faraday Soc.*, 1945, **41**, 384). There are four well-defined regions; one of very low intensity between 2650 and 2970 Å, a wide range (<1700—2650 Å) over which the absorption is of moderate intensity, and two regions of very intense absorption beginning at 1630 Å and 1120 Å. The last two were ascribed by Price and Walsh to Rydberg transitions, and the 1700—2650 Å absorption to an $N \longrightarrow V$ transition. Price and Walsh also examined hexa-2 : 4-diyne, which showed similar properties.

Solution spectra of a series of conjugated diacetylenic glycols were described by Bowden, Heilbron, Jones, and Sargent (*loc. cit.*); but the only general conclusion which can be drawn from their results is that these compound show complex absorption of low and very variable intensity in the 2200—3000-Å region, with important differences between compounds of very similar structures. In the course of the present work, and that described in Parts XXVIII and XXXIII, it became evident that these earlier results are misleading, and advantage was taken of the availability of many pure diacetylenic compounds to make a systematic study of the absorption of the diyne chromophore, by using photoelectric spectrophotometry. This proved somewhat difficult, because diacetylenes are often decidedly unstable and apparently decompose into ethylenic compounds showing high-intensity absorption. Accordingly, samples for examination were stored at —70° whenever necessary, and results inconsistent with those obtained for stable substances were checked by further purification or by the preparation of new samples. It then became evident that the light-absorption properties of diacetylenes are quite regular, and that their absorption does not extend, with appreciable intensity, beyond about 2650 Å.

The light-absorption properties of a number of diacetylenic hydrocarbons, alcohols, and glycols are summarised in Table 3. This includes results for the monosubstituted diacetylenes, which are unstable and for which the intensity values are doubtful to the extent of perhaps 20%, but contains no values which are likely to be grossly inaccurate. They suffice to show that the light-absorption of diacetylenes is approximately constant over a small range of substituents, and to permit the deduction that the substitution of alkyl for hydrogen in monosubstituted diacetylenes has only a small effect; the average bathochromic shift is 20 Å for the longest-wave-length band, as against 50 Å for alkyl-substitution in dienes. It also appears that α-hydroxyl groups have a detectable bathochromic effect (average + 15 Å); this is discussed in more detail in the following paper.

On the basis of the evidence presented in Table 3 a conclusion may be drawn regarding the structure of isanic or erythrogenic acid, first isolated from *Onguekoa gore* Engler by Steger and van Loon (*Fette und Seifen*, 1937, **44**, 344), and later examined by Castille (*Annalen*, 1939, **543**, 104) who proposed the alternative formulæ (IV) and (V) and recorded the light-absorption properties of his specimen. Comparison of these with those of typical

$$H_2C{=}CH{\cdot}C{\equiv}C{\cdot}[CH_2]_4{\cdot}C{\equiv}C{\cdot}[CH_2]_7{\cdot}CO_2H \quad (IV)$$
$$H_2C{=}CH{\cdot}[CH_2]_4{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}[CH_2]_7{\cdot}CO_2H \quad (V)$$

vinylacetylenes (Jones and McCombie, *J.*, 1943, 261) and with the diacetylene spectra recorded above eliminates (IV) and suggests that (V) is not the only substance present. On the other hand, the positions of the absorption bands are in very close agreement with those of propenyldiacetylene (Cook, Jones, and Whiting, forthcoming publication), and the intensity-ratios of the three maxima of longest wave-length are also very similar in the two cases (Table 4). It can therefore be concluded that the specimen of erythrogenic acid examined by Castille was heterogeneous, and contained about 6% of a (presumably) C_{18} acid possessing a —C=C—C≡C—C≡C— chromophore. The crude glycerides obtained from *Onguekoa gore* show similar (but more intense) light-absorption (Dr. E. M. Meade, private communication), and it therefore appears that the same chromophoric system does indeed occur in a natural fatty acid. Dr. J. P. Riley (private communication) independently reached the conclusion that erythrogenic acid is heterogeneous.

Fig. 1.

