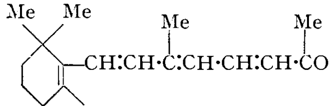
390. *Studies in the Polyene Series. Part XXIX. Ethoxyacetylenic Carbinols and their Conversion into αβ-Unsaturated Aldehydes and Acids.*

By Sir Ian Heilbron, E. R. H. Jones, M. Julia, and B. C. L. Weedon.

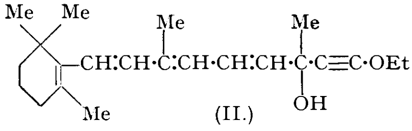
Condensation of ethoxyacetylene with acetone, methyl vinyl ketone, and *β*-ionone gives carbinols which, by semihydrogenation of the triple bond and treatment of the resulting ethoxyvinylcarbinols with dilute mineral acids, are converted into the *αβ*-unsaturated aldehydes (VII; R = Me), (VII; R = CH$_2$:CH), and *β*-ionylideneacetaldehyde (IV), respectively.

A novel synthesis of *αβ*-unsaturated acids from ketones is described. Hydration of the ethoxyacetylenic carbinols derived from acetone, methyl vinyl ketone, benzylideneacetone, *β*-ionone, and the C$_{15}$ ketone (X) occurs readily in the presence of dilute mineral acids, giving esters which, on hydrolysis, yield the *αβ*-unsaturated acids (VIII; R = Me), (VIII; R = CH$_2$:CH), (IX), *β*-ionylideneacetic acid (XI), and the C$_{17}$ acid (XII), respectively.

A new method for the preparation of polyene aldehydes was developed by Arens and van Dorp (*Nature*, 1947, **160**, 189) who showed that condensation of ethoxyacetylene with the C$_{18}$ ketone (I) gave the carbinol (II) which, by semihydrogenation of the triple bond and treatment of the ethoxyvinylcarbinol thus formed with dilute hydrochloric acid, was converted into vitamin A aldehyde (III) (retinene$_1$, cf. Morton *et al.*, *Nature*, 1944, **153**, 69, 405). Similarly, β-ionone yielded β-ionylideneacetaldehyde (IV). Since no details of this latter conversion have been published subsequently by Arens and van Dorp, we have repeated this preparation and also applied the method to both acetone and methyl vinyl ketone, each of which reacted readily with ethoxyacetylenylmagnesium bromide giving 1-*ethoxy*-3-*methylbut*-1-*yn*-3-*ol* (V; R = Me) and 1-*ethoxy*-3-*methylpent*-4-*en*-1-*yn*-3-*ol* (V; R = CH$_2$:CH), respectively, in 60 and 30% yield.



(I.)



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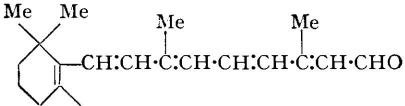

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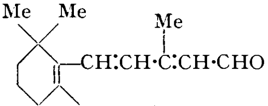
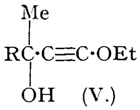
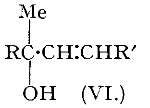


(IV.)

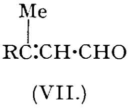
Partial hydrogenation of these carbinols, and treatment of the resulting ethoxyvinylcarbinols (VI; R = Me; R′ = OEt) and (VI; R = CH_2:CH; R′ = OEt) with dilute mineral acids, yielded β-methylcrotonaldehyde (VII; R = Me) and 3-methylpenta-2 : 4-dien-1-al (VII; R = CH_2:CH), respectively. It has previously been reported (Jones and Weedon, *J.*, 1946, 937) that the chlorovinylcarbinol (VI; R = Me, R′ = Cl) also gives β-methylcrotonaldehyde on treatment with dilute sulphuric acid.



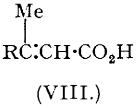
$\mathrm{R}\overset{\mathrm{Me}}{\underset{\mathrm{OH}}{\mathrm{C}}}\cdot\mathrm{C{\equiv}C\cdot OEt}$ (V.)



