717. *Studies on Compounds Related to Auxin-a and Auxin-b. Part II. Preparation of Analogues of Auxin-b Lactone.*

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Starting from δ-hydroxy-αβ-acetylenic acids, analogues of auxin-b lactone have been prepared, containing phenyl, propenyl, and *spirocyclo*hexyl groups in place of the di-*sec.*-butyl-*cyclo*pentenyl group. The phenyl analogue has been shown to be identical with "cinnamoylacetic acid" prepared by Schöpf and Thierfelder (*Annalen*, 1935, **518**, 217) from benzaldehyde and acetonedicarboxylic acid. Authentic cinnamoylacetic acid has been prepared by two methods. Some reactions of the phenyl analogue are described.

The preparation of analogues of auxin-b lactone [auxin-b (I), as formulated by Kögl, Haagen-Smit, and Erxleben, *Z. physiol. Chem.*, 1934, **225**, 215] containing phenyl and propenyl groups in place of the di-*sec.*-butyl*cyclo*pentenyl radical was undertaken to find out whether the methods employed in the preparation of the methyl analogue (Part I; Jones and Whiting, *J.*, 1949, 1419) could be extended to the synthesis of compounds more closely related to auxin-b. Such methods would then be applicable to the preparation of the *cyclo*pentenyl analogue (cf. succeeding paper), and eventually to the synthesis of auxin-b itself, although there are considerable stereochemical problems to surmount in preparing the natural compound, due to the presence of the five centres of asymmetry.

In the phenyl series, the chosen starting material was 1-phenylbut-3-yn-1-ol (II), prepared by a modified Reformatsky reaction between benzaldehyde and propargyl bromide in the presence of zinc (Henbest, Jones, and Walls, *J.*, 1949, 2696). This carbinol was carboxylated (Haynes and Jones, *J.*, 1946, 503) to give the crystalline acetylenic acid (III), converted in turn into its methyl ester (IV). Treatment of the latter with methanol in the presence of a boron trifluoride–mercuric oxide catalyst (Hennion and Zoss, *J. Amer. Chem. Soc.*, 1941, **63**, 1151) gave the crystalline methoxy-lactone (V).

Attempts to hydrolyse the methoxyl group in (V), to yield the desired hydroxy-lactone (X), by the method already successfully applied to the methyl analogue, *viz.*, hydrochloric acid in ether, were frustrated by the insolubility of (V) in ether. However, its greater solubility in chloroform enabled the acid hydrolysis to be carried out, but the crystalline product isolated from the reaction mixture was found to be cinnamoylacetic acid (VI), isomeric with the expected (X).

Alternative methods for the hydration of the triple bond in (III) or (IV) were then sought. Moureu and Delange (*Compt. rend.*, 1903, **136**, 753) were able to hydrate αβ-acetylenic acids to β-keto-acids by heating them under reflux in ethanol solution containing sodium hydroxide. Application of this method to (III) gave a low yield of cinnamoylacetic acid (VI), hydration of the triple bond being followed by dehydration of the δ-hydroxy-β-keto-acid, first formed. Substitution of methanol for ethanol in this reaction gave a greatly improved yield (60%) of cinnamoylacetic acid.

