16. *Researches on Acetylenic Compounds. Part IV. The Hydration of Some Acetylenylcarbinols Derived From αβ-Unsaturated Aldehydes.*

By I. M. Heilbron, E. R. H. Jones, Peter Smith, and B. C. L. Weedon.

Certain acetylenylcarbinols (*viz.*, vinylethynylcarbinol and propenylethynylcarbinol (X)) derived from αβ-unsaturated aldehydes give α-diketones on hydration with sulphuric acid and mercuric sulphate. On similar treatment, the anionotropic rearrangement product of propenylethynylcarbinol, *i.e.*, hex-3-en-5-yn-2-ol (XIII), is isomerised into 2 : 5-dimethylfuran, which can either be isolated as such or converted into acetonylacetone by varying the experimental conditions.

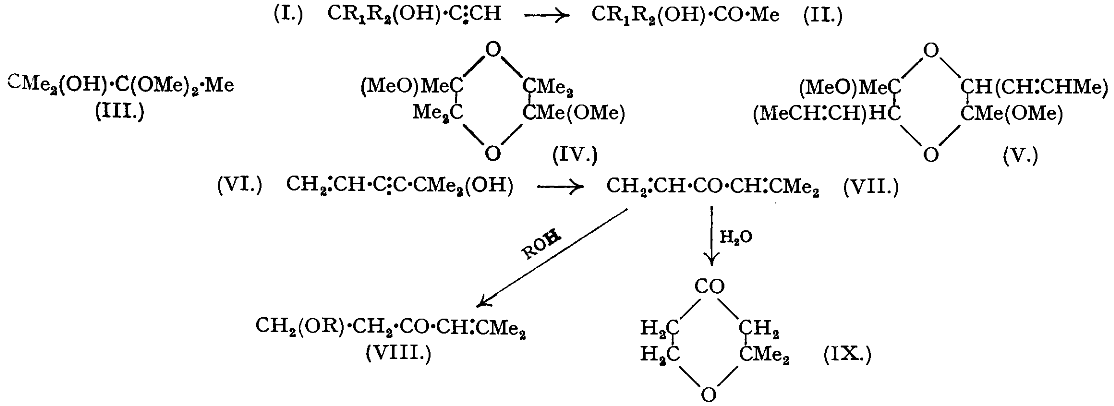
$$\mathrm{CH_2{:}CH{\cdot}CH(OH){\cdot}C{\vdots}CH \longrightarrow Me{\cdot}CH_2{\cdot}CO{\cdot}CO{\cdot}Me}$$

$$\text{(XIII.)}\quad \mathrm{Me{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}C{\vdots}CH \longrightarrow \text{dimethylfuran} \longrightarrow Me{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}Me}$$

The carbinol (XVII) derived from 2-ethylhexenal does not yield an α-diketone, but a furan (XIX) and also a 1 : 4-diketone (XX) are obtained on hydration of either the parent carbinol or its acid-rearrangement product (XVIII). In this case, the highly substituted furan does not appear to undergo hydrolysis to the diketone, and the latter must be formed independently of the furan during hydration. Poor yields of furan are obtained from the substituted carbinol, dec-3-en-5-yn-2-ol (XXII), but the use of the mercuric oxide–boron trifluoride catalyst gives a 30% yield of methylamylfuran.

The hydration of acetylenylcarbinols (I) to α-hydroxyketones (II) has received much attention, the most common method employing dilute sulphuric acid together with mercuric sulphate (Locquin and Sung, *Compt.*

rend., 1923, **176**, 516; *Rev. gen. sci.*, 1924, **35**, 170; Leers, *Bull. Soc. chim.*, 1926, **39**, 423; Colonge, *ibid.*, 1931, **49**, 441; Rupe and Kambli, *Annalen*, 1927, **459**, 216; Scheibler and Fischer, *Ber.*, 1922, **55**, 2903). Mercuric chloride (Hess and Munderloh, *Ber.*, 1918, **51**, 381) and mercury acetamide (Goldberg and Aeschbacher, *Helv. Chim. Acta*, 1939, **22**, 1185) have been employed for this purpose and mercuric acetate in acetic acid has also been used (Venus-Danilova and Danilov, *J. Gen. Chem. Russia*, 1932, **2**, 645; Ruzicka, Goldberg, and Hunziker, *Helv. Chim. Acta*, 1939, **22**, 707).