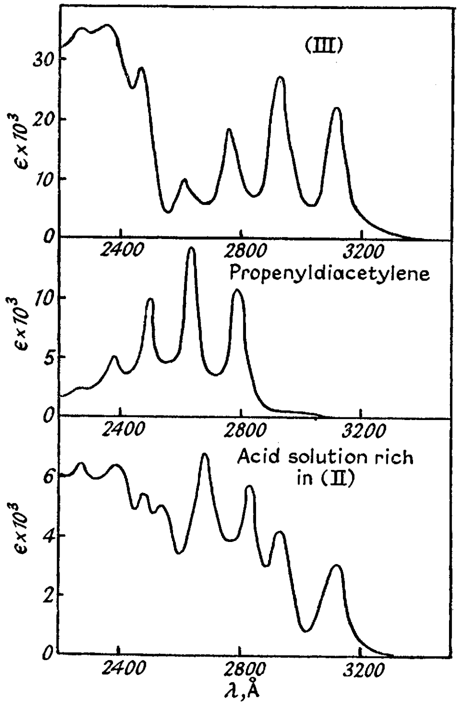
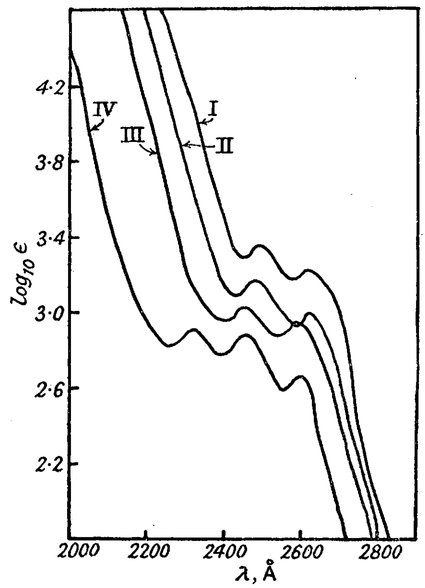


Fig. 2.



I. $HO{\cdot}CPh_2{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CPh_2{\cdot}OH$.
II. $HO{\cdot}CHPh{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CHPh{\cdot}OH$.
III. $HO{\cdot}CPhMe{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CPhMe{\cdot}OH$.
IV. $CH_3{\cdot}CH{=}CH{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH(OH){\cdot}CH{=}CH{\cdot}CH_3$.

The fine structure in the light absorption of simple diacetylenes (Table 3) corresponds (the average separation between maxima is 2300 cm.$^{-1}$) to the very strong 2264 cm.$^{-1}$ band observed by Meister and Cleveland (*J. Chem. Phys.*, 1950, **18**, 255) in the Raman spectrum of hexa-2 : 4-diyne and ascribed to the symmetrical (A_1) stretching of the molecule. Evidently the vibrational levels in this excited state show about the same spacing as in the ground state. In diacetylene itself prominent bands were observed at an interval of about 2100 cm.$^{-1}$ by Woo and Chu (*loc. cit.*) and were similarly assigned.

The aromatic diacetylenic glycols show light-absorption properties which deviate appreciably from those which might be predicted on the basis of the formally isolated chromophores present (Table 5 and Fig. 2). Similar deviations are observed in the case of dodeca-2 : 10-diene-5 : 7-diyne-4 : 8-diol; the presence of two isolated disubstituted ethylenic bonds does not sufficiently account for the intense absorption in the 2050—2200 Å region (Klevens, Platt, and Price, *J. Chem. Phys.*, 1949, **17**, 466, and unpublished work in these laboratories). It seems clear that these effects are the result of electronic interaction of a type expressible by such formulæ as that shown inset, and related to the pronounced auxochromic effects of propargylic substituents discussed in the next paper.

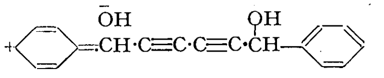
TABLE 3. *Light absorption of diacetylenes* ($R^1C{\equiv}C{\cdot}C{\equiv}CR^2$) (Wave-lengths in Å).