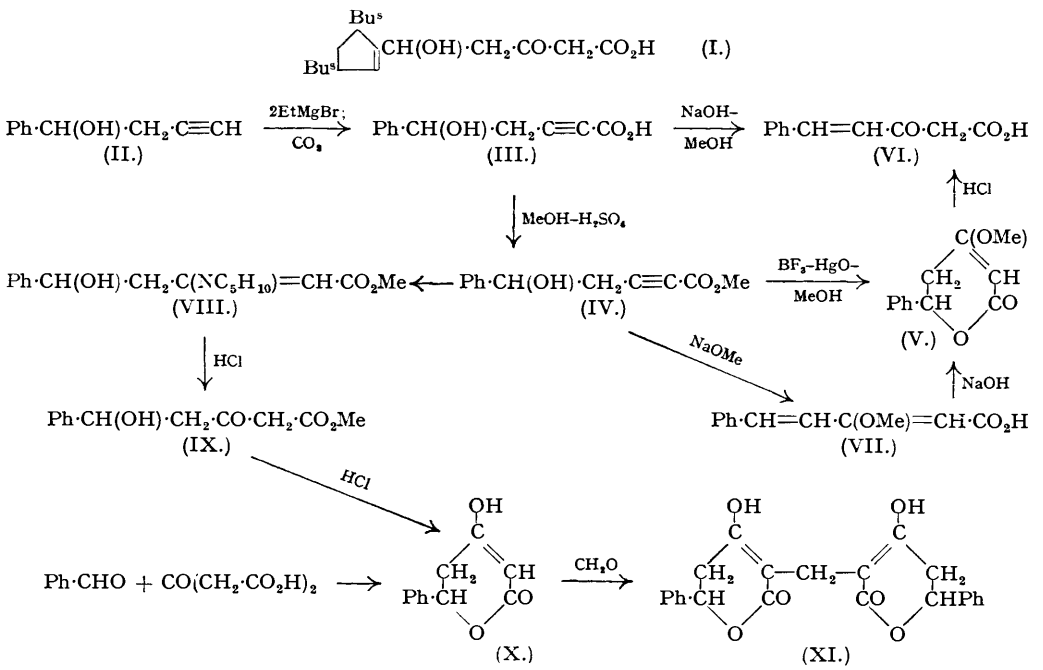
Another possible method for the hydration of the triple bond of a δ-hydroxy-αβ-acetylenic ester involves addition of a secondary amine to the triple bond to give an adduct, such as (VIII) (or its corresponding lactone), followed by mild acid hydrolysis (cf. Moureu and Lazennac, *Bull. Soc. chim.*, 1906, **35**, 1190) of the adduct. Jones and Whiting (*loc. cit.*) investigated this method in the methyl series, and found that addition of diethylamine followed by heating at 100° gave a diethylamino-lactone, convertible into the corresponding hydroxy-lactone in only 5% yield in the most favourable circumstances. However, the method has now been reinvestigated in the phenyl series, and by introduction of certain modifications it has proved to be a convenient hydration procedure. Addition of piperidine to the ester (IV) in ethereal solution at room temperature proceeded exothermically; diethylamine and morpholine appeared to be less reactive than piperidine and were not investigated further. The piperidine-adduct (VIII) (without further heating) was extracted from the ethereal mixture by 2N-hydrochloric acid, and the latter extract, containing an excess of mineral acid, was set aside at room temperature. After a short time the oily, open-chain keto-ester (IX) (since obtained crystalline, m. p. 48·5—49°) began to separate, which after a few hours was transformed by hydrolysis and lactonisation into a solid, the desired analogue, 5 : 6-dihydro-4-hydroxy-6-phenyl-2-pyrone (X). Isolation of the intermediate keto-ester (IX), whose structure was confirmed by analysis and light-absorption evidence, proves in turn that the piperidine adduct formed at room temperature has the open-chain structure (VIII). Lactonisation of the amine-adducts evidently only occurs with rapidity at 100°. This method of preparing analogues of auxin-b lactone has proved to be a general one, and has been successfully applied with *p*-chlorophenyl, *cyclo*pentenyl (succeeding paper), and propenyl groups (see below) in place of the phenyl group.

The phenyl-lactone (X), m. p. 136—141°, exhibited chemical and ultra-violet light-absorption properties in agreement with those expected for its structure. It gave a violet ferric chloride reaction, and dissolved readily in sodium hydrogen carbonate solution, being reprecipitated unchanged on acidification of the solution with mineral acid. Reaction with formaldehyde in the presence of a trace of piperidine (cf. Anschütz and Quitmann, *Annalen*, 1928, **462**, 97) gave 3 : 3′-methylenedi-(5 : 6-dihydro-4-hydroxy-6-phenyl-2-pyrone) (XI).

A number of reactions analogous to those carried out by Kögl, Haagen-Smit, and Erxleben (*loc. cit.*) on auxin-b have been performed with the phenyl-lactone (X) for purposes of comparison. A semicarbazone, m. p. 233—235°, was formed in quantitative yield, and a *p*-phenylphenacyl ester, m. p. 228—230°, in moderate yield. When a solution of the lactone in methanol containing hydrogen chloride (1·5%) was heated under reflux a small yield of the methoxy-lactone (V) was obtained. The latter was also formed in low yield by the action of diazomethane on the lactone (X). Hydrogenation of (X) in acetic acid in the presence of Adams's catalyst gave a heterogeneous product from which no single compound could be isolated. A fuller discussion of these comparative reactions is given in the succeeding paper.

