51. *Studies in the Polyene Series. Part XV. The Condensation of Carbonyl Compounds with Propenylethynylcarbinol and Hex-3-en-5-yn-2-ol.*

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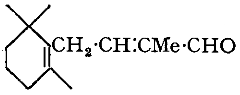
Propenylethynylcarbinol (III) has been condensed by the Grignard method with benzophenone, butaldehyde, benzaldehyde, and crotonaldehyde, the acetylenyl glycols (V)—(VIII) being obtained in yields ranging from 40 to 55%. In a similar manner the glycols (IX)—(XIII) and (XV) were isolated from condensation between hex-3-en-5-yn-2-ol (IV) and the appropriate aldehydes and ketones. By anionotropic rearrangement in the presence of acids the glycol (VI) has been converted into its isomer (IX), and both (VIII) and (XIII) have been isomerised to the symmetrical glycol (XIV). The products derived from hex-3-en-5-yn-2-ol, with the exception of (XV) which has been shown to dissociate into benzophenone on ultra-violet irradiation, exhibit light-absorption characteristics consistent with the presence of the conjugated vinylacetylene chromophore in their molecules.

One of the routes outlined in Part V (Heilbron, Johnson, Jones, and Spinks, J., 1942, 727) for the synthesis of polyenes of the vitamin A type involved condensations between substituted ethynylcarbinols, particularly vinylacetylenylcarbinols such as 3-methylpent-2-en-4-yn-1-ol (I), and carbonyl compounds, particularly

(I.) $HC{\vdots}C{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}OH$



(II.)

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

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

unsaturated aldehydes such as 3-(2′ : 6′ : 6′-trimethyl*cyclo*hexenyl)-1-methylcrotonaldehyde (II). As a preliminary, the condensation of the readily available acetylenic alcohols propenylethynylcarbinol (III) and hex-3-en-5-yn-2-ol (IV) (Jones and McCombie, J., 1942, 733; 1943, 261) with simple saturated and unsaturated aldehydes and ketones has been examined.

Marvel and his co-workers (*inter alia, J. Org. Chem.*, 1942, **7**, 93; *J. Amer. Chem. Soc.*, **1939**, **61**, 2006), employing the Grignard method, have provided innumerable examples of condensations between simple ethynylcarbinols, *e.g.*, 1-ethynyl*cyclo*hexanol, and saturated ketones. The method involves the addition of one mole of the ethynylcarbinol to two moles of ethylmagnesium bromide whereby both active hydrogen atoms are replaced by MgBr groups. The carbonyl compound (1 mole) is then added and condensation ensues, producing, after decomposition of the Grignard complex in the usual manner, the acetylenyl glycols, either symmetrical or unsymmetrical, in good yields. For other examples of Grignard condensations, see Zalkind and Gverdtsiteli (*J. Gen. Chem. Russia*, 1939, **9**, 855), who described the reaction of dimethylethynylcarbinol with *cyclo*pentanone, Zeile and Meyer (*Ber.*, 1942, **75**, 356), and Losac'h (*Bull. Soc. chim.*, 1941, **8**, 519). Condensing agents such as sodamide (Henecka, *Chem. Abstracts*, 1937, **31**, 2592), potassium *tert.*-butoxide (Burkhardt and Hindley, J., 1938, 989), potassium hydroxide (Babajan, *J. Gen. Chem. Russia*, 1940, **10**, 480, 1177), and copper and similar acetylides (General Aniline and Film Corp., U.S.P. 2,238,471) are applicable in certain simple cases. The only recorded employment of ethylenic ethynylcarbinols in such reactions is that by Teterin and Ivanov (*J. Gen. Chem. Russia*, 1937, **7**, 1629), who prepared 1 : 1-diphenylhept-5-en-2-yn-1 : 4-diol (V) from propenylethynylcarbinol (III) and benzophenone by the Grignard method. There is no mention in the literature of condensations between ethynylcarbinols and unsaturated carbonyl compounds. Similarly, condensations involving conjugated vinylacetylenylcarbinols such as (I) and (IV) have apparently never been attempted.