$\mathrm{R}\overset{\mathrm{Me}}{\underset{\mathrm{OH}}{\mathrm{C}}}\cdot\mathrm{CH{:}CHR'}$ (VI.)



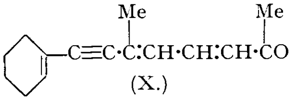
$\mathrm{R}\overset{\mathrm{Me}}{\mathrm{C}}\mathrm{{:}CH\cdot CHO}$ (VII.)

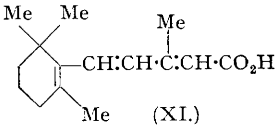


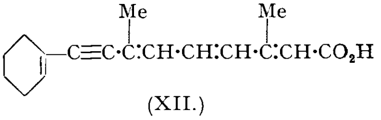
$\mathrm{R}\overset{\mathrm{Me}}{\mathrm{C}}\mathrm{{:}CH\cdot CO_2H}$ (VIII.)

The ease with which alkoxy- and phenoxy-acetylenes are hydrated in the presence of acids (Jacobs *et al.*, *J. Amer. Chem. Soc.*, 1940, **62**, 1849; 1942, **64**, 223; Favorski and Schtschukina, *J. Gen. Chem. Russia*, 1945, **15**, 385) prompted an investigation of the behaviour of ethoxyacetylenic carbinols under similar conditions. It was observed that on shaking an ethoxyacetylenic carbinol, *e.g.*, (V), with 10% sulphuric acid for a few minutes, an ester was formed which, after hydrolysis, yielded an αβ-unsaturated acid, *e.g.*, (VIII). Thus the carbinol (V; R = Me) gave β-methylcrotonic acid (VIII; R = Me) in 55% yield. In order to avoid the losses involved in attempted isolation of the ethoxyacetylenic carbinols, it was advantageous in the majority of cases to convert the crude products obtained by condensation of ketones with ethoxyacetylene directly into the acids. In this manner methyl vinyl ketone, benzylideneacetone, β-ionone, and the C_{15} ketone (X) were converted into *2-methylbuta-*1 : 3*-diene-*1*-carboxylic acid* (VIII; R = CH_2:CH) (35%), 4-phenyl-2-methylbuta-1 : 3-diene-1-carboxylic acid (IX) (65%), β-ionylideneacetic acid (XI), and the C_{17} acid (XII) (cf. Heilbron, Jones, and Richardson, *J.*, 1949, 287), respectively.

CHPh:CH·CMe:CH·CO_2H
(IX.)







This new synthesis of αβ-unsaturated acids from ketones thus constitutes an alternative method to the well known Reformatsky reaction with ethyl bromoacetate.*

Condensation of methyl vinyl ketone with zinc and ethyl bromoacetate gave, after dehydration and hydrolysis of the crude hydroxy-ester, the acid (VIII; R = CH_2:CH), identical with that prepared in the manner described above.

EXPERIMENTAL.

Light-absorption measurements were carried out in ethanol except where stated otherwise.

Ethoxyacetylene (cf. Jacobs, Cramer, and Hanson, *J. Amer. Chem. Soc.*, 1942, **64**, 223, 2635).—Bromoethoxyethylene (25 g.), prepared from dibromoacetal by the method of Jacobs *et al.* (*loc. cit.*, p. 223), was placed in a distilling flask (100 c.c.) and the free space in the bulb of the flask almost completely filled with powdered potassium hydroxide. The temperature of the flask and contents was slowly raised to 90—100° whereupon crude ethoxyacetylene (6—8 g.) distilled; b. p. 50°, n_D^{20} 1·395 (Favorski and Shostakovski, *J. Gen. Chem. Russia*, 1943, **13**, 1, give b. p. 48—50°; Jacobs *et al.*, *loc. cit.*, give n_D^{20} 1·3812 for the pure acetylene). The ethoxyacetylene was used without further purification.