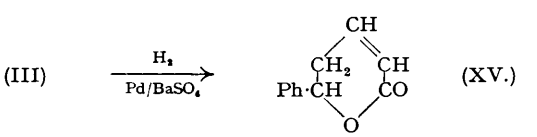
Mention has been made earlier in this paper of the isolation, from two experiments intended to produce the lactone (X), of the isomeric cinnamoylacetic acid (VI). Schöpf and Thierfelder (*Annalen*, 1935, **518**, 217), in the course of their extensive work on reactions taking place at " physiological pH's," found that the reaction between benzaldehyde and acetonedicarboxylic acid gave, amongst other products, a low yield of an acid, $C_{11}H_{10}O_3$, m. p. 139—141°, which they thought to be cinnamoylacetic acid. This experiment has been repeated, and it has been shown that Schöpf and Thierfelder's " cinnamoylacetic acid " is identical with the phenyl-lactone (X). The phenyl-lactone and cinnamoylacetic acid, indeed, show many points of resemblance; for instance, both dissolve in sodium hydrogen carbonate solution with liberation of carbon dioxide, both give violet ferric chloride colours, and both decompose above their

melting points to give benzylideneacetone. They are, however, clearly distinguishable by their ultra-violet light-absorption spectra, the former exhibiting a maximum at 2420 A., whereas



the latter has its main absorption band at 2810 A. Further confirmation of the structure of cinnamoylacetic acid was obtained by comparing its methyl ester (prepared from the acid with diazomethane) with the ethyl ester prepared by Borsche and Lewinsohn's method (*Ber.*, **1933**, **66**, 1792) from cinnamoyl chloride and ethyl acetoacetate, an unambiguous route. The similarity of the ultra-violet light-absorption spectra of the two esters confirmed the structure assigned to the parent acid, and, incidentally, indicates that these esters must exist predominantly in the enolic form, $PhCH{=}CH{\cdot}C(OH){=}CH{\cdot}CO_2R$ (XII).

The propenyl analogue (XIII) of auxin-b lactone has been obtained by starting from crotonaldehyde, by the route described above for the phenyl analogue; its chemical and light-absorption properties closely parallel those of the latter compound. Starting from *cyclo*hexanone, the pentamethylene analogue (XIV; R = H) has been prepared *via* the methoxy-lactone (XIV; R = Me) by Jones and Whiting's procedure (*loc. cit.*).



Partial hydrogenation of the acetylenic acid (III), in the presence of a palladium–barium sulphate catalyst, followed by distillation (cf. preparation of δ-$\Delta^{\alpha\beta}$-hexenolactone; Haynes and Jones, *J.*, **1946**, 954) gave the crystalline lactone (XV), previously obtained by Fittig and Perrin (*Annalen*, **1894**, **283**, 318) by starting from cinnamaldehyde and malonic acid. By their method of preparation, Fittig and Perrin were not certain of the position of the double bond in this lactone, but the above synthesis *via* an $\alpha\beta$-acetylenic acid shows that it must be $\alpha\beta$ to the potential carboxylic acid group. The hydroxylation of the lactone (XV) is being investigated

with a view to obtaining phenyl analogues of auxin-a lactone, and some success in this direction has already been achieved.

$$\underset{\text{(XVI.)}}{R'R''C(OH)\cdot CH_2\cdot C{\equiv}C\cdot CO_2Me} \xrightarrow{\text{NaOMe}} \underset{\text{(XVII.)}}{R'R''C{=}CH\cdot C(OMe){=}CH\cdot CO_2H}$$

A study has also been made of the reaction between sodium methoxide and the δ-hydroxy-αβ-acetylenic esters (as XVI) obtained as intermediates in this work. In all the examples examined, addition of methanol to the triple bond with concomitant dehydration of the hydroxyl group took place, β-methoxy-unsaturated acids (XVII) being obtained. The phenyl-acid (VII) was also obtained from the methoxy-lactone (V) by warming it in sodium hydroxide solution. The acids so prepared together with their light-absorption properties are given in the table.

