23. *Studies in the Polyene Series. Part XX. The Formation of Ethers and Esters from Propenylvinylcarbinol and Related Compounds, and the Simultaneous Rearrangements.**

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Treatment of propenylvinylcarbinol (III; R = OH) with alcohols and sulphuric acid gives ethers of hexa-3 : 5-dien-2-ol (IV; R = OH) which exhibit high-intensity ultra-violet absorption characteristic of conjugated dienes and, unlike the corresponding carbinols, form normal adducts with maleic anhydride. The acetate (III; R = OAc), prepared with acetic anhydride and pyridine in the cold, is isomerised to the acetate (IV; R = OAc) with acetic anhydride at 100°. This also gives a normal Diels–Alder adduct, but when either the anhydride or the corresponding acid (V; R = OAc) is hydrolysed with boiling hydrochloric acid a lactonic acid (VI) is produced, which is probably a stereoisomer of that prepared directly from the dienol (Part XIX).

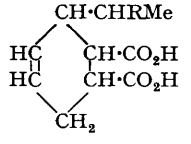
The behaviour of divinylcarbinol (VII; R = OH) provides a striking contrast in that no rearrangement accompanies the formation of either the methyl ether or the acetyl derivative, even when the latter is prepared in boiling acetic anhydride.

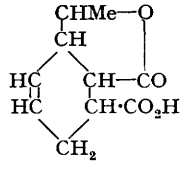
The rearrangement of propenylethynylcarbinol (I) with concentrated sulphuric acid in the presence of alcohols has been shown (Part XVIII) to result in the formation of ethers of the conjugated vinylacetylenylcarbinol (II). The enhanced mobility of the anionotropic system of propenylvinylcarbinol (III; R = OH) when compared with that of (I) suggested that in this case ether formation and the accompanying rearrangement would be easy to effect. When (III; R = OH) is treated with alcoholic sulphuric acid at room temperature

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

(III.) $CH_3{\cdot}CH{:}CH{\cdot}CHR{\cdot}CH{:}CH_2$ $\qquad$ $CH_3{\cdot}CHR{\cdot}CH{:}CH{\cdot}CH{:}CH_2$ (IV.)

(V.)





(VI.)

the *ether* (IV; R = OEt), is obtained in about 60% yield, and the 2-*methoxy*-analogue can be prepared in a similar manner. Both ethers are probably formed in practically theoretical yields but losses occur during isolation owing to their high volatility. With ethylene chlorohydrin and sulphuric acid 2-β-*chloroethoxyhexa*-3 : 5-*diene* (IV; R = $CH_2Cl{\cdot}CH_2{\cdot}O$) is obtained from (III; R = OH). These diene-ethers all exhibit high-intensity light absorption in the ultra-violet (Table) and from the ethyl ether and maleic anhydride, a

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
2-Ethoxyhexa-3 : 5-diene (IV; R = OEt)	2230	26,000
2-Methoxyhexa-3 : 5-diene (IV; R = OMe)	2235	30,000
2-β-Chloroethoxyhexa-3 : 5-diene (IV; R = $CH_2Cl{\cdot}CH_2O$)	2280	34,000
2-Acetoxyhexa-3 : 5-diene (IV; R = OAc)	2235	27,500
Hexa-3 : 5-dien-2-ol [1] (IV; R = OH)	2230	27,500
Hydrogen phthalate of (IV; R = OH) *	2230	39,500

[1] Part XIX. * In N-alcoholic KOH.

normal adduct, the *anhydride* of 3-α-*ethoxyethyl*-Δ^4-cyclo*hexene*-1 : 2-*dicarboxylic acid*, giving the *acid* (V; R = OEt) on refluxing with water, is formed. Similarly the *acid* (V; R = OMe) and the corresponding *anhydride* are obtained from the methyl ether.

