20. *Studies in the Polyene Series. Part XVII. Replacement Halogenation and Simultaneous Anionotropic Rearrangements of Acetylenylcarbinols and Glycols derived from αβ-Unsaturated Aldehydes.**

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When the acetylenyl- or vinylacetylenyl-carbinols or acetylenyl glycols derived from *αβ*-unsaturated aldehydes are shaken with concentrated hydrochloric acid, at room temperature, replacement halogenation of the hydroxyl group accompanies the usual anionotropic rearrangement (see Parts VIII onwards). In the case of vinylethynylcarbinol (IV), which is unaffected by 25% sulphuric acid even at 100°, the rearranged chloro-compound (V) is readily obtained and is converted *via* the acetate into the primary acetylenylvinylcarbinol (VI), giving *n*-amyl alcohol on hydrogenation. The related glycol (XIV) from acraldehyde behaves analogously, leading eventually to octane-1 : 8-diol.

The expected light-absorption properties were observed with all the halogeno-compounds containing the conjugated vinylacetylene and *s*.-divinylacetylene chromophores.

THE rearrangements of acetylenylcarbinols and glycols derived from αβ-unsaturated carbonyl compounds so far described in this series (Part VIII onwards, J., 1943—1944) consist almost entirely of examples involving a migrating hydroxyl anion. It has been postulated that the mobility of anionotropic systems increases with increasing stability of the mobile anion X, and hence with increasing strength of the acid HX (Burton and Ingold, J., 1928, 904; Burton, J., 1928, 1650). Consequently, it was to be expected that replacement-halogenation of propenylethynylcarbinol (I) and related compounds with reagents such as thionyl chloride or phosphorus pentachloride would lead to products, *e.g.*, (II), which, if they existed at all, would readily undergo rearrangement to chloro-alkylvinylacetylenes, *e.g.*, (III).

(I.) $\mathrm{CH_3{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}C{\vdots}CH}$
(II.) $\mathrm{CH_3{\cdot}CH{:}CH{\cdot}CHCl{\cdot}C{\vdots}CH}$
(III.) $\mathrm{CH_3{\cdot}CHCl{\cdot}CH{:}CH{\cdot}C{\vdots}CH}$

$\mathrm{CH_2{:}CH{\cdot}CH(OH){\cdot}C{\vdots}CH}$ (IV.)
$\mathrm{CH_2Cl{\cdot}CH{:}CH{\cdot}C{\vdots}CH}$ (V.)
$\mathrm{OH{\cdot}CH_2{\cdot}CH{:}CH{\cdot}C{\vdots}CH}$ (VI.)

Reactions of this type with vinylethynylcarbinol (IV) were of particular interest, since this had been found to be unaffected by 25% sulphuric acid (Jones and McCombie, J., 1943, 261), and since its isomerisation product (VI) was required for syntheses of primary alcohols related to vitamin-A. When (IV) was caused to react in cold dilute ethereal solution with thionyl chloride in the presence of pyridine, a product was obtained which decomposed on attempted distillation, but under more vigorous conditions a mixture containing a high proportion of the chloro-hydrocarbon (V) resulted, as indicated by the ultra-violet absorption of the product (see below).

Since Campbell, Campbell, and Eby (*J. Amer. Chem. Soc.*, 1938, **60**, 2882) reported that treatment of methylethylethynylcarbinol with concentrated hydrochloric acid gave a 40% yield of 3-chloro-3-methylpent-

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* See I.C.I. Ltd., Jones, and McCombie, B.P. 560,081.

1-yne, vinylethynylcarbinol (IV) was shaken with this acid for 40 minutes at 20—40°, whereby 1-*chloropent*-2-*en*-4-*yne* (V) was obtained in 50% yield. An indication of the structure of the chloro-compound was provided by its absorption spectrum (Table I) characteristic of the conjugated vinylacetylene system (see Parts VIII, X, XIV—XVI), and complete proof was furnished by its conversion into *n*-amyl alcohol by the following reactions.

TABLE I.