Acid (XVII).	$\lambda_{max.}$, A.	$\varepsilon_{max.}$	Acid (XVII).	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
R′ = Me R″ = H [1]	2650	15,000	R′ = Ph R″ = H	{2290 {3080	{17,500 {24,500
R′ = R″ = Me	2700	14,500			
R′R″ = <[CH$_2$]$_5$	2690	14,500	R′ = PhCH:CH R″ = H [2]	{2510 {3220	{ 9,500 {40,000
R′ = MeCH:CH R″ = H	2940	30,000			

[1] Jones and Whiting (*loc. cit.*). [2] Fowler and Henbest (*J.*, 1950, 3642).

Experimental.

(All m. p.s were taken on a Köfler block and are corrected, and all light-absorption data were determined in alcoholic solutions).

4-Hydroxy-4-phenylbut-1-yne-1-carboxylic Acid (III).—1-Phenylbut-3-yn-1-ol (20 g.) (Henbest, Jones, and Walls, *loc. cit.*) was carboxylated by the general method (Haynes and Jones, *loc. cit.*), except that the Grignard complex was prepared in ether–benzene at 0°, and not heated under reflux. The *acid* (19·8 g.; 77% conversion) crystallised from ethyl acetate–light petroleum (b. p. 60—80°) or benzene as prisms, m. p. 104° (Found: C, 69·45; H, 5·25. $C_{11}H_{10}O_3$ requires C, 69·5; H, 5·3%). Its *methyl* ester (IV), prepared with methanol containing sulphuric acid (1%) (95% yield), was a viscous liquid, b. p. 100° (bath temp.; short-path still)/10^{-5} mm., n_D^{18} 1·5400 (Found: C, 70·35; H, 6·15. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·95%). A skin sensitivity developed after working with this ester for some weeks; small amounts of liquid (and even vapour) then produced an intense irritation on the hands, followed later by peeling of the affected skin.

Benzoylation of the methyl ester (3 g.) was effected with benzoyl chloride (4 c.c.) in dry pyridine (10 c.c.), the mixture being kept at 0° overnight. The product was isolated with ether, volatile materials were removed at 100°/10^{-2} mm., and the residue triturated with light petroleum (b. p. 40—50°). The solid was recrystallised from aqueous methanol (3·6 g.; m. p. 71—72°) and then light petroleum (b. p. 60—80°) to give the *benzoate* as needles, m. p. 72—73° (Found: C, 73·8; H, 5·35. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·25%).

5 : 6-Dihydro-6-phenyl-2-pyrone (XV).—4-Hydroxy-4-phenylbut-1-yne-1-carboxylic acid (3·8 g.) was hydrogenated at atmospheric pressure in the presence of palladium–barium sulphate (0·5 g.; 5% Pd) until 460 c.c. (reduced to N.T.P.; theoretical for one double bond, 448 c.c.) had been absorbed. Isolation by distillation at 1 mm. gave a distillate (3·2 g.) which readily solidified; crystallisation from aqueous methanol gave the lactone in small plates (2·45 g.), m. p. 59°. Recrystallisation from light petroleum (b. p. 60—80°) gave hair-like needles, m. p. 59° (Fittig and Perrin, *loc. cit.*, give m. p. 60°).

5 : 6-Dihydro-4-methoxy-6-phenyl-2-pyrone (V).—One drop of boron trifluoride–ether complex, mercuric oxide (10 mg.), and a small crystal of trichloroacetic acid were dissolved in methanol (1·5 c.c.) by gentle warming. Methyl 4-hydroxy-4-phenylbut-1-yne-1-carboxylate (IV) (1·5 g.) was added to the catalyst solution, which was then warmed to 50°, whereupon a slight exothermic reaction commenced. The temperature was kept at 50° by slight external cooling, and then kept at room temperature for 48 hours. The deposited solid (1·05 g.; m. p. 144—146°) was recrystallised from ethanol or aqueous acetone; it gave the *methoxy-lactone* (V) as prisms, m. p. 146—147° (Found: C, 70·35; H, 6·1. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·95%). Light absorption: Maximum, 2350 A.; $\varepsilon_{max.}$ = 12,000.