(I.) $CR_1R_2(OH){\cdot}C{\vdots}CH \longrightarrow CR_1R_2(OH){\cdot}CO{\cdot}Me$ (II.)

$CMe_2(OH){\cdot}C(OMe)_2{\cdot}Me$ (III.)

(IV.) (V.)

(VI.) $CH_2{:}CH{\cdot}C{\vdots}C{\cdot}CMe_2(OH) \longrightarrow CH_2{:}CH{\cdot}CO{\cdot}CH{:}CMe_2$ (VII.)

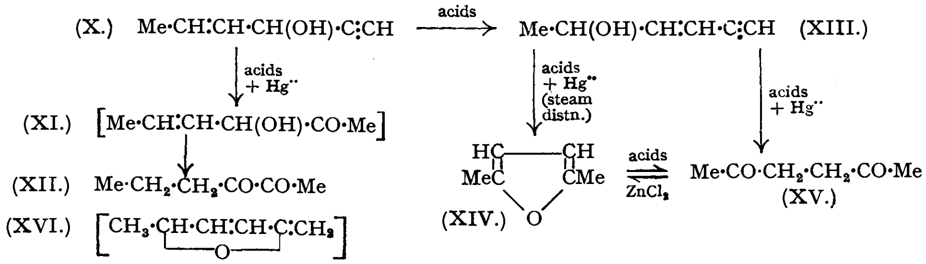
$CH_2(OR){\cdot}CH_2{\cdot}CO{\cdot}CH{:}CMe_2$ (VIII.)

(IX.)

Additions of alcohols and carboxylic acids to acetylenic linkages can be effected conveniently by using the mercuric oxide–boron trifluoride catalyst (Hennion, Nieuwland *et al.*, *J. Amer. Chem. Soc.*, 1934, **56**, 1130, 1384, 1786, 1802; 1935, **57**, 2006; 1936, **58**, 80, 892, 1658, etc. For summary, see Spring, *Ann. Reports*, 1942, **39**, 128), and this method has recently been applied to effect the addition of alcohols to simple ethynylcarbinols (Froning and Hennion, *J. Amer. Chem. Soc.*, 1940, **62**, 653; Nazarov and Elizarova, *Bull. Acad. Sci. U.R.S.S.*, 1940, 195). Treatment of dimethylethynylcarbinol (I; $R_1 = R_2 =$ Me) with methyl alcohol and the above catalyst gives mainly the hydroxyketal (III) together with some of the substituted dioxan (IV). Hennion and Lieb (*J. Amer. Chem. Soc.*, 1944, **66**, 1289) applied the same process to propenylethynylcarbinol (X), but only the dioxan derivative (V) was isolated, and that in comparatively small yield.

Nazarov and his co-workers (*Bull. Acad. Sci. U.R.S.S.*, 1940, 453, 545, 552; **1941**, 314, 423; **1943**, 50) have intensively investigated the reactions of vinylacetylenylcarbinols (*e.g.*, VI) in the presence of both mercuric salts and also the mercuric oxide–boron trifluoride catalyst. Under all conditions, the primary reaction involved appears to be isomerisation to the ketone (VII), which may then add alcohols or water to give either alkoxyketones (VIII) or tetrahydropyrone derivatives, such as (IX).

When either propenylethynylcarbinol (X) or vinylethynylcarbinol is treated with mercuric sulphate and dilute sulphuric acid, hydration of the acetylenic bond is apparently accompanied by a simultaneous prototropic rearrangement giving hexane-2 : 3-dione (XII) and pentane-2 : 3-dione (15 and 70% yields, respectively). Under the sole influence of acids, propenylethynylcarbinol has been shown to be isomerised readily to the conjugated vinylacetylenic alcohol (XIII) (Jones and McCombie, *J.*, 1943, 261) but, in the presence of mercuric salts, this isomerisation would, on account of the simultaneous hydration of the acetylenic bond, appear to be suppressed appreciably. The hypothetical intermediate (XI) would not be expected to undergo anionotropic rearrangement readily because of the strongly electron-attracting nature of the carbonyl group. The much slower isomerisation rate of vinylethynylcarbinol accounts for the appreciably higher yield of α-diketone in this case.


(X.) $Me{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}C{\vdots}CH \xrightarrow{\text{acids}} Me{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}C{\vdots}CH$ (XIII.)

(XI.) $[Me{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CO{\cdot}Me]$

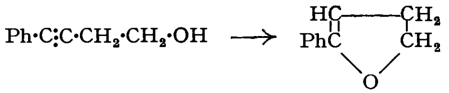
(XII.) $Me{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CO{\cdot}Me$

(XVI.)