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
1-Chloropent-2-en-4-yne (V)	2280	10,500
2-Chlorohex-3-en-5-yne (III)	2260	14,000
2-Chlorodec-3-en-5-yne (IX)	2350 2400*	17,500 17,000

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
Pent-2-en-4-yn-1-ol (VI)	2230	14,000
,, acetate	2225	21,500
Hex-3-en-5-yn-2-ol [1]	2230 2300*	13,500 9,500

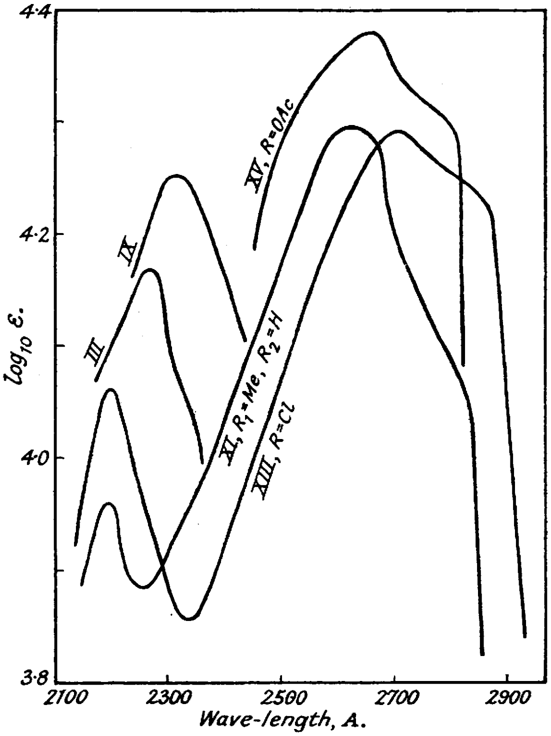
* Inflexion.

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

Treatment of (V) with potassium acetate in methyl-alcoholic solution gave the *acetate* of pent-2-en-4-yn-1-ol (VI), together with a low-boiling fraction, probably the corresponding methyl ether. Both the acetate and the primary *alcohol* (VI) (α-*naphthylurethane*), obtained from it by alkaline hydrolysis, exhibit light absorption (Table I) similar to that of the parent chloro-hydrocarbon, indicating that all three substances contain the same conjugated system and that they must be interrelated in the manner prescribed. A Zerewitinoff determination on (VI) showed the presence of two active hydrogen atoms and on complete hydrogenation it gave *n*-amyl alcohol.

In order to ascertain at this stage whether (VI) reacts normally with carbonyl compounds, a Grignard reaction with butaldehyde was attempted according to the method evolved in Part XV. This gave a 30% yield of *non*-2-*en*-4-*yne*-1 : 6-*diol* (VII) (*bisphenylurethane*) with properties in accord with the suggested structure.

When propenylethynylcarbinol (I) was treated either with concentrated hydrochloric acid or with thionyl chloride and pyridine in the cold, good yields of 2-*chlorohex*-3-*en*-5-*yne* (III) (for absorption spectrum, see Table I and Fig.) were obtained. On the other hand, the action of hydrochloric acid on hex-3-en-5-yn-2-ol, the rearrangement product of (I), gave only a 45% yield of (III), accompanied by much material formed by addition of hydrogen chloride to the unsaturated system. With potassium acetate in methyl-alcoholic solution (III) gave the acetate of hex-3-en-5-yn-2-ol, identical in physical properties with that obtained by direct acetylation of the carbinol. A study has been made of various replacement reactions of (III), particularly those with amines, and this work will be described in due course.



The substituted propenylethynylcarbinol (VIII) is converted smoothly (85% yield) with concentrated hydrochloric acid into 2-*chlorodec*-3-*en*-5-*yne* (IX) (see Table I and Fig. for light absorption). Carbinols (X) prepared by condensing crotonaldehyde with vinylacetylenes also undergo rearrangement-chlorination and

$$CH_3\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot C{\vdots}C\cdot CH{:}CH\cdot CH_2\cdot OH \quad \text{(VII.)}$$
$$CH_3\cdot[CH_2]_3\cdot C{\vdots}C\cdot CH(OH)\cdot CH{:}CH\cdot CH_3 \quad \text{(VIII.)}$$
$$CH_3\cdot[CH_2]_3\cdot C{\vdots}C\cdot CH{:}CH\cdot CHCl\cdot CH_3 \quad \text{(IX.)}$$