Dibromoacetal.—The method used was a modification of that employed by Wizinger and Yousef-el-Attar (*Helv. Chim. Acta*, 1947, **30**, 189) for the preparation of monobromoacetal. Bromine (1060 g.) was added dropwise with vigorous stirring to paraldehyde (225 g.), cooled in an ice–salt bath. The rate of addition was such that the temperature of the mixture did not exceed 10—15° and no permanent colour developed in the mixture. Absolute alcohol (1 l.) was added, and the mixture was set aside at 20° overnight and then poured into water (4 l.). The oil thus precipitated was separated, washed thoroughly with water, dried, and distilled, giving dibromoacetal (350 g.), b. p. 102—104°/15 mm., n_D^{22} 1·4845 (Jacobs *et al.*, *loc. cit.*, give b. p. 94—97°/12 mm., n_D^{25} 1·4790), together with a low-boiling fraction (190 g.) consisting mainly of mono- and di-bromoacetal.

1*-Ethoxy-*3*-methylbut-*1*-yn-*3*-ol* (V; R = Me).—A solution of ethoxyacetylene (7·4 g.) in ether (50 c.c.) was added during 30 minutes to a well stirred solution of ethylmagnesium bromide (prepared from

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* [Added, June 27th, 1949.] Two recent papers (Schtschukina and Rubtsov, *J. Gen. Chem. Russia*, 1948, **18**, 1645, Preobrazhenskii and Rubtsov, *ibid.*, p. 1719), received since the present communication was submitted, have also described the conversion of acetylenic ethoxy-carbinols into aldehydes and acids.

2·3 g. of magnesium) in ether (100 c.c.), and the mixture was heated under reflux for 2½ hours during which the complex separated as an oil. After the mixture had been cooled, acetone (5 g.) in ether (50 c.c.) was added dropwise during 30 minutes; the mixture was heated under reflux for 1½ hours and then cooled to 0°. The complex was decomposed by addition of ammonium chloride (20 g.) in water (100 c.c.), and the product isolated in the usual manner with ether, giving 1-*ethoxy*-3-*methylbut*-1-*yn*-3-*ol* (6·7 g.) as a mobile liquid, b. p. 72°/11 mm., n_D^{20} 1·4420 (Found : C, 65·25; H, 9·35. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4%).

β-Methylcrotonaldehyde (VII; R = Me).—The above carbinol (0·9 g.) in ethyl acetate (20 c.c.) was shaken in an atmosphere of hydrogen in the presence of a palladium–calcium carbonate catalyst (0·1 g.; 2% Pd) until 168 c.c. (20°/777 mm.) had been absorbed (equivalent to 1 double bond). After removal of the catalyst and evaporation of the solvent under reduced pressure, the residue was dissolved in methanol and treated with methanolic 2 : 4-dinitrophenylhydrazine sulphate. The resulting precipitate was crystallised from alcohol, giving dark red needles (1·0 g.), m. p. 179°, undepressed on admixture with an authentic specimen of the 2 : 4-dinitrophenylhydrazone of β-methylcrotonaldehyde (Braude and Jones, *J.*, 1945, 498, give m. p. 179°).

β-Methylcrotonic acid (VIII; R = Me).—1-Ethoxy-3-methylbut-1-yn-3-ol (1·2 g.) was shaken with 10% (w/v) sulphuric acid (10 c.c.) for 3 minutes. The ester thus formed was isolated by means of ether and hydrolysed by heating under reflux for 3 hours with a solution of potassium hydroxide (2 g.) in methanol (15 c.c.). After cooling, the solution was diluted with water (100 c.c.), and the non-hydrolysable material extracted with ether. The aqueous solution was then acidified with 10% (w/v) sulphuric acid and distilled. The first 100 c.c. of distillate were collected and extracted thoroughly with ether. Drying and evaporation of the ethereal solution gave β-methylcrotonic acid (0·5 g.) which crystallised from water in needles, m. p. 68°, undepressed on admixture with an authentic specimen (Ives, Linstead, and Riley, *J.*, 1933, 561, give m. p. 70°).