(XIV.)

$Me{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}Me$ (XV.)

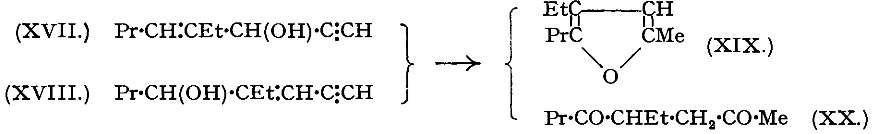
The hydration of the rearrangement product (XIII) of propenylethynylcarbinol proceeds in an entirely different manner. When a mixture of hex-3-en-5-yn-2-ol (XIII), mercuric sulphate and dilute sulphuric acid is heated and the product distilled with steam as it is formed, 2 : 5-dimethylfuran (XIV) can be isolated in 45% yield which is raised to 55% by a similar procedure employing aqueous alcoholic mercuric chloride. This process can be regarded either as a direct intramolecular hydration to (XVI) followed by isomerisation to the dimethylfuran, or as comprising normal hydration of the acetylenic linkage, followed by cyclodehydration to [XVI). The formation of 4 : 5-dihydrofurans as by-products in reactions between acetylenylmagnesium halides and ethylene oxide (Danehy, Vogt, and Nieuwland, *J. Amer. Chem. Soc.*, 1934, **56**, 2790) is in some respects analogous to the above reaction.



Dimethylfuran (25% yield) is also formed when the rearranged carbinol (XIII) is treated with the mercuric oxide–boron trifluoride catalyst in methanol. The poor yield of the dioxan derivative (V) obtained from propenylethynylcarbinol by the same method (Hennion and Lieb, *loc. cit.*) may be attributable to the formation of the furan, the separation of which from the methanol used is not easily effected by distillation, owing to the formation of an azeotrope.

If hex-3-en-5-yn-2-ol (XIII) be heated with mercuric sulphate and sulphuric acid without steam distillation, hydrolysis of the dimethylfuran occurs and acetonylacetone (XV) can be isolated in a yield of about 55%. In the absence of mercuric salts a poor yield of the diketone can be obtained. This conversion can be effected directly from propenylethynylcarbinol (X) by treatment with sulphuric acid followed by the addition of mercuric sulphate, an overall yield of 55% of acetonylacetone being obtained. In the preparation of hexane-2 : 3-dione from propenylethynylcarbinol, some dimethylfuran and appreciable quantities of acetonylacetone are produced simultaneously.

To exemplify further the furan and diketone formation referred to above, a study has been made of the hydration of the ethynylcarbinol (XVII) from 2-ethylhexenal (Jones and McCombie, *J.*, 1942, 733) and its rearrangement product (XVIII) (*idem, J.*, 1943, 261). With neither of these carbinols has it been possible to isolate any α-diketone from hydration experiments.



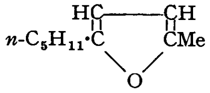
When either the un-rearranged or the rearranged carbinol (XVII or XVIII) is steam-distilled with 1% sulphuric acid, *5-methyl-3-ethyl-2-*n*-propylfuran* (XIX) (*maleic anhydride adduct*) is produced in 20—25% yield, the remainder of the product in each case consisting essentially of the isomerised carbinol (XVIII). No improvement in the yield of furan is obtained by carrying out the steam-distillation under partial reflux or in the presence of mercuric sulphate. Hydration of the unrearranged carbinol (XVII) at 100° with more concentrated acid (10%), in the presence of a comparatively large amount of mercuric sulphate, gives a similar yield of furan, but this is accompanied by 40% of the 1 : 4-diketone, *4-ethyloctane-2 : 5-dione* (XX) (*monosemicarbazone*).

Yields of up to 64% of the furan can be achieved by carrying out the hydration under reflux with 1% acid in aqueous alcohol containing mercuric sulphate, better yields resulting from the use of the rearranged carbinol (XVIII) than from its isomer. As would be expected, refluxing with a solution of mercuric chloride in aqueous alcohol leads to similar results. Some of the diketone (XX) is formed in all of these experiments but the yield never exceeds 25%.