		D		*C*		*B*		*A*	
R^1	R^2	$\lambda_{max.}$	(ε)	$\lambda_{max.}$	(ε)	$\lambda_{max.}$	(ε)	$\lambda_{max.}$	(ε)
Me	H	—		2270	(370)	2365	(390)	2490	(210)
Et	H	—		2280	(300)	2375	(340)	2505	(210)
Bu	H	—		2295	(300)	2380	(300)	2510	(200)
Me	Me	2185	(300)	2265	(360)	2360	(330)	2500	(160)
Et	Et	—		2275	(360)	2385	(340)	2530	(230)
Bu	Bu	—		2280	(440)	2395	(390)	2540	(240)
$CH_2{\cdot}OH$	H	—		2280	(415)	2390	(415)	2530	(230)
$CHMe{\cdot}OH$	H	—		2300	(280)	2390	(300)	2515	(190)
$CHPr{\cdot}OH$	H	—		2275	(305)	2385	(325)	2525	(200)
$CMe_2{\cdot}OH$	H	—		2290	(360)	2355	(300)	2520	(170)
$CH_2{\cdot}OH$	Me	—		2305	(395)	2415	(385)	2550	(245)
$CMe_2{\cdot}OH$	Me	—		2290	(310)	2395	(330)	2530	(190)
$CH_2{\cdot}OH$	$CH_2{\cdot}OH$	2205	(295)	2320	(410)	2440	(440)	2575	(260)
$CHMe{\cdot}OH$	$CHMe{\cdot}OH$ [1]	2205	(225)	2305	(320)	2425	(330)	2560	(210)
$CHMe{\cdot}OH$	$CHMe{\cdot}OH$ [2]	—		2320	(320)	2425	(330)	2560	(210)
$CHPr{\cdot}OH$	$CHPr{\cdot}OH$	—		2330	(430)	2435	(470)	2565	(290)
$CMe_2{\cdot}OH$	$CMe_2{\cdot}OH$	2230	(230)	2315	(330)	2420	(365)	2550	(215)
$CMeEt{\cdot}OH$	$CMeEt{\cdot}OH$	—		2315	(290)	2420	(330)	2550	(190)
$CMe(OH){\cdot}C_9H_{19}$	$CMe(OH){\cdot}C_9H_{19}$	—		2320	(390)	2420	(405)	2560	(265)
$CMeBu^t{\cdot}OH$	$CMeBu^t{\cdot}OH$	—		2325	(300)	2430	(325)	2560	(195)
$C(OH)[CH_2]_5$	$C(OH)[CH_2]_5$	—		2325	(320)	2430	(345)	2570	(220)
$CH_2{\cdot}CH_2{\cdot}OH$	$CH_2{\cdot}CH_2{\cdot}OH$	2155	(330)	2280	(450)	2395	(490)	2540	(330)
$CH_2{\cdot}CHMe{\cdot}OH$	$CH_2{\cdot}CHMe{\cdot}OH$	2165	(300)	2285	(420)	2405	(455)	2550	(295)

[1] α-Form, m. p. 103—106°. [2] β-Form, m. p. 67·5—68·5°.

TABLE 4. *Constitution of erythrogenic acid* (Wave-lengths in Å).

	$\lambda_{max.}$	(ε)	$\lambda_{max.}$	(ε)	$\lambda_{max.}$	(ε)	$\lambda_{max.}$	(ε)	$\lambda_{max.}$	(ε)
Erythrogenic acid	2275	(1167)	2400	(870)	2530	(700)	2666	(870)	2820	(700)
Propenyldiacetylene	2300	(2250)	2380	(5000)	2510	(10,000)	2640	(14,000)	2800	(11,000)



It is convenient at this point to refer to a remarkable property of some di- and polyacetylenes briefly mentioned in Part XII (*loc. cit.*) and occasionally noted by earlier workers. Certain of these form crystals which are photolabile, giving intensely-coloured pigments, usually vivid red or blue. It now seems clear that this process is associated with the crystal lattice of the substance concerned. Thus octa-3 : 5-diyne-1 : 8-diol is stable to light in the liquid state, whether in solution, above its melting point, or even as a supercooled liquid; yet a deep red colour rapidly develops on the surface of the solid unless

TABLE 5. *Light-absorption properties of* $(HO{\cdot}CR^1R^2{\cdot}C{\equiv}C)_2$ (Wave-lengths in Å).

R^1	R^2	$\lambda_{max.}$	(ε)	$\lambda_{max.}$	(ε)	$\lambda_{max.}$	(ε)
H	CHMe=CH	2325	(830)	2450	(790)	2590	(495)
H	Ph	—		2475	(1300)	2605	(920)
Me	Ph	—		2445	(1020)	2580	(900)
Ph	Ph	—		2485	(2240)	2610	(1660)

light is carefully excluded. Octa-3 : 5-diyne-2 : 7-diol exists in two crystalline forms, the relationship of which is discussed below. The lower-melting form becomes pink on exposure to bright light—it is perhaps 100 times less sensitive than the diprimary isomer—while the higher-melting form is quite stable to light. These forms differ only in relative configuration at the mutually rather distant •CHMe•OH groupings, and it seems impossible that this could imply any significant differences in chemical behaviour. Moreover, the possession of this property is quite unpredictable in incidence; thus octa-3 : 5-diyne-1 : 8-diol forms a photostable ditoluene-*p*-sulphonate (forthcoming publication), while hexa-2 : 4-diyne-1 : 6-diol, which is itself quite stable in light, forms a ditoluene-*p*-sulphonate which rapidly assumes an intense magenta colour in light.

The general nature of the products of the action of light seems to be fairly constant over a wide range of di- and poly-acetylenes; they are always amorphous films, insoluble in organic solvents and in the fused acetylenic compound. The process by which these materials are formed is not understood. Oxygen, at least in more than minute traces, is not necessary, since pigment formation has been observed even when the substance was in a flask evacuated to 0·1 mm. (octa-3 : 5-diyne-1 : 8-diol) or during sublimation at 10^{-5} mm. (deca-2 : 4 : 6 : 8-tetrayne). In many cases, but not, for example, when tetra-acetylenic compounds are involved, the pigment itself shows considerable stability and has no tendency to undergo further decomposition. The most plausible mechanism at present envisaged involves the cross-linking of poly-yne chains, which in a favourable crystal lattice are perhaps held close to each other, as a consequence of photochemical activation.