In spite of the ease of rearrangement of propenylvinylcarbinol (III; R = OH), when treated in the cold with acetic anhydride in the presence of pyridine it is quantitatively converted into the *acetate* (III; R = OAc), without isomerisation. The latter remains unchanged after heating in benzonitrile at 100° for 18 hours, but in acetic anhydride at the same temperature it undergoes isomerisation † to 2-*acetoxyhexa*-3 : 5-*diene* (IV; R = OAc) (for light absorption, see Table), which can also be prepared directly from the carbinol (III; R = OH) in this way. This rearranged acetate (IV; R = OAc) is best obtained, however, by acetylation of the isomerised carbinol (IV; R = OH) in the cold with acetic anhydride in the presence of pyridine, for in many acetylation experiments, particularly those carried out at elevated temperatures, variable quantities of high-boiling products were produced. Nazarov (*Bull. Acad. Sci. U.R.S.S.*, 1938, 695) observed ether formation accompanying the acetylation of a vinylacetylenylcarbinol, but with neither propenylvinylcarbinol nor its isomer could any homogeneous C_{12} ether, corresponding to that described in Part XVIII, be isolated, almost certainly owing to the greater ease with which polymerisation reactions take place in the dienol series.

The unrearranged acetate (III; R = OAc) is hydrolysed by refluxing with methyl-alcoholic potassium

* Patent application pending.

† The failure of the acetate (III; R = OAc) to isomerise on heating in benzonitrile is difficult to reconcile with its behaviour in acetic anhydride and with the experience of Burton (J., 1928, 1650), who observed the ready rearrangement of α-phenylallyl *p*-nitrobenzoate on heating in either benzonitrile or acetic anhydride, the similar behaviour in the two solvents being attributed to their similarly high dielectric constants and ionising powers.

carbonate, but with methyl alcohol alone some of the rearranged methyl ether (IV; R = OMe) is formed. Such etherifications have been effected with acetates of acetylenylcarbinols (cf. Moureu, Dufraisse, and Houghton, *Bull. Soc. chim.*, **1927**, **41**, 53), and the isomerisation observed here must be brought about by the acetic acid originally liberated.

Condensation between the rearranged acetate (IV; R = OAc) and maleic anhydride in benzene gives the *anhydride* of the acid (V; R = OAc), which is converted into the *acid* on refluxing with water. On the other hand, when the addition reaction is effected in alcoholic solution a *monoethyl* ester of the acid (V; R = OAc) results. Hydrolysis of either the acetate-anhydride or the acetate-acid by heating for a few minutes with concentrated hydrochloric acid gives a lactonic *acid*, m. p. 176·5° (VI), rather unexpectedly different from that (m. p. 157—158°) obtained directly from the corresponding carbinol (Part XIX). Its *monomethyl* ester has practically the same m. p. as that of the isomeric compound, but the *mono*-p-*toluidide* is readily distinguishable from the corresponding derivative of the other form. Mixtures of the acids, the esters, or the toluidides melt at temperatures intermediate between the m. p.'s of the two components.

These two forms of (VI) are almost certainly stereoisomerides, and it seems likely that the treatment with boiling hydrochloric acid permits the assumption of the more stable configuration before lactonisation. The possibility of interconversions between the two forms and their inter-relationship will be examined as occasion permits.

A further indication of the great mobility of the system present in propenylvinylcarbinol is provided when, in attempts to prepare its hydrogen phthalate in pyridine solution at room temperature, the *hydrogen phthalate* of the rearranged alcohol (IV; R = OH), exhibiting intense light absorption in the ultra-violet (Table), is produced.