2-*chloro-octa*-3 : 7-*dien*-5-*yne* (XI; $R_1 = R_2 = H$), 2-*chloro*-7-*methylocta*-3 : 7-*dien*-5-*yne* (XI; $R_1 = Me$, $R_2 = H$), and 2-*chloro*-7-*methylnona*-3 : 7-*dien*-5-*yne* (XI; $R_1 = R_2 = Me$) have been prepared in this way. The structures of the rearranged chloro-compounds (IX and XI) are assumed by analogy with the simpler

$$\text{(X.)}\ CHR_2{:}CR_1\cdot C{\vdots}C\cdot CH(OH)\cdot CH{:}CH\cdot CH_3 \qquad CHR_2{:}CR_1\cdot C{\vdots}C\cdot CH{:}CH\cdot CHCl\cdot CH_3\ \text{(XI.)}$$

cases where rigid proof has been provided, and the correctness of these assumptions is substantiated by light-absorption evidence (Table II and Fig.). The chloro-hydrocarbons of structure (XI) exhibit maximal absorption at about 2620 A. with inflexions at slightly longer wave-lengths, analogous to that already described for compounds containing the symmetrical dienyne chromophore (Parts X, XI, and XIV). The additional maxima at about 2200 A. of comparatively low intensity observed with these compounds appear to be characteristic.

In Part XI (Heilbron, Jones, and Raphael, J., 1943, 268) a dual rearrangement of the acetylenyl glycol (XII) from crotonaldehyde leading to a *s.*-divinylacetylenyl glycol (XIII; R = OH) was described. It has

TABLE II.

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
2-Chloro-octa-3 : 7-dien-5-yne (XI; $R_1 = R_2 = H$)	2200 2620 2750*	6,000 17,000 13,500
2-Chloro-7-methylnona-3 : 7-dien-5-yne (XI; $R_1 = R_2 = Me$)	2680 2780*	18,000 15,500
2-Chloro-7-methylocta-3 : 7-dien-5-yne (XI; $R_1 = Me$, $R_2 = H$)	2190 2625 2750*	7,500 18,000 14,000
7-Methylnona-3 : 7-dien-5-yn-2-ol [1]	2640 2690*	16,500 15,500

* Inflexion.

[1] Heilbron, Johnson, Jones, and Raphael, J., **1943**, 265.

now been established that a similar change takes place on replacement halogenation of (XII) by treatment with concentrated hydrochloric acid, giving 2 : 9-*dichlorodeca*-3 : 7-*dien*-5-*yne* (XIII; R = Cl) in 85% yield, the light absorption-properties (Table III and Fig.) of which are similar, both in location and in intensity of the

(XII.) $CH_3\cdot CH{:}CH\cdot CH(OH)\cdot C{\vdots}C\cdot CH(OH)\cdot CH{:}CH\cdot CH_3$ $\qquad$ $CH_3\cdot CHR\cdot CH{:}CH\cdot C{\vdots}C\cdot CH{:}CH\cdot CHR\cdot CH_3$ (XIII.)

main maximum, to those described (Part XI) for the corresponding glycol (XIII; R = OH), and the diacetate of the latter was obtained by treating the dichloro-compound with potassium acetate in alcohol.

TABLE III.

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
1 : 8-Dichloro-octa-2 : 6-dien-4-yne (XV; R = Cl)	2690 2780*	17,500 15,500
2 : 9-Dichlorodeca-3 : 7-dien-5-yne (XIII; R = Cl)	2210 2700 2760	11,500 19,500 18,500
Deca-3 : 7-dien-5-yne-2 : 9-diol [1] (XIII; R = OH)	2180 2650 2800	11,000 21,500 19,000
1 : 8-Diacetoxyocta-2 : 6-dien-4-yne (XV; R = OAc)	2650 2770*	24,000 21,000
Octa-2 : 6-dien-4-yne-1 : 8-diol (XV; R = OH) (crude)	2190 2290 2650 2790	7,500 6,500 16,000 12,500
Diacetate [1] of deca-3 : 7-dien-5-yne-2 : 9-diol [1] (XIII; R = OAc)	2560 2650 2780	14,000 22,000 18,500

* Inflexions.

[1] Heilbron, Jones, and Raphael, J., **1943**, 268.

The glycol (XIV) (Dupont, *Ann. Chim.*, **1913**, **30**, 485) derived from acraldehyde failed to undergo rearrangement on treatment with 25% sulphuric acid, thus behaving analogously to the related ethynylcarbinol (Jones and McCombie, *loc. cit.*) and phenylvinylcarbinol (Burton and Ingold, *loc. cit.*). With concentrated hydrochloric acid, however, rearrangement-chlorination occurred, although the 1 : 8-*dichloro-octa*-2 : 6-*dien*-4-*yne* (XV; R = Cl) could not effectively be separated from the small quantity of unchanged glycol present in the product. It seems possible that in this case the reaction proceeds to an equilibrium point. However, when the dichloro-compound was treated with potassium acetate in methyl alcohol, 1 : 8-*diacetoxyocta*-2 : 6-*dien*-4-*yne* (XV; R = OAc) was readily isolated in a pure condition, and on complete hydrogenation, followed by hydrolysis of the di-ester, octane-1 : 8-diol (bisphenylurethane) was obtained. Direct hydrolysis of the diacetate gave a diol (*bisphenylurethane*) which underwent extensive polymerisation on distillation even in a high vacuum, presumably owing to formation of a polymeric ether.