1-*Ethoxy*-3-*methylpent*-4-*en*-1-*yn*-3-*ol* (V; R = CH_2:CH).—A solution of methyl vinyl ketone (7·0 g.) in ether (50 c.c.) was added at 0° during 30 minutes to a well stirred suspension of ethoxyacetylenylmagnesium bromide (prepared from 2·3 g. of magnesium and 7·3 g. of ethoxyacetylene) in ether (200 c.c.), and the mixture was heated under reflux for 1½ hours. After the mixture had been cooled to 0°, the complex was decomposed by addition of ammonium chloride (20 g.) in water (100 c.c.), and the product isolated with ether in the usual way. Distillation, accompanied by some decomposition, gave 1-*ethoxy*-3-*methylpent*-4-*en*-1-*yn*-3-*ol* (4·3 g.), b. p. 54—55°/0·1 mm., n_D^{20} 1·4590 (Found : C, 68·2; H, 8·8. $C_8H_{12}O_2$ requires C, 68·55; H, 8·65%).

1-*Ethoxy*-3-*methylpenta*-1 : 4-*dien*-3-*ol and* 3-*Methylpenta*-2 : 4-*dien*-1-*al*.—The above carbinol (3·1 g.) in ethyl acetate (25 c.c.) was shaken in an atmosphere of hydrogen in the presence of a palladium–calcium carbonate catalyst (0·5 g.; 2% Pd) until 525 c.c. (20°/765 mm.) had been absorbed (equivalent to 1 double bond). The reaction was then interrupted, the catalyst and solvent were removed, and the residue was distilled, giving 1-*ethoxy*-3-*methylpenta*-1 : 4-*dien*-3-*ol* (2 g.), b. p. 35°/0·1 mm., n_D^{24} 1·4530 (Found : C, 68·05; H, 9·85. $C_8H_{14}O_2$ requires C, 67·6; H, 9·9%). When a small portion of the carbinol was shaken with 5% (w/v) hydrochloric acid for 5 minutes, a pungent liquid was obtained. Treatment of the latter with 2 : 4-dinitrophenylhydrazine sulphate in methanol gave the 2 : 4-dinitrophenylhydrazone of 3-methylpenta-2 : 4-dien-1-al which crystallised from ethyl acetate as deep-red needles, m. p. 130—131°, undepressed on admixture with a specimen prepared by the method of Heilbron, Jones, and Julia (this vol., p. 1430). Treatment of the crude aldehyde with a solution of semicarbazide acetate in methanol gave a *semicarbazone* which crystallised from ethyl acetate in needles, m. p. 180—182° (Found : N, 27·6. $C_7H_{11}ON_3$ requires N, 27·45%). Light absorption of the semicarbazone: Maximum, 2810 A.; ε, 27,000. Inflexion, 2950 A.; ε, 22,000. This derivative is isomeric with that, m. p. 166—167° (light absorption : Maximum 2940 A.; ε, 38,000), previously described for 3-methylpenta-2 : 4-dien-1-al (*idem, loc. cit.*).

2-*Methylbuta*-1 : 3-*diene*-1-*carboxylic Acid* (VIII; R = CH_2:CH).—(*a*) Methyl vinyl ketone (6 g.) was condensed with ethoxyacetylenylmagnesium bromide (prepared from 2·3 g. of magnesium and 7 g. of ethoxyacetylene) in the manner described above. After the Grignard complex had been decomposed, the crude ethoxyacetylenic carbinol was extracted with ether, and the ethereal solution (200 c.c.) shaken with 10% (w/v) sulphuric acid (100 c.c.) for 10 minutes, heat being evolved in the process. After cooling to 20°, the ethereal layer was separated, washed well with water, dried, and evaporated. Distillation of the residue gave *ethyl* 2-*methylbuta*-1 : 3-*diene*-1-*carboxylate* (6 g.) with a slightly pungent smell, b. p. 74°/15 mm., n_D^{22} 1·4799 (Found : C, 68·55; H, 8·85. $C_8H_{12}O_2$ requires C, 68·55; H, 8·65%). Light absorption : Maximum 2510 A.; ε, 20,000.