On the other hand, the lower mobility of divinylcarbinol (VII; R = OH) is clearly demonstrated in that with methyl-alcoholic sulphuric acid only the *methyl ether* (VII; R = OMe) of the unrearranged carbinol is produced, and refluxing with acetic anhydride gives only the unrearranged *acetate* (VII; R = OAc). The structures of both compounds follow from their inability to absorb in the ultra-violet and their failure to react with maleic anhydride. This stability of divinylcarbinyl acetate (VII; R = OAc) in boiling acetic anhydride is unexpected in view of the ready isomerisation of the parent carbinol (VII; R = OH), and this result would appear to be contrary to the postulates of Burton and Ingold (J., 1928, 904) that the mobility of the anion X increases in the order X = OH < OAc < Cl < Br, *i.e.*, in the order of increasing ionic stability. However, the basis on which true comparisons could be made is not obvious and, if the prediction is intended to apply to spontaneous rearrangements, *i.e.*, in the absence of acids, as well it might, it is probably true.

$CH_2{:}CH{\cdot}CHR{\cdot}CH{:}CH_2$
(VII.)

Experimental.

(Absorption spectra were determined in alcoholic solutions.)

2-*Ethoxyhexa*-3 : 5-*diene* (IV; R = OEt).—Propenylvinylcarbinol (116 g.; preceding paper) was added slowly to a cold solution of concentrated sulphuric acid (4 g.) in alcohol (400 c.c.), the mixture set aside at room temperature for 20 hours, then diluted with water, and the product isolated with ether. Removal of the latter through a column, and distillation of the product through a 24-cm. Dufton column, gave 2-*ethoxyhexa*-3 : 5-*diene* (85 g.) as a mobile liquid with a pronounced ethereal odour; b. p. 62—62·5°/77 mm., $n_D^{17°}$ 1·4484 (Found: C, 75·9; H, 11·05. $C_8H_{14}O$ requires C, 76·15; H, 11·2%).

2-*Methoxyhexa*-3 : 5-*diene* (IV; R = OMe).—Prepared by the above method from propenylvinylcarbinol (30 g.), methyl alcohol (100 c.c.), and sulphuric acid (1 g.), the *ether* (18 g.) had b. p. 61—62°/100 mm., $n_D^{19°}$ 1·4488 (Found: C, 74·75; H, 10·9. $C_7H_{12}O$ requires C, 74·95; H, 10·8%).

2-*β-Chloroethoxyhexa*-3 : 5-*diene* (IV; R = $CH_2Cl{\cdot}CH_2O$).—A mixture of propenylvinylcarbinol (30 g.), ethylene chlorohydrin (100 c.c.), and sulphuric acid (1 g.) was kept at room temperature for 2½ days. Isolation in the usual manner, followed by careful fractionation, gave the *β-chloroethyl ether* (9 g.), b. p. 79·5°/7·5 mm., $n_D^{22·5°}$ 1·4910 (Found: C, 59·8; H, 8·0. $C_8H_{13}OCl$ requires C, 59·85; H, 8·15%).

3-*α-Ethoxyethyl*-Δ^4-cyclo*hexene*-1 : 2-*dicarboxylic Acid* (V; R = OEt).—Equimolecular quantities of the above ethyl ether and maleic anhydride were brought to reaction in benzene solution. The crystals which separated on evaporation were recrystallised several times from light petroleum (b. p. 40—60°), giving the *anhydride* as needles, m. p. 68° (Found: C, 64·35; H, 7·3. $C_{12}H_{16}O_4$ requires C, 64·25; H, 7·2%). Refluxing with water gave the *acid*, which formed hexagonal plates, m. p. 165·5—166° (Found: C, 59·55; H, 7·5. $C_{12}H_{18}O_5$ requires C, 59·5; H, 7·5%).

3-*α-Methoxyethyl*-Δ^4-cyclo*hexene*-1 : 2-*dicarboxylic Acid* (V; R = OMe).—The *anhydride*, prepared as above, formed prismatic needles, from light petroleum (b. p. 80—100°), m. p. 85—86° (Found: C, 62·9; H, 6·55. $C_{11}H_{14}O_4$ requires C, 62·85; H, 6·7%). Refluxing with water gave the *acid* as rectangular prisms, m. p. 163—164° (Found: C, 57·9; H, 6·85. $C_{11}H_{16}O_5$ requires C, 57·9; H, 7·05%).