Since hex-3-en-5-yn-2-ol, on hydration, gives 2 : 5-dimethylfuran and acetonylacetone it is clear that, unless the comparatively easily hydrolysable furan is removed from the reaction medium as formed, it is converted into the diketone. This does not apply apparently to the carbinols derived from 2-ethylhexenal. Appreciable yields of the furan are always produced under a wide variety of conditions and all attempts to hydrolyse the furan (XIX) to the diketone (XX) separately have been unsuccessful. The failures are probably related to its very low solubility in aqueous media. The two hydration products would thus appear to be produced by distinct reactions, the diketone formation proceeding most readily in strongly acidic media. There is some evidence that higher yields of the diketone are invariably obtained from the un-rearranged rather than the rearranged carbinol.

(XXI.) Me·CH:CH·CH(OH)·C⋮C·C_4H_9

(XXII.) Me·CH(OH)·CH:CH·C⋮C·C_4H_9



(XXIII.)

Further extension of the hydration experiments to the carbinols (XXI and XXII) derived from condensation of 1-hexyne with crotonaldehyde, followed by rearrangement to give (XXII), resulted in only very poor conversions into the furan. Under most of the conditions mentioned above, the carbinol (XXII) gave, at the most, a 10% yield of *2-methyl-5-*n*-amylfuran* (XXIII), the bulk of the starting material being recovered unchanged. Prolonged treatment of the rearranged carbinol (XXII) with the mercuric oxide–boron trifluoride catalyst did, however, give a 30% yield of the furan.

EXPERIMENTAL.

Hexane-2 : 3-dione (XII).—A mixture of propenylethynylcarbinol (10 g.; Heilbron, Jones, and Weedon, *J.*, 1945, 81), mercuric sulphate (5 g.) and sulphuric acid (100 c.c., 10% w/v) was distilled with steam in an atmosphere of nitrogen.

After saturation of the distillate with salt, isolation by means of ether gave hexane-2 : 3-dione (1·5 g.) as a yellow oil, b. p. 128—130° (Dufraisse and Moureu, *Bull. Soc. chim.*, 1927, **41** 1375, give b. p. 127·5—129°). The dioxime crystallised from aqueous alcohol in needles, m. p. 169—170° (Fileti and Ponzio, *Gazzetta*, 1895, **25**, 242, give m. p. 170—171°) (Found : N, 18·4. Calc. for $C_6H_{12}O_2N_2$: N, 18·4%). The *mono*-2 : 4-*dinitrophenylhydrazone* separated from either aqueous alcohol or ligroin (b. p. 100—120°) as pale yellow needles, m. p. 101—102° (Found : N, 19·5. $C_{12}H_{14}O_5N_4$ requires N, 19·05%). The *quinoxaline derivative* prepared from the diketone and *o*-phenylenediamine in ethereal solution, crystallised from aqueous methanol in buff-coloured prisms, m. p. 63—64° (Found : N, 14·75. $C_{12}H_{14}N_2$ requires N, 15·05%).

Pentane-2 : 3-*dione*.—A mixture of vinylethynylcarbinol (6·3 g.; Jones and McCombie, *J.*, 1942, 733) and mercuric sulphate (1 g.) in sulphuric acid (50 c.c., 10% w/v) was heated on the steam-bath for an hour after which it was distilled until the distillate was colourless. The distillate was saturated with salt giving pentane-2 : 3-dione (5·4 g.), b. p. 110—112°, $n_{\mathrm{D}}^{19^\circ}$ 1·4081 (Dufraisse and Moureu, *loc. cit.*, give b. p. 110—112° and Brühl, *J. pr. Chem.*, 1894, **50**, 140, gives $n_{\mathrm{D}}^{19^\circ}$ 1·40135). The dioxime formed needles, m. p. 172—173° from aqueous alcohol (Fileti and Ponzio, *loc. cit.*, give m. p. 172—173°) and the osazone was obtained from aqueous alcohol as pale yellow prisms, m. p. 165—166° (von Pechmann and Dahl, *Ber.*, 1890, **23**, 2426, give m. p. 166—167°). The *quinoxaline derivative*, prepared in boiling acetic acid, crystallised from aqueous methanol in yellow prismatic needles, m. p. 53—54° (Found : N, 16·45. $C_{11}H_{12}N_2$ requires N, 16·3%). The *bis*-2 : 4-*dinitrophenylhydrazone* separated from aqueous dioxan in small dark red prisms, m. p. 280—281° decomp. (Found : N, 24·6. $C_{17}H_{16}O_8N_8$ requires N, 24·35%).