Repetition of Teterin and Ivanov's work (*loc. cit.*) gave the glycol (V), m. p. 131° (*lit.*, m. p. 124°), which contains two active hydrogen atoms as estimated by the Zerewitinoff method. In this respect all the glycols subsequently described in this paper behaved normally. Condensation between butaldehyde and propenylethynylcarbinol (III) by the Grignard method, which was used without exception for all the condensations herein described, furnished *dec-2-en-5-yn-4 : 7-diol* (VI) in 55% yield. The glycol was obtained as a viscous oil, which gave two *bisphenylurethanes* [m. p.'s 153° (decomp.) and 125°] probably derived from the two theoretically possible *dl*-forms of the glycol. When benzaldehyde reacted with (III) a 40% yield of *1-phenylhept-5-en-2-yn-1 : 4-diol* (VII) (m. p. 108°) was obtained, and in this case there was little evidence of the presence of stereoisomerides in the reaction mixture. A similar experiment employing crotonaldehyde gave a 40% yield of

$CPh_2(OH)\cdot C{\vdots}C\cdot CH(OH)\cdot CH{:}CH\cdot CH_3$ (V.)
$CH_3\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot C{\vdots}C\cdot CH(OH)\cdot CH{:}CH\cdot CH_3$ (VI.)
$CHPh(OH)\cdot C{\vdots}C\cdot CH(OH)\cdot CH{:}CH\cdot CH_3$ (VII.)
$CH_3\cdot CH{:}CH\cdot CH(OH)\cdot C{\vdots}C\cdot CH(OH)\cdot CH{:}CH\cdot CH_3$ (VIII.)

mixed isomers of deca-2 : 8-dien-5-yn-4 : 7-diol (VIII), from which the pure crystalline glycol, m. p. 91°, was isolated (cf. Heilbron, Jones, and Raphael, J., 1943, 268; Dupont, *Ann. Chim.*, 1913, **30**, 499).

When hex-3-en-5-yn-2-ol (IV), prepared by anionotropic rearrangement of propenylethynylcarbinol (III) with acids (Jones and McCombie, J., 1943, 261), was condensed with butaldehyde, a 45% yield of *dec-3-en-5-yn-2 : 7-diol* (IX) was obtained; this was also prepared by isomerisation of (VI) with either 2·5% or 10% sulphuric acid. Replacement of the acetylenic hydrogen atom of propenylethynylcarbinol by a propylcarbinol group thus appears to have no profound effect on the ease of anionotropic rearrangement in systems such as $\cdot C{\vdots}C\cdot CH(OH)\cdot CH{:}CH\cdot CH_3$. Comparison of the products obtained by the two methods could only be made by means of refractive index and light-absorption measurements since no crystalline derivatives were obtainable from either specimen of glycol. These are certainly mixtures of stereoisomerides and it might be expected that, since the ethylenic linkage in these compounds has been involved in the isomerisation, geometrical isomerides of the two possible *dl*-forms would be encountered.

By similar condensations, benzaldehyde was converted into *1-phenylhept-4-en-2-yn-1 : 6-diol* (X) in 60% yield, anisaldehyde gave a 30% yield of the *p-methoxy-analogue* (XI), m. p. 19—20°, and methyl ethyl ketone yielded 70% of the theoretical amount of *3-methylnon-6-en-4-yn-3 : 8-diol* (XII). From crotonaldehyde a 50% yield of *deca-3 : 8-dien-5-yn-2 : 7-diol* (XIII) was obtained, and on shaking this glycol with 4% sulphuric acid

$CH_3\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot C{\vdots}C\cdot CH{:}CH\cdot CH(OH)\cdot CH_3$ (IX.)
$CHPh(OH)\cdot C{\vdots}C\cdot CH{:}CH\cdot CH(OH)\cdot CH_3$ (X.)
$(p)\text{-}OMe\cdot C_6H_4\cdot CH(OH)\cdot C{\vdots}C\cdot CH{:}CH\cdot CH(OH)\cdot CH_3$ (XI.)
$CH_3\cdot CH_2\cdot C(OH)Me\cdot C{\vdots}C\cdot CH{:}CH\cdot CH(OH)\cdot CH_3$ (XII.)
$CH_3\cdot CH{:}CH\cdot CH(OH)\cdot C{\vdots}C\cdot CH{:}CH\cdot CH(OH)\cdot CH_3$ (XIII.)
$CH_3\cdot CH(OH)\cdot CH{:}CH\cdot C{\vdots}C\cdot CH{:}CH\cdot CH(OH)\cdot CH_3$ (XIV.)
$CPh_2(OH)\cdot C{\vdots}C\cdot CH{:}CH\cdot CH(OH)\cdot CH_3$ (XV.)

it was converted into deca-3 : 7-dien-5-yn-2 : 9-diol (XIV), previously prepared by a dual anionotropic rearrangement of the acetylenyl glycol from crotonaldehyde (Heilbron, Jones, and Raphael, J., 1943, 268). *1 : 1-Diphenylhept-4-en-2-yn-1 : 6-diol* (XV) was isolated (50% yield) from the condensation of benzophenone with (IV), but attempts to obtain it by isomerisation of (V), even with 25% sulphuric acid, gave only unchanged material. However, it cannot be stated definitely that the diphenylcarbinol group has a powerful deactivating effect on the mobility of the anionotropic system since it appears likely that solubility factors would be of importance in this case. Experiments carried out in homogeneous media have so far proved inconclusive.