Cinnamoylacetic Acid (2-*Keto*-4-*phenylbut*-3-*ene*-1-*carboxylic Acid*) (VI).—(a) *From the methoxy-lactone* (V). The methoxy-lactone (500 mg.) dissolved in chloroform (10 c.c.) was treated with saturated hydrogen chloride in ether (10 c.c.); the solution being kept at room temperature for three hours. After removal of mineral acid by washing the solution with water, the organic acid (231 mg.) was extracted with potassium hydrogen carbonate solution, followed by acidification and isolation with ether. The solid acid was recrystallised by dissolving it in ethyl acetate at 40°, adding light petroleum (b. p. 40—60°) and cooling to 0°. *Cinnamoylacetic acid* formed colourless leaflets, m. p. 113—116° (decomp.) (Found: C, 69·7; H, 5·55. $C_{11}H_{10}O_3$ requires C, 69·5; H, 5·3%). Light absorption: Maxima, 2240 and 2810 A.; $\varepsilon_{max.}$ = 10,500 and 23,000, respectively. Inflexion, 2910 A.; $\varepsilon_{inf.}$ = 21,500. Some unchanged methoxy-lactone was recovered from the neutral product of this reaction.

A small sample of cinnamoylacetic acid was heated at 120° for one minute; carbon dioxide (baryta test) was rapidly evolved. The residue solidified on cooling and after crystallisation from light petroleum (b. p. 40—60°) had m. p. 42°, undepressed on admixture with pure benzylideneacetone, m. p. 42°.

(b) *From* 4-*hydroxy*-4-*phenylbut*-1-*yne*-1-*carboxylic acid.* The acid (380 mg.) was heated under reflux in a solution of sodium hydroxide (250 mg.) in methanol (10 c.c.) for five hours. The acid fraction (360 mg.) was isolated with ether, and this solid product was crystallised from methanol–water (2 : 1) to

give cinnamoylacetic acid (210 mg.), m. p. 108—109° (decomp.). The melting point was not raised by recrystallisation, and the light absorption indicated that this product was somewhat impure: Maxima, 2820 and 2910 A.; $\varepsilon_{max.} = 17,500$ in each case. On admixture with a sample of cinnamoylacetic acid prepared by method (*a*), the m. p. was 110—113° (decomp.).

Methyl Cinnamoylacetate.—This was prepared from cinnamoylacetic acid (m. p. 108—109° or 113—116°) (50 mg.) with diazomethane in ether. After two recrystallisations from light petroleum (b. p. 40—60°) the *ester* formed pale-yellow needles, m. p. 73—74° (Found: C, 70·75; H, 6·0. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·95%). Light absorption: Maxima, 2260 and 3060 A.; $\varepsilon_{max.} = 10,500$ and 25,500, respectively.

Ethyl Cinnamoylacetate.—This *ester* was prepared from ethyl acetoacetate and cinnamoyl chloride by Borsche and Lewinsohn's method (*loc. cit.*). It had m. p. 44—46° (Borsche and Lewinsohn give m. p. 46°). Light absorption: Maxima, 2270 and 3060 A.; $\varepsilon_{max.} = 10,000$ and 24,500, respectively.

2-Methoxy-4-phenylbuta-1 : 3-diene-1-carboxylic Acid (VII).—(*a*) Methyl 4-hydroxy-4-phenylbut-1-yne-1-carboxylate (500 mg.) was added to a solution of sodium methoxide [prepared from sodium (250 mg.) dissolved in methanol (3 c.c.)] at 0°. After three days at room temperature, the solution was diluted with water and extracted with ether, the latter extract being rejected. Acidification of the aqueous solution gave the *methoxy-acid* (0·36 g.), which, after two crystallisations from aqueous methanol, formed long needles, m. p. 173° (decomp.) (Found: C, 70·45; H, 6·3. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·95%). Light absorption: see Table.

(*b*) The methoxy-lactone (V) (100 mg.) was dissolved in 2N-sodium hydroxide solution (5 c.c.) by being heated at the boiling point for five minutes. Cooling and acidification of the solution gave a solid, which, after two crystallisations from aqueous methanol, had m. p. 172—173° (decomp.), undepressed on admixture with a sample prepared by method (*a*).