(XIV.) $CH_2{:}CH\cdot CH(OH)\cdot C{\vdots}C\cdot CH(OH)\cdot CH{:}CH_2$ $\qquad$ $CH_2R\cdot CH{:}CH\cdot C{\vdots}C\cdot CH{:}CH\cdot CH_2R$ (XV.)

Attempts were made to obtain the dichloro-diene (XVI), which can be regarded as a substituted chloroprene, by more vigorous treatment of hex-3-en-5-yn-2-ol or 2-chlorohex-3-en-5-yne (III) with hydrochloric acid. From either the former with concentrated acid at 55°, or from (III) under conditions similar to those used by Carothers, Berchet, and Collins (*J. Amer. Chem. Soc.*, **1932**, **54**, 4066) for the conversion of vinylacetylene into 2-chlorobutadiene, complex mixtures were obtained. By careful fractionation, however, a dichloro-diene, provisionally designated by analogy as 2 : 5-*dichlorohexa*-1 : 3-*diene* (XVI), and showing the expected high-intensity light absorption, was isolated.

$CH_3\cdot CHCl\cdot CH{:}CH\cdot CCl{:}CH_2$ (XVI.)

Several attempts have been made to prepare bromo-compounds corresponding to the various chloro-compounds described above, but when (I), (IV), and (XII) were treated with hydrobromic acid, highly unstable heterogeneous products, decomposing on attempted distillation, resulted. In this connection the work of Favorskaya *et al.* (*J. Gen. Chem. Russ.*, **1940**, **10**, 461; **1939**, **9**, 386) is of interest, since they observed that by treating dimethylethynylcarbinol (XVII) with hydrobromic acid, the bromo-compound rapidly isomerised through the allene (XVIII) to the 1 : 3-butadiene derivative (XIX). The primary chloro-compound, on the other hand, prepared with hydrochloric acid in the presence of cuprous and ammonium chlorides, was much more stable, giving the allene only after a reaction time of some days and isomerising to the conjugated diene only after three weeks. The instability of the bromo-compounds obtained in the present study may well be occasioned by the ease with which rearrangements of the above type occur.

$$\underset{\text{(XVII.)}}{CMe_2(OH)\cdot C{\vdots}CH} \longrightarrow \underset{\text{(XVIII.)}}{CMe_2{:}C{:}CHBr} \longrightarrow \underset{\text{(XIX.)}}{CH_2{:}CMe\cdot CH{:}CHBr}$$

EXPERIMENTAL.

(Absorption spectra were determined in alcoholic solutions.)

1-*Chloropent-2-en-4-yne* (V).—A mixture of vinylethynylcarbinol (40 g.; Jones and McCombie, J., 1942, 733) and concentrated hydrochloric acid (200 c.c.) was shaken at 20° for 30 minutes under nitrogen and finally for 10 minutes at 40°. The product, isolated by means of ether, gave 1-*chloropent-2-en-4-yne* (30 g.), b. p. 82—84°/200 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4842 (Found ; Cl, 35·0. C_5H_5Cl requires Cl, 35·3%). Even at 0° in the presence of quinol, the chloro-compound darkened rapidly.

1-*Acetoxypent-2-en-4-yne.*—A solution of 1-chloropent-2-en-4-yne (24 g.) and anhydrous potassium acetate (60 g.) in methyl alcohol (300 c.c.) was heated under reflux for 18 hours under nitrogen. The potassium chloride was filtered off, the major portion of the solvent distilled off through a column, and the residue poured into water. Distillation of the product obtained by isolation with ether gave three fractions : (1) B. p. 82—86°/100 mm., $n_{\mathrm{D}}^{22^\circ}$ 1·4446; (2) b. p. 86—90°/100 mm., $n_{\mathrm{D}}^{22^\circ}$ 1·4567; (3) 1-*acetoxypent-2-en-4-yne* (8 g.), b. p. 72°/18 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·4863 (Found : C, 67·4; H, 6·6. $C_7H_8O_2$ requires C, 67·75; H, 6·5%). *Active hydrogen* (Zerewitinoff) : The acetate (145 mg.) gave (without heating) 29·2 c.c. of methane at 23°/767 mm. (1·0 active hydrogen atom per mol.).