With the exception of the glycol (XV) derived from benzophenone, the products obtained from condensations with hex-3-en-5-yn-2-ol (IV) all exhibit light absorption (see table) characteristic of the conjugated vinylacetylene chromophore (Parts VIII—X), although inflexions were not observed in every case, attributable possibly to the presence of stereoisomerides.

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$	$\lambda_{infl.}$, A.	$\varepsilon_{infl.}$
Hex-3-en-5-yn-2-ol [1] (IV)	2230	13,000	2300	9,500
Dec-3-en-5-yn-2 : 7-diol (IX)	2280	15,000	2380	11,500
1-Phenylhept-4-en-2-yn-1 : 6-diol (X)	2240	12,500	2350	11,500
1-(*p*-Methoxyphenyl)hept-4-en-2-yn-1 : 6-diol (XI)	2250	17,500	—	—
3-Methylnon-6-en-4-yn-3 : 8-diol (XII)	2285	12,500	2350	11,000
Deca-3 : 8-dien-5-yn-2 : 7-diol (XIII)	2280	13,000	—	—
1 : 1-Diphenylhept-4-en-2-yn-1 : 6-diol (XV)	2510	21,000	—	—
	3315	13,500	—	—
Benzophenone [2]	2520	20,000	—	—
	3300	160	—	—

[1] Jones and McCombie, J., 1943, 261.

[2] Scheibe, *Ber.*, 1926, **59**, 2617.

The absorption spectrum of (XV) appeared to be distinctly anomalous, and, in fact, bore a resemblance to that of the parent ketone, benzophenone. It had been noted during the preparation of (XV) that much of the latter ketone was present in the product, but there was no doubt that the spectrographic and analytical samples were free from ketone. It was then ascertained from refractive-index measurements that some fission of the glycol took place during distillation even in a high vacuum, benzophenone distilling over first, followed by the glycol, the quantity of the latter decreasing progressively on repeated distillation. That a similar fission took place by the action of ultra-violet light during the light-absorption measurements was proved by irradiating a solution of the pure glycol in alcohol in a quartz cell with light from a mercury arc, whereupon benzophenone was readily detected in the solution by testing with 2 : 4-dinitrophenylhydrazine, the original solution failing to give any trace of the ketonic derivative.

The reversion of acetylenic carbinols into the constituent carbonyl compounds and acetylenes by the action of alkalis is well known and cases of cleavage on distillation have been recorded (Armour and Co., E.P. 529,794), but fission simply by ultra-violet irradiation does not appear to have been observed hitherto. In this case the effect of the two phenyl groups in weakening the carbon–carbon bond must be accentuated by the adjacent conjugated vinylacetylene group, since no decomposition of the unrearranged glycol (V) was observed.

EXPERIMENTAL.

(Absorption spectra were determined in alcoholic solutions.)

1 : 1-*Diphenylhept*-5-*en*-2-*yn*-1 : 4-*diol* (V).—Propenylethynylcarbinol (24 g.) was added during 1 hour to an ethereal solution of ethylmagnesium bromide (from 12 g. of magnesium), and the mixture refluxed for 2 hours. After ice-cooling, a solution of benzophenone (45 g.) in ether was added dropwise, the mixture was set aside overnight, and finally refluxed for 1 hour. The Grignard complex was decomposed with ammonium chloride solution (ice), and isolation by the normal procedure yielded the glycol (43 g.), after crystallisation from benzene, as needles, m. p. 131° (Teterin and Ivanov, *loc. cit.*, give m. p. 124°) (Found : C, 81·5; H, 6·45. Calc. for $C_{19}H_{18}O_2$: C, 81·95; H, 6·5%). *Active hydrogen* (Zerewitinoff) : The glycol (98·5 mg.) evolved 18·7 c.c. of methane at 22°/750 mm., equivalent to 2·1 active hydrogen atoms per mol. *Light absorption :* Maximum 2210 A.; ε = 12,500. Inflexion, 2280 A.; ε = 10,500.