5 : 6-Dihydro-4-hydroxy-6-phenyl-2-pyrone (X).—A solution of the methyl ester (IV) (0·7 g.) in dry ether (2 c.c.) was treated with pure piperidine (0·5 g.) at room temperature; a mild exothermic reaction was observed. Four hours later more ether was added, and the piperidine adduct was extracted with 2N-hydrochloric acid (20 c.c.). The clear acid extract became turbid after ten minutes owing to separation of keto-ester (IX) (see below). The mixture was then shaken mechanically for 48 hours at room temperature; solid began to separate from the oil after about four hours. The collected solid (0·41 g.; m. p. 128—135°) was washed with a little dry ether, to remove some gummy material, and then recrystallised by adding it to water preheated to 90°, filtering the solution, and cooling it rapidly to 0°. The *pyrone* (X) was obtained as a granular solid, m. p. 136—141° (decomp.) (Found: C, 69·55; H, 5·6. $C_{11}H_{10}O_3$ requires C, 69·5; H, 5·3%). Light absorption: Maximum, 2420 A.; $\varepsilon_{max.} = 10,500$. A sample heated above its melting point for a few minutes gave benzylideneacetone (m. p. and mixed m. p. 42°). A specimen of the pyrone prepared by Schöpf and Thierfelder's method (*loc. cit.*) had m. p. (and mixed m. p.) 136—140°. Light absorption: Maximum, 2410 A.; $\varepsilon_{max.} = 10,500$.

The keto-ester (IX), formed as an intermediate in the above hydration reaction, was isolated with ether after the piperidine adduct had been left in the acid solution for two hours. Evaporation of the dry ethereal solution gave an oil which solidified on trituration with methanol–water (1 : 1). Recrystallisation from benzene–light petroleum (b. p. 60—80°) (2 : 1) gave the *keto*-ester as needles, m. p. 48·5—49° (Found: C, 65·05; H, 5·7. $C_{12}H_{14}O_4$ requires C, 64·85; H, 6·35%). Light absorption: Maximum, 2480 A., $\varepsilon_{max.} = 2,000$.

Reactions of 5 : 6-Dihydro-4-hydroxy-6-phenyl-2-pyrone (X).—(a) *With formaldehyde.* The lactone (150 mg.) was dissolved in methanol (5 c.c.) and water (2 c.c.), formalin solution (0·5 c.c.) and one small drop of piperidine were then added in that sequence. *3 : 3'-Methylenedi-(5 : 6-dihydro-4-hydroxy-6-phenyl-2-pyrone)* (XI) (110 mg.; m. p. 187—196°) began to crystallise after five minutes. Recrystallisation from ethyl acetate–light petroleum (b. p. 60—80°) (1 : 1) gave needles, m. p. 188—196° (Found: C, 70·35; H, 5·15. $C_{23}H_{20}O_6$ requires C, 70·4; H, 5·15%). Light absorption: Maximum, 2440 A.; $\varepsilon_{max.} = 16,500$; inflexion, 2500 A.; $\varepsilon_{inf.} = 15,500$. The above reaction proceeded at a greatly reduced rate in the absence of piperidine, but the same product was obtained.

(b) *With semicarbazide.* A solution of the lactone (30 mg.) in ethanol (1·5 c.c.) was treated with a solution of semicarbazide hydrochloride (30 mg.) and potassium acetate (30 mg.) in water (0·5 c.c.). A crystalline precipitate began to appear after five minutes. After one hour at room temperature the *semicarbazone* (37 mg.) was filtered off, and then had m. p. 230—232°. It was purified by being washed with boiling water and boiling ethanol, in both of which it was quite insoluble, followed by recrystallisation from ethylene glycol. The pure derivative formed plates, m. p. 233—235° (slight decomp.) (Found: C, 58·1; H, 5·35. $C_{12}H_{13}O_3N_3$ requires C, 58·3; H, 5·3%).

(c) *With p-phenylphenacyl bromide.* The lactone (38 mg.) and potassium hydrogen carbonate (20 mg.) were dissolved in warm 80% ethanol (5 c.c.). *p*-Phenylphenacyl bromide (43 mg.) was added and the solution heated under reflux for 1·5 hours. An amorphous solid separated on cooling, and was extracted with boiling ethanol–*n*-butanol (1 : 1). The insoluble part (36 mg.) had m. p. 223—226°; recrystallisation from nitromethane gave the *ester* as small needles, m. p. 228—230° (Found: C, 76·95; H, 5·4. $C_{25}H_{20}O_4$ requires C, 78·1; H, 5·25%).