Pent-2-en-4-yn-1-ol (VI).—The above acetate (8 g.) was shaken for 1 hour with aqueous potassium hydroxide (400 c.c.; 2·5%) under nitrogen. The reaction mixture was saturated with salt and repeatedly extracted with small portions of ether, and from the extracts there were obtained 4·5 g. of *pent-2-en-4-yn-1-ol*, b. p. 103°/100 mm., 90°/50 mm., $n_{\mathrm{D}}^{23^\circ}$ 1·4933 (Found : C, 73·05; H, 7·2. C_5H_6O requires C, 73·15; H, 7·35%). *Active hydrogen* (Zerewitinoff) : The carbinol (56 mg.) gave 30·3 c.c. of methane at 20°/767 mm. (1·9 active hydrogen atoms per mol.). The *α-naphthylurethane* crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 110—111° (Found : N, 5·8. $C_{16}H_{13}O_2N$ requires N, 5·6%). The overall yield of (VI) from acraldehyde is only about 4%.

The carbinol (3·4 g.) in methyl acetate (20 c.c.) was shaken with hydrogen in the presence of platinic oxide (100 mg.) until absorption was complete. The catalyst and solvent were removed, the latter through a column, and the residual *n*-amyl alcohol had b. p. 136—138°, $n_{\mathrm{D}}^{18^\circ}$ 1·4103 (lit. b. p. 137·8°, $n_{\mathrm{D}}^{15^\circ}$ 1·4117). The α-naphthylurethane had m. p. 68°, undepressed on admixture with an authentic specimen (Bicket and French, *J. Amer. Chem. Soc.*, 1926, **48**, 747, give m. p. 68°).

*Non-2-en-4-yne-*1 : 6-*diol* (VII).—A solution of pent-2-en-4-yn-1-ol (4·5 g.) in ether (100 c.c.) was added slowly with stirring to ethylmagnesium bromide (from 2·7 g. of magnesium) in an atmosphere of nitrogen; the reaction was completed by heating under reflux for 2 hours. *n*-Butaldehyde (4 g.) in ether (100 c.c.) was then added in the cold, and the mixture subsequently refluxed for 1½ hours. The dark red reaction mixture was decomposed with ammonium chloride, and isolation of the product with ether gave the *glycol* (2·5 g.) as a colourless viscous oil, b. p. 85° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{20^\circ}$ 1·5112 (Found : C, 69·85; H, 9·3. $C_9H_{14}O_2$ requires C, 70·1; H, 9·2%). *Active hydrogen* (Zerewitinoff) : The glycol (68 mg.) gave 19·1 c.c. of methane at 23°/758 mm. (1·8 active hydrogen atoms per mol.). *Quantitative hydrogenation :* A mixture of the glycol (500 mg.) and platinic oxide (100 mg.) in ethyl acetate (10 c.c.) absorbed 218 c.c. of hydrogen at 21°/765 mm. ($|^{=}$ 2·8). *Light absorption :* Maximum, 2280 A.; ε = 16,000. Inflexion, 2380 A.; ε = 10,000. The *bisphenylurethane* crystallised from benzene–light petroleum (b. p. 60—80°) in needles, m. p. 84° (Found : N, 7·4. $C_{23}H_{24}O_4N_2$ requires N, 7·15%).

2-*Chlorohex-3-en-5-yne* (III).—(*a*) A mixture of propenylethynylcarbinol (70 g.; Jones and McCombie, *loc. cit.*) and concentrated hydrochloric acid (200 c.c.) was shaken at 20° under nitrogen for 20 minutes, and the oily layer separated by means of ether. After washing and drying, evaporation yielded 2-*chlorohex-3-en-5-yne* (62 g.), b. p. 72—75°/100 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·4832, as a colourless oil which rapidly darkened on standing, although the pure colourless chloro-compound can be recovered almost quantitatively on redistillation (Found : Cl, 31·1. C_6H_7Cl requires Cl, 31·0%).

(*b*) To a solution of propenylethynylcarbinol (20 g.) and anhydrous pyridine (22 g.) in dry ether (150 c.c.) at 0°, redistilled thionyl chloride (29·5 g.) was added during an hour with stirring after which the mixture was set aside overnight at 0°. After treatment with ice the ethereal solution was worked up in the usual manner, yielding 2-chlorohex-3-en-5-yne (13·5 g.), b. p. 131°, 111°/400 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4824.