Dec-2-*en*-5-*yn*-4 : 7-*diol* (VI.)—By using the method employed above, butaldehyde (9 g.) was condensed with propenylethynylcarbinol (12·5 g.), giving *dec*-2-*en*-5-*yn*-4 : 7-*diol* (12 g.) as a viscous liquid, b. p. 52° (bath temp.)/10^{-4} mm., $n_D^{17^\circ}$ 1·4666 (Found : C, 71·1; H, 9·8. $C_{10}H_{16}O_2$ requires C, 71·35; H, 9·6%). *Active hydrogen* (Zerewitinoff) : The glycol (42·1 mg.) evolved 11·2 c.c. of methane at 18°/777 mm. (1·95 active hydrogen atoms per mol.). The glycol exhibited no absorption of appreciable intensity in the ultra-violet. Two *bisphenylurethanes* were obtained from the glycol by reaction with phenyl *iso*cyanate; the more insoluble form separated from methyl alcohol as needles, m. p. 125° (Found : N, 6·8. $C_{24}H_{26}O_4N_2$ requires N, 6·9%), and the other form crystallised from alcohol in rhombic plates, m. p. 153° (decomp.) (Found : N, 6·95%). Only one *bis-a-naphthylurethane* could be obtained in a pure condition. It separated from alcohol in needles, m. p. 194° (decomp.) (Found : N, 5·75. $C_{32}H_{30}O_4N_2$ requires N, 5·55%).

1-*Phenylhept*-5-*en*-2-*yn*-1 : 4-*diol* (VII).—This was prepared by the general method from propenylethynylcarbinol (12 g.) and benzaldehyde (13 g.). Distillation of the crude glycol gave an oil (10·5 g.), b. p. 80—90° (bath temp.)/10^{-4} mm., which solidified, and when crystallised from benzene yielded 1-*phenylhept*-5-*en*-2-*yn*-1 : 4-*diol* as prismatic needles, m. p. 108° (Found : C, 77·5; H, 6·9. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%). *Active hydrogen* (Zerewitinoff) : The glycol (100 mg.) evolved 25·3 c.c. of methane at 22°/762 mm. (2·1 active hydrogen atoms per mol.). *Light absorption :* Maximum, 2180 A.; ε = 5000. Inflexion, 2240 A.; ε = 2000.

Deca-2 : 8-*dien*-5-*yn*-4 : 7-*diol* (VIII).—Condensation of propenylethynylcarbinol (12 g.) with crotonaldehyde (8·8 g.) gave the glycol (9 g.), b. p. 90—100° (bath temp.)/10^{-4} mm., which solidified on cooling and, when crystallised from carbon tetrachloride or benzene, formed needles, m. p. 91° (Dupont, *loc. cit.*, gives m. p. 90—92°). It gave no depression in m. p. on admixture with an authentic specimen prepared by Dupont's method and exhibited no light absorption of appreciable intensity in the ultra-violet.

Dec-3-*en*-5-*yn*-2 : 7-*diol* (IX).—(a) When prepared from hex-3-en-5-yn-2-ol (6 g.) and butaldehyde (4·5 g.) in the usual manner, *dec*-3-*en*-5-*yn*-2 : 7-*diol* (4·5 g.) was isolated with b. p. 72° (bath temp.)/10^{-4} mm., $n_D^{16^\circ}$ 1·5038 (Found : C, 70·9; H, 9·4. $C_{10}H_{16}O_2$ requires C, 71·35; H, 9·6%). *Active hydrogen* (Zerewitinoff) : The glycol (114 mg.) evolved 34·0 c.c. of methane at 22°/777 mm. (2·1 active hydrogen atoms per mol.). *Light absorption :* see table.

(b) A mixture of dec-2-en-5-yn-4 : 7-diol (1·5 g.) and sulphuric acid (60 c.c.; 2·5% w/v) was shaken at 20° for 15 hours. Isolation of the product with ether gave dec-3-en-5-yn-2 : 7-diol (1·2 g.), b. p. 75° (bath temp.)/10^{-4} mm., $n_D^{18^\circ}$ 1·5032. *Light absorption :* Maximum, 2275 A; ε = 15,000. Inflexion, 2360 A.; ε = 12,500. Shaking with 10% sulphuric acid for the same time gave a glycol with identical properties.