The ester (3·3 g.) was dissolved in a solution of potassium hydroxide (10 g.) in methanol (100 c.c.) and set aside at 20° for 48 hours. Water (200 c.c.) was then added, the non-hydrolysable material extracted with ether, and the aqueous layer acidified with 10% (w/v) sulphuric acid. The liberated acid was isolated by means of ether, giving 2-*methylbuta*-1 : 3-*diene*-1-*carboxylic acid* (1·8 g.), b. p. 60°/0·05 mm., n_D^{22} 1·5186, which crystallised in needles when kept at 0° (Found : C, 63·95; H, 7·4. $C_6H_8O_2$ requires C, 64·15; H, 7·2%). Light absorption : Maximum, 2490 A.; ε, 20,500 (cf. light absorption in hexane of sorbic acid : Maximum 2610 A.; ε, 50,000; Hausser *et al.*, *Z. physikal. Chem.*, 1935, *B*, **29**, 371). The S-*benzylthiuronium* salt crystallised from aqueous alcohol (50%) in needles, m. p. 162° (Found : N, 10·15. $C_{14}H_{18}O_2N_2S$ requires N, 10·0%).

(*b*) A portion (*ca.* 10 c.c.) of a solution of methyl vinyl ketone (9 g.) and ethyl bromoacetate (20 g.) in dry thiophen-free benzene (50 c.c.) was added to activated zinc turnings (8·5 g.), mercuric chloride (*ca.* 0·1 g.), and benzene (100 c.c.), and the mixture was heated under reflux until reaction commenced. The remainder of the ketone–bromoacetate solution was then added dropwise during 30 minutes, and the mixture heated under reflux for a further hour during which most of the zinc dissolved. The liquid was cooled, decanted from unchanged zinc, and shaken with a solution of acetic acid (30 g.) in water (600 c.c.). The benzene layer was washed free from acid, dried, and evaporated. Distillation of the residue gave the crude hydroxy-ester (6·5 g.), b. p. 82°/15 mm., n_D^{23} 1·436.

The crude ester was heated under reflux with anhydrous oxalic acid (15 g.) at 95—100°/15 mm. for

2 hours. After cooling, the residue was extracted with light petroleum (b. p. 60—80°), and the extract washed, dried, and evaporated. Distillation gave the crude dehydrated ester (1·0 g.), b. p. 72—75°/15 mm., n_D^{25} 1·460. Light absorption : Maximum, 2510 A. ; $E^{1\%}_{1\,\text{cm.}}$, 710. The ester was hydrolysed and the acid (0·8 g.) isolated in the manner described above. It was converted into the *S*-benzylthiuronium salt which crystallised from aqueous alcohol (50%) in needles (0·7 g.), m. p., and mixed m. p. with a specimen from (*a*), 162°.