2-*Acetoxyhex-3-en-5-yne.*—2-Chlorohex-3-en-5-yne (20 g.) was added to a solution of anhydrous sodium acetate (25 g.) in alcohol (120 c.c.) which was then heated under reflux for 6 hours. After dilution with water, the product was isolated with ether and the ethereal solution dried and evaporated. On distillation the material boiled over a wide range, owing probably to the presence of the ethyl ether, but redistillation of the fraction, b. p. 85—97° (mainly 92—97°)/50 mm. (8·2 g.), gave 2-acetoxyhex-3-en-5-yne (5 g.), b. p. 94—96°/50 mm., $n_{\mathrm{D}}^{18\cdot5^\circ}$ 1·4589 (Jones and McCombie, *loc. cit.*, give b. p. 101—103°/70 mm., $n_{\mathrm{D}}^{18\cdot5^\circ}$ 1·4578). *Light absorption :* Maximum, 2240 A., ε = 12,500.

2-*Chlorodec-3-en-5-yne* (IX).—A mixture of dec-2-en-5-yn-4-ol (5 g.; Heilbron, Jones, and Raphael, J., 1943, 264) and concentrated hydrochloric acid (25 c.c.) was shaken at 20° for 30 minutes in an atmosphere of nitrogen. Isolation of the product with ether gave 2-*chlorodec-3-en-5-yne* (4·7 g.), b. p. 58°/1 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4947 (Found : Cl, 20·75. $C_{10}H_{15}Cl$ requires Cl, 20·85%).

2-*Chloro-octa-*3 : 7-*dien-5-yne* (XI; $R_1 = R_2 =$ H).—Octa-2 : 7-dien-5-yn-4-ol (10 g.; Heilbron, Jones, and Weedon, J., 1944, 140) was shaken with concentrated hydrochloric acid (50 c.c.) and ether (5 c.c.) under nitrogen for 1 hour. After dilution with water the product was isolated by ether extraction, 2-*chloro-octa-*3 : 7-*dien-5-yne* (8 g.) being obtained as a colourless liquid, b. p. 48—50°/3 mm., $n_{\mathrm{D}}^{16^\circ}$ 1·5406 (Found : C, 68·15; H, 6·55. C_8H_9Cl requires C, 68·35; H, 6·45%).

2-*Chloro-7-methylocta-*3 : 7-*dien-5-yne* (XI; $R_1 =$ Me, $R_2 =$ H).—An experiment similar to that described above employing 7-methylocta-2 : 7-dien-5-yn-4-ol (8 g.; Heilbron, Jones, and Weedon, *loc. cit.*) yielded 2-*chloro-7-methylocta-*3 : 7-*dien-5-yne* (5 g.), b. p. 46°/3 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·5302 (Found : C, 70·15; H, 7·1. $C_9H_{11}Cl$ requires C, 69·9; H, 7·2%).

2-*Chloro-7-methylnona-*3 : 7-*dien-5-yne* (XI; $R_1 = R_2 =$ Me).—A mixture of 7-methylnona-2 : 7-dien-5-yn-4-ol (8 g.; Heilbron, Johnson, Jones, and Raphael, J., 1943, 265) and concentrated hydrochloric acid (40 c.c.) was shaken at 20° for 30 minutes under nitrogen. 2-*Chloro-7-methylnona-*3 : 7-*dien-5-yne* (7 g.), isolated in the usual manner, had b. p. 71—72°/1 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·5262 (Found : Cl, 21·3. $C_{10}H_{13}Cl$ requires Cl, 21·05%).

2 : 9-*Dichlorodeca-*3 : 7-*dien-5-yne* (XIII; R = Cl).—A solution of deca-2 : 8-dien-5-yn-4 : 7 -diol (2 g.; Heilbron, Jones, and Raphael, J., 1943, 268) in ether (10 c.c.) was shaken with concentrated hydrochloric acid (30 c.c.) for 45 minutes at 20° under nitrogen. The reaction mixture was diluted with water and extracted with ether. From the washed and dried ethereal phase 2 : 9-*dichlorodeca-*3 : 7-*dien-5-yne* (2·1 g.) was isolated as a mobile liquid which gradually darkened on keeping; b. p. 100—102°/10^{-2} mm., $n_{\mathrm{D}}^{25^\circ}$ 1·5500 (Found : C, 59·5; H, 6·2. $C_{10}H_{12}Cl_2$ requires C, 59·1; H, 5·9%). The dichloro-compound gives an immediate precipitate with cold aqueous silver nitrate.