3-*Acetoxyhexa*-1 : 4-*diene* (III; R = OAc).—Acetic anhydride (68 g.) was gradually added to a cooled solution of propenylvinylcarbinol (65 g.) in pyridine (60 g.), and the mixture kept for 5 days at about 20°. After shaking with water for 30 mins., isolation with ether gave 3-*acetoxyhexa*-1 : 4-*diene* (85·5 g.), b. p. 60°/20 mm., $n_D^{19°}$ 1·4384 (Found: C, 68·75; H, 8·75. $C_8H_{12}O_2$ requires C, 68·55; H, 8·65%). *Light absorption:* Doubtful max. 2230 A.; ε = 1,500.

When this acetate (10 g.) was heated under reflux for 6 hours in methyl alcohol (10 c.c.) in the presence of anhydrous potassium carbonate (5 g.), there was obtained propenylvinylcarbinol (6·7 g.), b. p. 96—98°/150 mm., $n_D^{18°}$ 1·4542. The α-naphthylurethane had m. p. 94—95°, undepressed on admixture with an authentic specimen (Part XIX).

Refluxing the acetate (10 g.) in methyl alcohol (15 c.c.) for 7 hours gave a heterogeneous product from which on fractionation 2-methoxyhexa-3 : 5-diene (2·2 g.), b. p. 77—78°/150 mm., $n_D^{15°}$ 1·4508, was obtained. *Light absorption:* Maximum, 2230 A., ε = 24,000. With maleic anhydride in benzene it gave the adduct, m. p. 84—85°, undepressed on admixture with an authentic specimen (see above).

2-*Acetoxyhexa*-3 : 5-*diene* (IV; R = OAc).—(*a*) A solution of hexa-3 : 5-dien-2-ol (65 g.; Heilbron, Jones, McCombie, and Weedon, preceding paper) in pyridine (60 g.) was treated with acetic anhydride (68 g.), and the mixture kept at

about 20° for 2 days. This yielded *2-acetoxyhexa-3 : 5-diene* (77 g.), b. p. 66—70°/20 mm., $n_D^{20.5°}$ 1·4579 (Found: C, 68·25; H, 8·5. $C_8H_{12}O_2$ requires C, 68·55; H, 8·65%).

(*b*) When hexa-3 : 5-dien-2-ol (10 g.) was heated with acetic anhydride (12 g.) on a steam-bath for 5 hours in an atmosphere of nitrogen, 2-acetoxyhexa-3 : 5-diene (9·5 g.), b. p. 68—70°/20 mm., $n_D^{17°}$ 1·4597, was obtained.

(*c*) A solution of propenylvinylcarbinol (100 g.) in acetic anhydride (120 g.) was heated for 3 hours on a steam-bath in an atmosphere of nitrogen, giving 2-acetoxyhexa-3 : 5-diene (60 g.), b. p. 63—66°/20 mm., $n_D^{18°}$ 1·4583.

(*d*) A solution of 3-acetoxyhexa-1 : 4-diene (10·7 g.) in acetic anhydride (15 c.c.) was heated on a steam-bath for 40 hours. Isolation in the usual manner gave 2-acetoxyhexa-3 : 5-diene (5·5 g.), b. p. 58·5—60·5°/13 mm., $n_D^{15°}$ 1·4632. This material was slightly contaminated with an impurity of higher refractive index, but it gave the expected maleic anhydride adduct (see below), m. p. 142—143°, undepressed on admixture with an authentic specimen.