4-*Phenyl*-2-*methylbuta*-1 : 3-*diene*-1-*carboxylic Acid* (IX).—A solution of benzylideneacetone (2 g.) in ether (50 c.c.) was added during 15 minutes to a well stirred suspension of ethoxyacetylenylmagnesium bromide (prepared from 1·3 g. of magnesium and 4·5 g. of ethoxyacetylene) in ether (125 c.c.), and the mixture was stirred at 20° for 3 hours. The complex was decomposed by the addition of ammonium chloride (15 g.) in water (75 c.c.). The crude carbinol (2·6 g.), isolated by means of ether, was dissolved in methanol (10 c.c.) containing 1 drop of 10% (w/v) sulphuric acid, and the solution was kept for ½ hour, whereafter 10% (w/v) sulphuric acid (10 c.c.) was added and the product was extracted with ether. Evaporation of the ethereal solution gave a crude ester which was dissolved in a solution of potassium hydroxide (3 g.) in methanol (30 c.c.) and heated under reflux for 2 hours. After cooling, the solution was diluted with water, the non-hydrolysable portion was extracted with ether, and the acid, liberated from the aqueous solution by 10% (w/v) sulphuric acid, was isolated in the usual manner with ether. Crystallisation from light petroleum (b. p. 60—80°) gave 4-phenyl-2-methylbuta-1 : 3-diene-1-carboxylic acid (1·7 g.) as prisms, m. p. 122—124° (Kuhn and Hoffer, *Ber.*, 1932, **65**, 651, give m. p. 123·5—124·5°). Light absorption : Maxima, 2290 and 3090 A. ; ε, 13,500 and 28,000, respectively.

β-*Ionylideneacetaldehyde* and β-*Ionylideneacetic Acid*.—A solution of β-ionone (9·5 g.) (n_D^{18} 1·5200. Light absorption : Maxima 2230 and 2960 A. ; ε, 6,500 and 10,000) in ether (50 c.c.) was added dropwise to a well stirred suspension of ethoxyacetylenylmagnesium bromide (prepared from 1·8 g. of magnesium and 5·3 g. of ethoxyacetylene) in ether (50 c.c.), and the mixture was heated under reflux for 2½ hours and then cooled. A solution of ammonium chloride (50 g.) in water (150 c.c.) was added slowly and the product isolated in the usual manner. Distillation gave a pale yellow oil (7·5 g.), b. p. 80—100° (bath temp.)/10^{-6} mm., n_D^{15} 1·5143, exhibiting general absorption in the 2350—2490 A. region ($E^{1\%}_{1\,\text{cm.}}$, 300) ; Maximum, 2960 A. ; $E^{1\%}_{1\,\text{cm.}}$, 440 ; inflexion, 3080 A. ; $E^{1\%}_{1\,\text{cm.}}$, 410.

A portion of the crude carbinol (2·25 g.) in ethyl acetate (40 c.c.) was shaken in an atmosphere of hydrogen in the presence of palladium–calcium carbonate (0·5 g. ; 2% Pd) until 80 c.c. (20°/765 mm.) of gas had been absorbed. After removal of the catalyst and evaporation of the solvent, the residue was dissolved in ether (40 c.c.), and the ethereal solution was shaken with 10% (w/v) sulphuric acid for 5 minutes, washed with water, dried, and evaporated. The residue was divided into two equal parts. One was treated with a solution of 2 : 4-dinitrophenylhydrazine sulphate in methanol and gave β-*ionylideneacetaldehyde* 2 : 4-*dinitrophenylhydrazone* (0·4 g.) which crystallised from ethyl acetate in red needles, m. p. 198—200° (Found : N, 14·5. $C_{21}H_{26}O_4N_4$ requires 14·05%). Light absorption (in chloroform) : Maxima 2550, 3230, and 4100 A. ; ε, 20,500, 15,000, and 42,000, respectively. The second part was treated with a solution of semicarbazide acetate in alcohol and gave β-ionylideneacetaldehyde semicarbazone (0·2 g.) which crystallised from benzene in needles, m. p. 193—195° (Kuhn and Morris, *Ber.*, 1937, **70**, 853, and Arens and van Dorp, *Nature*, 1947, **160**, 189, give m. p. 193—195°). Light absorption : Maximum, 3170 A., ε, 38,000. Inflexion, 3250 A. ; ε, 36,000 (Arens and van Dorp, *loc. cit.*, give maximum 3230 A.).