Experimental

Light-absorption data were determined in alcoholic solutions, except where otherwise stated (hexa-2 : 4-diyne showed almost identical spectra in alcoholic and hexane solutions), a Beckman Model D.U. or a Unicam Spectrophotometer being used and corrected for scattered light below 2130 A. Melting points were determined on a Kofler block.

Coupling reactions were effected by the method exemplified for dodeca-2 : 10-diene-5 : 7-diyne-4 : 9-diol below, but with modifications in the method of isolation indicated in Table 1. The results of varying the pH and the copper-salt concentration in the coupling of ethynylmethylcarbinol are shown in Table 6; similar variations in pH in the case of ethynylpropenylcarbinol have effects summarised in Table 7.

Table 6. *Coupling of ethynylmethylcarbinol* (*quantities in moles*).

Carbinol	CuCl	NH_4Cl	pH	Time [1]	Yield, %
0·2	0·5	1·5	13	4	28
0·2	0·5	1·5	7	12	56
0·2	0·5	1·5	4	4	78
0·2	0·5	1·5	3	4	94
0·2	0·5	1·5	2	4	90
0·2	0·05	0·4	2	14	70
0·4	0·2	1·5	2	40	90

Table 7. *Coupling of ethynylpropenylcarbinol.*

			Product,[3] %		
pH	Time [1]	Total yield, % [2]	(I)	(II)	(III)
<1	6	68	~0	~0	100 [3]
1	3	81	~0	~0	100 [3]
3·5	4	88	95·5	6	0·4
4·5	8	88	97	3	0·2
6·5	10	93	99·5	0·5	0·05

[1] To approximate completion, in hours. [2] After isolation with ether and recrystallisation from benzene. [3] Analysed spectroscopically. Note that the detection of small quantities of (I) and (II) in (III) is impossible.

Dodeca-2 : 10-*diene*-5 : 7-*diyne*-4 : 9-*diol* (I).—A solution of ammonium chloride (80 g.) and commercial cuprous chloride (50 g.) in water (200 c.c.) was brought to pH 6·5 by adding ammonia solution (*d* 0·88; 25 c.c.), transferred to a 1-l. flask with a side-arm, and connected to a standard quantitative hydrogenation apparatus which was filled with oxygen. Ethynylpropenylcarbinol (Jones and McCombie, *J.*, 1942, 733) (19·2 g.) was now added and the contents of the flask were shaken until the uptake of oxygen ceased. The resultant blue-green suspension was extracted with ether (6 × 100 c.c.) without preliminary filtration, which is unnecessary and rather difficult, and the dried extract evaporated and heated to 50° at 0·1 mm. to remove unreacted carbinol. The product (19 g.) crystallised during evaporation and was recrystallised from benzene, giving the *glycol* (17·6 g., 93%) as needles, m. p. 125° (Found : C, 76·05; H, 7·6. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%).

Dodeca-3 : 9-*diene*-5 : 7-*diyne*-2 : 11-*diol* (III).—The above experiment was repeated, except that before the carbinol was added the solution was adjusted to pH 1 by addition of concentrated hydrochloric acid (5 c.c.). Isolation of the product gave a slightly brown solid (19·0 g.) which was crystallised from benzene to give the pure glycol (15·6 g., 81%), m. p. 95° (Bowden, Heilbron, Jones, and Sargent, *loc. cit.*, give m. p. 94—95°).

The other glycols were prepared essentially as described above, but with the modifications indicated in Table 1. Octa-3 : 5-diyne-2 : 7-diol can be obtained in two forms, as stated by Zalkind and Gverdsiteli [*loc. cit.* (*b*)], who give m. p. 67·5—68° and 108—109°, and their interconversion was studied in collaboration with Mr. E. B. Bates. As normally prepared the glycol is a mixture, which is converted by sublimation very largely into the lower-melting form; after two such sublimations, in each of which only half the total material was sublimed, the lower-melting isomer was obtained as a photolabile crystalline powder, m. p. 67·5—68·5°. This may be recrystallised from benzene or carbon disulphide, giving well-formed rosettes of needles which, however, have m. p. 70—72°; continuing the sublimation gives material with m. p. 74—93°. The higher-melting form is best prepared by crystallisation from hot water, then from benzene, and forms needles, m. p. 103—106°, which are stable in light. Mixtures of the two forms have an intermediate melting point. The most probable explanation for these phenomena is that the two forms are *meso*- and racemic isomers which form solid solutions and are fairly easily equilibrated at higher temperatures.

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