3-α-Acetoxyethyl-Δ⁴-cyclohexene-1 : 2-dicarboxylic Acid (V; R = OAc).—A mixture of 2-acetoxyhexa-3 : 5-diene (10 g.) and maleic anhydride (7·5 g.) was dissolved in benzene (25 g.) and after the solution had stood for 3 days at about 20° a mass of needles separated. These, together with a further quantity obtained on concentrating the benzene solution, when recrystallised from methyl alcohol gave the *anhydride* (8·4 g.) of the above acid, as needles, m. p. 142—143° (Found: C, 60·7; H, 6·0. $C_{12}H_{14}O_5$ requires C, 60·5; H, 5·9%). The *acid* crystallised from water in plates, m. p. 152·5—154° (Found: C, 56·4; H, 6·65. $C_{12}H_{16}O_6$ requires C, 56·25; H, 6·3%). The *dimethyl* ester, prepared with diazomethane, separated from aqueous methyl alcohol in needles, m. p. 103—103·5° (Found: C, 59·05; H, 7·35. $C_{14}H_{20}O_6$ requires C, 59·15; H, 7·1%). *Monoethyl ester.* Equimolecular quantities of the acetate and maleic anhydride were dissolved in alcohol. The crystalline deposit which soon separated redissolved on standing for 3 weeks at about 20°, and evaporation of the solution and crystallisation of the residue from water gave the *monoethyl* ester as needles, m. p. 120—121° (Found: C, 59·15; H, 7·25. $C_{14}H_{20}O_6$ requires C, 59·15; H, 7·1%).

γ-Lactone of 3-α-Hydroxyethyl-Δ⁴-cyclohexene-1 : 2-dicarboxylic Acid (VI).—When either the anhydride or the acid described above was refluxed with concentrated hydrochloric acid for 5 minutes the lactonic *acid* was formed. It was purified by sublimation at 100° (bath temp.)/10^{-4} mm. and by recrystallisation from water and formed plates, m. p. 176·5° [Found: C, 61·35; H, 6·2; *M* (titration), 194·5. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·15%; *M*, 196]. The *methyl* ester had m. p. 140·5—141° (Found: C, 62·9; H, 7·0. $C_{11}H_{14}O_4$ requires C, 62·85; H, 6·7%). The *p-toluidide* crystallised from aqueous alcohol as needles, m. p. 185—186° (Found: C, 71·55; H, 6·7. $C_{17}H_{19}O_3N$ requires C, 71·55; H, 6·7%).

Hydrogen Phthalate of Hexa-3 : 5-dien-2-ol.—Phthalic anhydride (15 g.) was added to a solution of propenylvinylcarbinol (10 g.) in pyridine (10 c.c.), the mixture kept at about 20° until homogeneous (5 days), and diluted with ether; the ethereal solution was washed with water, dilute hydrochloric acid, and dilute ammonium hydroxide. The alkaline washings were extracted with ether and acidified with dilute hydrochloric acid; the product (11 g.), isolated with chloroform, was an oil which gradually solidified when kept in a vacuum desiccator. Repeated crystallisation from light petroleum (b. p. 40—60°) gave the *hydrogen phthalate* of *hexa-3 : 5-dien-2-ol* as crystals, m. p. 78—80° (Found: C, 68·15; H, 6·05. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·75%).

3-Methoxypenta-1 : 4-diene (VII; R = OMe).—A mixture of divinylcarbinol (5 g.; preceding paper), methyl alcohol (10 c.c.), and concentrated sulphuric acid (0·1 g.) was kept at about 20° for one week. Isolation by means of ether gave *3-methoxypenta-1 : 4-diene* (2·7 g.), b. p. 80—82°/200 mm., $n_D^{17·5°}$ 1·4397 (Found: C, 73·5; H, 10·65. $C_6H_{10}O$ requires C, 73·4; H, 10·25%).

3-Acetoxypenta-1 : 4-diene (VII; R = OAc).—Divinylcarbinol (5·3 g.) was heated under reflux for 4 hours with acetic anhydride (10·8 g.) in the presence of anhydrous potassium acetate (1 g.). Isolation by means of ether gave *3-acetoxypenta-1 : 4-diene* (6 g.), b. p. 132°/750 mm., 74—75°/100 mm., $n_D^{16°}$ 1·4247 (Found: C, 66·85; H, 8·2. $C_7H_{10}O_2$ requires C, 66·65; H, 8·0%).

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