A further portion of the crude carbinol (2 g.) was dissolved in methanol (8 c.c.), containing a few drops of 10% (w/v) sulphuric acid. After 15 minutes the product was isolated by means of ether, and distillation gave crude ethyl β-ionylideneacetate as a pale yellow oil (1·6 g.), b. p. 130—150° (bath temp.)/0·03 mm., $n_D^{15°}$ 1·5342. Light absorption: Maxima, 2230, 3000, and 3150 A. ; $E^{1\%}_{1\,\text{cm.}}$, 500, 550, and 450, respectively ; inflexion, 2650 A. ; $E^{1\%}_{1\,\text{cm.}}$, 400. The crude ester was dissolved in a solution of potassium hydroxide (2·5 g.) in methanol (20 c.c.), and the mixture was kept at 20° for 24 hours. After dilution with water (100 c.c.) and extraction of the non-hydrolysable portion with ether, the acid, liberated from the aqueous solution by dilute sulphuric acid, was isolated with ether. Trituration of the resulting oil (0·55 g.) with light petroleum (b. p. 40—60°) gave β-ionylideneacetic acid which crystallised from light petroleum (b. p. 60—80°) in needles (0·1 g.), m. p. 124° (Karrer, Salomon, Morf, and Walker, *Helv. Chim. Acta*, 1932, **15**, 878, give m. p. 125°). Light absorption : Maxima, 2600 and 2900—2980 A. ; ε, 16,500 and 17,500, respectively (Young, Andrews, and Cristol, *J. Amer. Chem. Soc.*, 1944, **66**, 520, give maxima, 2600 and 2940 A. ; ε, 12,900 and 13,700, respectively).

8-cyclo*Hex*-1′-*enyl*-2 : 6-*dimethylocta*-1 : 3 : 5-*trien*-7-*yne*-1-*carboxylic Acid* (XII).—A solution of 8-*cyclo*hex-1′-enyl-6-methylocta-3 : 5-dien-7-yn-2-one (7 g.) (Heilbron, Jones, and Richardson, this vol., p. 287) in ether (100 c.c.) was added over a period of 45 minutes to a well stirred suspension of ethoxyacetylenylmagnesium bromide (prepared from 3 g. of magnesium and 9·5 g. of ethoxyacetylene), and the mixture was heated under reflux for 1½ hours. After cooling to 0°, the complex was decomposed by the addition of ammonium chloride (50 g.) in water (200 c.c.), and the crude ethoxyacetylenic carbinol (8·6 g.) was isolated in the usual manner with ether. Light absorption : Maximum, 2900 A. ; $E^{1\%}_{1\,\text{cm.}}$, 510.

This carbinol was dissolved in methanol (50 c.c.), 10% (w/v) sulphuric acid (0·5 c.c) added, and the solution allowed to stand at 20° for 30 minutes. The crude hydroxy-ester, isolated, after dilution with water (100 c.c.), by ether, was heated with anhydrous oxalic acid (35 g.) at 95—100°/0·1 mm. for 3 hours. The residue was extracted with light petroleum (b. p. 60—80°), and the extract was washed with water, dried, and evaporated, giving a crude ester (6·5 g.). Light absorption : Maxima, 3410 and 3480 A. ; $E^{1\%}_{1\,\text{cm.}}$, 440.

The ester was dissolved in a solution of potassium hydroxide (20 g.) in methanol (200 c.c.) and kept at 20° for 48 hours. Water (500 c.c.) was then added, the non-hydrolysable material extracted with ether, and the aqueous layer acidified to pH 4 with phosphoric acid. The liberated acid was taken up in ether, and the solution was washed and dried. On concentrating the ethereal solution, 8-*cyclo*hex-1′-enyl-2 : 6-dimethylocta-1 : 3 : 5-trien-7-yne-1-carboxylic acid separated and was recrystallised from methanol giving yellow needles (0·15 g.), m. p. 179—180° (Heilbron, Jones, and Richardson, this vol., p. 287, give m. p. 179° for the " *A* form "). Light absorption : Maxima, 3380 and 2580 A. ; ε, 33,000 and 14,000, respectively (*idem, loc. cit.*, give maxima 3390, 2600, and 2570 A. ; ε, 27,500, 12,000, and 11,000, respectively).

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