(d) *Methylation experiments.* The lactone (40 mg.) was dissolved in methanol (2 c.c.) containing hydrogen chloride (1·5%), and the solution heated under reflux for 1·5 hours. Evaporation of the solvent in a vacuum gave a product which solidified on trituration with methanol; it had m. p. 136—142°. Recrystallisation from methanol gave the methoxy-lactone (V) (8 mg.), m. p. 145—146°; the mixed m. p. with authentic material was 145—147°.

The lactone (50 mg.) dissolved in chloroform (10 c.c.) was treated with a slight excess of diazomethane in ether. Evaporation in a vacuum gave a solid, which after two crystallisations from aqueous methanol had m. p. 146—147°, undepressed on admixture with the methoxy-lactone (V).

4-Hydroxyhept-5-en-1-yne-1-carboxylic Acid.—Hept-5-en-1-yn-4-ol (11 g.) (Henbest, Jones, and Walls, *loc. cit.*), dissolved in dry benzene (75 c.c.), was added at 0° to a solution of ethylmagnesium bromide (from 5 g. of magnesium) in ether (50 c.c.); the resulting Grignard complex (without further heating) was carboxylated in the usual way. The acetylenic *acid* (8·1 g.) was obtained as a pale-brown viscous liquid. Only small quantities could be distilled, from a short-path still, without appreciable decomposition; a sample had b. p. 120° (bath temp.)/10^{-5} mm., n_D^{20} 1·4960 (Found: C, 62·35; H, 6·85. $C_8H_{10}O_3$ requires C, 62·3; H, 6·55%). The methyl ester was prepared from the crude acid (13·9 g.) and methanol (100 c.c.), containing concentrated sulphuric acid (1 c.c.), the solution being set aside overnight at room temperature and then heated under reflux for two hours. Isolation with ether and distillation gave *methyl 4-hydroxyhept-5-en-1-yne-1-carboxylate* (11·7 g.) as a pleasant-smelling liquid, b. p. 98—99°/0·1 mm., n_D^{21} 1·4828 (Found: C, 64·45; H, 7·2. $C_9H_{12}O_3$ requires C, 64·25; H, 7·2%).

5 : 6-Dihydro-4-hydroxy-6-propenyl-2-pyrone (XIII).—Pure piperidine (0·4 c.c.) was added to a solution of the foregoing ester (0·5 g.) in dry ether (1 c.c.), and the mixture was then kept at room temperature for one hour. The piperidine adduct was extracted with 2N-hydrochloric acid (5 c.c.), chloroform (5 c.c.) was added to the acid extract, and the mixture was kept at room temperature for 48 hours with intermittent shaking. The aqueous solution was twice extracted with chloroform, and the extracts were dried (Na_2SO_4) and evaporated *in vacuo*. The residue became solid on trituration with a little dry ether. Recrystallisation from ethyl acetate–light petroleum (b. p. 60—80°) gave material (25 mg.) with m. p. 114—120°. Further recrystallisation from benzene gave the pure *pyrone*, m. p. 120—122°, as a microcrystalline material (Found: C, 62·25; H, 6·6. $C_8H_{10}O_3$ requires C, 62·3; H, 6·55%). Light absorption: Maximum, 2400 A.; $\varepsilon_{max.}$ = 11,500.

2-Methoxyhepta-1 : 3 : 5-triene-1-carboxylic Acid (XVII; R′ = Me·CH:CH, R″ = H).—Sodium (0·2 g.) was dissolved in methanol (3 c.c.), and the solution cooled to 0°. Methyl 4-hydroxyhept-5-en-1-yne-1-carboxylate (0·55 g.) was added and the solution was kept at room temperature for 40 hours. Addition of 2N-sulphuric acid gave a solid (0·32 g.), m. p. 143—147°, which after three recrystallisations from benzene–light petroleum (b. p. 60—80°) (1 : 1) gave the pure *acid* as needles, m. p. 155—156° (Found: C, 63·65; H, 7·1. $C_9H_{10}O_3$ requires C, 64·25; H, 7·2%). Light absorption: see table.