2 : 9-*Diacetoxydeca-*3 : 7-*dien-5-yne* (XIII; R = OAc).—The above dichloro-compound (2 g.) was added to a solution of anhydrous potassium acetate (2·5 g.) in methyl alcohol (30 c.c.), which was then heated under reflux for 30 minutes. After dilution with water the product was extracted with ether, yielding the diacetate (1·8 g.), b. p. 138—139°/10^{-2} mm., $n_{\mathrm{D}}^{22^\circ}$ 1·4995 (when prepared from the rearranged glycol it had b. p. 131—132°/10^{-3} mm., $n_{\mathrm{D}}^{27^\circ}$ 1·5005).

*Octa-*1 : 7-*dien-4-yne-*3 : 6-*diol* (XIV) (cf. Dupont, *loc. cit.*).—To an ethereal solution of acetylenedimagnesium bromide (from magnesium, 12 g.), a solution of acraldehyde (28 g.) in ether (30 c.c.) was added during 30 minutes with vigorous stirring, which was continued for a further 4 hours. The Grignard complex was decomposed with a saturated solution of ammonium chloride (200 c.c.), and the acraldehyde polymer (15 g.) filtered off. The ethereal solution furnished octa-1 : 7-dien-4-yne-3 : 6-diol (10 g.), a viscous liquid, b. p. 131°/5 mm., 112—114°/1 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·5011 (Dupont, *loc. cit.* gives b. p. 146°/15 mm., n_{D} 1·5040). It shows no absorption of high intensity in the ultra-violet. The glycol was recovered unchanged on shaking for 24 hours with 25% sulphuric acid.

1 : 8-*Dichloro-octa*-2 : 6-*dien*-4-*yne* (XV; R = Cl).—A solution of the above glycol (5 g.) in ether (5 c.c.) was shaken with concentrated hydrochloric acid (25 c.c.) at 20° for 45 minutes under nitrogen. The reaction mixture was extensively diluted with water, and the product, obtained by extraction with ether and repeated distillation, was slightly impure 1 : 8-*dichloro-octa*-2 : 6-*dien*-4-*yne* (6 g.), b. p. 95—97°/10^{-2} mm., $n_{\mathrm{D}}^{24^\circ}$ 1·5700 (Found : C, 56·3, 56·3; H, 5·0, 5·4. $C_8H_8Cl_2$ requires C, 54·9; H, 4·6%). It has not been found possible to separate the pure dichloro-compound from the small quantity of glycol which it undoubtedly contains. The product gives an immediate precipitate with cold aqueous silver nitrate.

1 : 8-*Diacetoxyocta*-2 : 6-*dien*-4-*yne* (XV; R = OAc).—The above dichloro-compound (6 g.) was heated under reflux for 8 hours in nitrogen with a solution of anhydrous potassium acetate (10 g.) in methyl alcohol (100 c.c.). The reaction mixture was diluted with water and extracted with ether, and distillation of the washed and dried ethereal phase gave two fractions : (i) B. p. 82—84°/10^{-4} mm. (2 g.), $n_{\mathrm{D}}^{20^\circ}$ 1·5691, and (ii) 1 : 8-*diacetoxyocta*-2 : 6-*dien*-4-*yne* (3 g.), b. p. 118—120°/10^{-4} mm., $n_{\mathrm{D}}^{20^\circ}$ 1·5301 (Found : C, 64·5; H, 6·5. $C_{12}H_{14}O_4$ requires C, 64·85; H, 6·35%). When the diacetate (4 g.) was heated under reflux, in nitrogen, with methyl-alcoholic potassium hydroxide (50 c.c.; 6%) for 4 hours, the product, isolated with ether, underwent extensive decomposition on distillation, even at 10^{-4} mm. A small amount (200 mg.) of the glycol, not sufficiently pure to justify analysis, was obtained which had b. p. 110—112°/10^{-4} mm., $n_{\mathrm{D}}^{16^\circ}$ 1·5430. The *bisphenylurethane* of *octa*-2 : 6-*dien*-4-*yne*-1 : 8-*diol* could be obtained, however, and it formed prismatic plates or needles, m. p. 162°, from benzene (Found : N, 7·8. $C_{22}H_{10}O_4N_2$ requires N, 7·45%).