1-*Phenylhept*-4-*en*-2-*yn*-1 : 6-*diol* (X).—Prepared by condensation of hex-3-en-5-yn-2-ol (6 g.) with benzaldehyde (6 g.), this *diol* (7·5 g.) was obtained after 3 distillations as a pale yellow oil, b. p. 78° (bath temp.)/10^{-4} mm., $n_D^{17^\circ}$ 1·5694 (Found : C, 77·1; H, 7·3. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%). *Active hydrogen* (Zerewitinoff) : The glycol (112 mg.) evolved 26·45 c.c. of methane at 20°/763 mm. (2·0 active hydrogen atoms per mol.).

1-(p-*Methoxyphenyl*)*hept*-4-*en*-2-*yn*-1 : 6-*diol* (XI.)—Reaction between hex-3-en-5-yn-2-ol (6 g.) and anisaldehyde (8·5 g.) yielded a crude product (12 g.), the non-aldehydic portion of which, separated by means of Girard reagent P, yielded the *diol* (XI) (4 g.), b. p. 60° (bath temp.)/10^{-4} mm., $n_D^{16^\circ}$ 1·5424. On standing at 0° it solidified to needles, m. p.

19 - 20° (Found : C, 72·3; H, 7·45. $C_{14}H_{16}O_3$ requires C, 72·35; H, 6·95%). *Active hydrogen* (Zerewitinoff) : The glycol (94 mg.) evolved 20·0 c.c. of methane at 20°/737 mm. (2·0 active hydrogen atoms per mol.).

3-*Methylnon*-6-*en*-4-*yn*-3 : 8-*diol* (XII).—Condensation between hex-3-en-5-yn-2-ol (6 g.) and methyl ethyl ketone (4 g.) yielded the *glycol* as a viscous oil (6·5 g.), b. p. 63° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{17^\circ}$ 1·4989 (Found : C, 71·7; H, 9·75. $C_{10}H_{16}O_2$ requires C, 71·35; H, 9·6%). *Active hydrogen* (Zerewitinoff) : The glycol (79 mg.) evolved 20·1 c.c. of methane at 21°/753 mm. (1·9 active hydrogen atoms per mol.).

Deca-3 : 8-*dien*-5-*yn*-2 : 7-*diol* (XIII).—Condensation between hex-3-en-5-yn-2-ol (6 g.) and crotonaldehyde (4 g.) yielded the *diol* (XIII) (4·8 g.) as a pale yellow oil, b. p. 75° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{19^\circ}$ 1·5309 (Found : C, 72·3; H, 8·75. $C_{10}H_{14}O_2$ requires C, 72·25; H, 8·5%). *Active hydrogen* (Zerewitinoff) : The glycol (121 mg.) gave 34·15 c.c. of methane at 16°/755 mm. (2·0 active hydrogen atoms per mol.).

Deca-3 : 7-*dien*-5-*yn*-2 : 9-*diol* (XIV).—A mixture of deca-3 : 8-dien-5-yn-2 : 7-diol (200 mg.) and sulphuric acid (20 c.c.; 4% w/v) was shaken under nitrogen for 25 hours at 20°. Isolation by means of ether yielded the diol (XIV) (100 mg.) as a pale yellow viscous oil, b. p. 110—115° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{21^\circ}$ 1·5501 (Heilbron, Jones, and Raphael, *loc. cit.*, give $n_{\mathrm{D}}^{21^\circ}$ 1·5511). *Light absorption :* Maxima, 2660 and 2790 A.; ε = 17,500 and 15,000, respectively.

1 : 1-*Diphenylhept*-4-*en*-2-*yn*-1 : 6-*diol* (XV).—Prepared as described above from hex-3-en-5-yn-2-ol (12 g.) and benzophenone (21 g.), after two distillations this *diol* (12 g.) was obtained as a pale yellow viscous oil, b. p. 85° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{17^\circ}$ 1·6468 (Found : C, 82·15; H, 6·45. $C_{19}H_{18}O_2$ requires C, 81·95; H, 6·5%). *Active hydrogen* (Zerewitinoff) : The glycol (109·5 mg.) evolved 19·5 c.c. of methane at 20°/763 mm. (2·05 active hydrogen atoms per mol.). A portion of a solution of the glycol (20 mg.) in alcohol (4 c.c.) gave no positive ketonic reaction when treated with an alcoholic solution of 2 : 4-dinitrophenylhydrazine sulphate. After irradiation in a quartz cell with light from a mercury vapour lamp for 10 minutes, similar treatment gave the 2 : 4-dinitrophenylhydrazone of benzophenone, which crystallised from acetic acid in red crystals, m. p. 234° (decomp.), undepressed on admixture with an authentic specimen.

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