3-1′-Hydroxycyclohexylprop-1-yne-1-carboxylic Acid.—Recrystallised 1-propargylcyclohexanol (15 g.) was carboxylated by the general method described above, the Grignard complex being completely soluble in ether–benzene. The acetylenic *acid* (13·7 g., 70%) crystallised from benzene or ethyl acetate–light petroleum (b. p. 60—80°) in granular prisms (12·5 g.), m. p. 124—125° (Found: C, 66·05; H, 7·8. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·75%). The *methyl* ester was prepared by heating a methanol solution of the acid containing concentrated sulphuric acid (1%) for six hours. The product was a viscous oil, b. p. 130° (bath temp.; short-path still)/10^{-2} mm., n_D^{18} 1·4962 (Found: C, 67·15; H, 8·3. $C_{11}H_{16}O_3$ requires C, 67·3; H, 8·2%).

5 : 6-Dihydro-4-methoxy-6 : 6-pentamethylene-2-pyrone (XIV; R = Me).—The forgoing methyl ester (1 g.) was treated with methanol (1 c.c.), containing one drop of boron trifluoride–ether complex, and mercuric oxide (10 mg.). On gentle warming, an exothermic reaction commenced, the temperature rising quickly to 70°. After 24 hours at room temperature the product was isolated with ether. Two recrystallisations from light petroleum (b. p. 60—80°) gave the *lactone* (0·68 g.) as long needles, m. p. 80° (Found: C, 67·0; H, 8·2. $C_{11}H_{16}O_3$ requires C, 67·3; H, 8·2%). Light absorption: Maximum, 2360 A.; $\varepsilon_{max.}$ = 10,500.

5 : 6-Dihydro-4-hydroxy-6 : 6-pentamethylene-2-pyrone (XIV; R = H).—A solution of the foregoing methoxy-lactone (250 mg.) in ether (10 c.c.), to which one drop (50 mg.) of concentrated hydrochloric acid had been added, was kept at room temperature for four days. Ether and potassium hydrogen carbonate solution were added and the mixture shaken vigorously to extract the pyrone from the ethereal solution. The latter was extracted once more with potassium hydrogen carbonate solution, the combined extracts were acidified with dilute sulphuric acid, and the liberated pyrone extracted twice with ether. Evaporation of the dried ethereal extract gave a solid which was triturated with ether–light petroleum (1 : 1). Recrystallisation from ethyl acetate–light petroleum gave the pure *pyrone* (85 mg.) as feathery needles, m. p. 121—123° (Found: C, 70·05; H, 8·0. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·75%). Light absorption: Maximum, 2430 A.; $\varepsilon_{max.}$ = 11,000.

3-cyclohexylidene-2-methoxyprop-1-ene-1-carboxylic Acid (XVII; R′R″ = $<[CH_2]_5$) (With Dr. R. A. Raphael).—Methyl 3-1′-hydroxycyclohexylprop-1-yne-1-carboxylate (2·5 g.) was slowly added to a solution of sodium methoxide [from sodium (0·9 g.) in methanol (15 c.c.)] at 0°, the solution then being kept at room temperature for three days. Addition of 2N-sulphuric acid precipitated a solid which after recrystallisation fron light petroleum (b. p. 60—80°) gave the *acid* (1·26 g.) as needles, m. p. 122° (Found: C, 67·1; H, 8·1. $C_{11}H_{16}O_3$ requires C, 67·35; H, 8·2%). Light absorption: see table.

2-Methoxy-4-methylpenta-1 : 3-diene-1-carboxylic Acid (XVII; R′ = R″ = Me) (With Dr. R. A. Raphael).—2-Methylpent-4-yn-2-ol (Henbest, Jones, and Walls, *loc. cit.*) was carboxylated and esterified. The ester (2 g.) (b. p. 131°/0·2 mm.) was added slowly to a solution of sodium methoxide [from sodium (0·9 g.) in methanol (15 c.c.)] at 0°. After being kept for three days at room temperature the solution was treated with 2N-sulphuric acid. The precipitate was recrystallised from light petroleum (b. p. 60—80°) to give the *acid* (1·55 g.) as needles, m. p. 115° (Found: C, 61·6; H, 7·8. $C_8H_{12}O_3$ requires C, 61·55; H, 7·75%). Light absorption: see table.

Microanalyses were carried out by Mr. E. S. Morton and Mr. H. Swift.

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