Octane-1 : 8-*diol*.—A solution of 1 : 8-diacetoxyocta-2 : 6-dien-4-yne (2 g.) in methyl alcohol (10 c.c.) was hydrogenated in the presence of platinic oxide (10 mg.). When absorption ceased the solution was freed from catalyst by filtration, a solution of potassium hydroxide (2 g.) in methyl alcohol (30 c.c.) was added, and the mixture heated under reflux for 3 hours. Isolation by means of ether and subsequent distillation gave octane-1 : 8-diol, b. p. 170—171°/16 mm., which solidified in contact with light petroleum (b. p. 40—60°), and on crystallisation from a mixture of this solvent with benzene it separated as needles, m. p. 62° (Lespieau, *Ann. Chim.*, 1914, **2**, 287, gives b. p. 172°/20 mm., m. p. 62—63°). The bisphenylurethane crystallised from ethyl acetate as plates, m. p. 173° (Lespieau, *loc. cit.*, gives m. p. 172—172·5°).

Reaction of Hex-3-*en*-5-*yn*-2-*ol with Concentrated Hydrochloric Acid*.—(*a*) A mixture of the carbinol (30 g.; Jones and McCombie, J., 1943, 261) and concentrated hydrochloric acid (100 c.c.) was shaken at 20° for 20 minutes. Distillation of the product obtained by isolation with ether gave two fractions : (i) Mainly 2-chlorohex-3-en-5-yne, b. p. 85—87°/150 mm. (15 g.), $n_{\mathrm{D}}^{20^\circ}$ 1·4801; (ii) b. p. 91°/50 mm., 76°/18 mm. (8 g.), $n_{\mathrm{D}}^{20^\circ}$ 1·5097.

(*b*) The carbinol (95 g.) was added during 10 minutes to vigorously stirred concentrated hydrochloric acid at 55° under nitrogen, stirring and heating being continued for 30 minutes. The mixture was then diluted with water, the product isolated by means of ether, and distilled through a Widmer column. Two main fractions were collected : (i) Mainly 2-chlorohex-3-en-5-yne, b. p. 70—97°/100 mm. (33 g.), $n_{\mathrm{D}}^{19^\circ}$ 1·4826; (ii) b. p. 68—78°/15 mm. (66·5 g.), $n_{\mathrm{D}}^{18^\circ}$ 1·5190. Further fractionation of (ii) through the packed column described below gave a product (27 g.) consisting essentially of dichloro-diene, probably 2 : 5-*dichlorohexa*-1 : 3-*diene*, b. p. 79—81°/17 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·5225 (Found : Cl, 47·2. $C_6H_8Cl_2$ requires Cl, 47·0%). *Light absorption* : Maximum, 2445 A.; $E_{1\,\mathrm{cm.}}^{1\%}$ 1420.

Addition of Hydrogen Chloride to 2-*Chlorohex*-3-*en*-5-*yne*.—The chloro-compound (150 g.) was shaken at about 20° for 4 hours with a solution of cuprous chloride (75 g.) and ammonium chloride (30 g.) in concentrated hydrochloric acid (500 c.c.), the product being isolated with ether after steam-distillation. The residual oil was fractionated through a well-lagged column containing a 40 × 1·8 cm. packing of single-turn glass helices and fitted with a total condensation–variable take-off head adjusted to give a reflux ratio of about 8 : 1. After much starting material had been stripped off, the following fractions were obtained : (i) B. p. 55—68°/15 mm. (10 g.), $n_{\mathrm{D}}^{21^\circ}$ 1·4988; (ii) b. p. 68—75°/15 mm. (14 g.), $n_{\mathrm{D}}^{21^\circ}$ 1·5092; (iii) b. p. 75—76°/15 mm. (19 g.), $n_{\mathrm{D}}^{21^\circ}$ 1·5179; (iv) b. p. 76—78°/15 mm. (10 g.), $n_{\mathrm{D}}^{21^\circ}$ 1·5251; (v) b. p. 78—79°/15 mm. (14·5 g.), $n_{\mathrm{D}}^{21^\circ}$ 1·5273. Attempts further to fractionate (iii), (iv), and (v) resulted in no appreciable variation in physical constants.

Light absorption : Fraction (iii). Maximum, 2380 A.; $E_{1\,\mathrm{cm.}}^{1\%}$ 1300 (Found : Cl, 44·6. Calc. for $C_6H_8Cl_2$: Cl, 47·0%). Fraction (iv). Maximum, 2410 A.; $E_{1\,\mathrm{cm.}}^{1\%}$ 1450 (Found : Cl, 46·7%). Fractions (iv) and (v) are considered to consist essentially of 2 : 5-dichlorohexa-1 : 3-diene.

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