2 : 5-*Dimethylfuran* (XIV).—(*a*) An authentic specimen, prepared in 46% yield from acetonylacetone (7 g.) and anhydrous zinc chloride (3 g.), by the method of Dietrich and Paal (*Ber.*, 1887, **20**, 1085) who obtained a 25% yield, had b. p. 93—94°, $n_{\mathrm{D}}^{19^\circ}$ 1·4424 (von Auwers, *Annalen*, 1915, **408**, 271, gives b. p. 93—94°, $n_{\mathrm{D}}^{21 \cdot 6^\circ}$ 1·43508; Nasini and Carrara, *Gazzetta*, 1894, **24**, 271, give $n_{\mathrm{D}}^{17 \cdot 7^\circ}$ 1·4427). In spite of repeated crystallisation from ether and sublimation at 50° (bath temp.)/10^{-4} mm., the maleic anhydride adduct had m. p. 73° (Diels and Alder, *Ber.*, 1929, **62**, 560, give m. p. 78°). Light absorption in alcohol : Max. 2195 A.; ε = 8000.

(*b*) Steam was passed slowly into a mixture of hex-3-en-5-yn-2-ol (10·4 g.; see below for improved method of preparation), mercuric sulphate (200 mg.) and sulphuric acid (40 c.c.; 0·5% w/v) until the distillate (total volume *ca.* 12 c.c.) no longer separated into two layers. The upper layer was removed, dried over calcium chloride and distilled (finally from sodium) giving 2 : 5-dimethylfuran (4·6 g.), b. p. 93·5—94°, $n_{\mathrm{D}}^{19^\circ}$ 1·4420, which had light absorption properties as described above.

(*c*) A solution of hex-3-en-5-yn-2-ol (20 g.) and mercuric chloride (1·5 g.) in water (60 c.c.) and alcohol (55 c.c.) was stirred and heated on the steam-bath in such a manner as to maintain a slow rate of distillation. A further quantity of mercuric chloride (1·5 g.) was added after 2 hours and the distillation continued until the distillate no longer separated into two layers on dilution with water. The distillate was poured into brine and the upper layer separated, washed with water and dried over calcium chloride. Distillation gave 2 : 5-dimethylfuran (11·4 g.), b. p. 94—96°, $n_{\mathrm{D}}^{23^\circ}$ 1·4417.

(*d*) The catalyst, prepared by heating together for a few minutes a mixture of mercuric oxide (2 g.), boron trifluoride–ether complex (0·8 c.c.) and methanol (0·8 c.c.) together with a few crystals of trichloroacetic acid (cf. *e.g.*, Hennion and Lieb, *loc. cit.*), was dissolved in methanol (80 c.c.) and a solution of hex-3-en-5-yn-2-ol (33 g.) in the same solvent (80 c.c.) was added during an hour at 50—55°. Stirring was continued for another hour at this temperature, powdered potassium carbonate (5 g.) was added and after 30 minutes, the solid material was allowed to settle. The decanted solution was carefully fractionated through an 18 inch column packed with glass helices and the fraction having b. p. 61—65° was freed from methanol by washing with water. Drying over calcium chloride followed by distillation from sodium gave 2 : 5-dimethylfuran (9 g.), b. p. 93—94°, $n_{\mathrm{D}}^{17^\circ}$ 1·4432. Some 12 g. of hex-3-en-5-yn-2-ol were recovered.

Acetonylacetone (XV).—(*a*) An authentic specimen prepared from diethyl diacetosuccinate according to Knorr (*Ber.*, 1900, **33**, 1219) had b. p. 190°/780 mm., 75°/13 mm., $n_{\mathrm{D}}^{17 \cdot 5^\circ}$ 1·4286, constants in reasonable agreement with the published values.

(*b*) A mixture of hex-3-en-5-yn-2-ol (10·7 g.), mercuric sulphate (0·2 g.) and sulphuric acid (40 c.c.; 2% w/v) was heated on the steam-bath with vigorous stirring in an atmosphere of nitrogen until it became homogeneous (4—5 hours). After saturation with salt the product was isolated with ether giving acetonylacetone (7·2 g.), b. p. 75—76°/14 mm., $n_{\mathrm{D}}^{15^\circ}$ 1·4292. The dioxime had m. p. 138°, undepressed on admixture with an authentic specimen (Lipp and Schiller, *Ber.*, 1909, **42**, 1967, give m. p. 137°).

(*c*) A mixture of propenylethynylcarbinol (10·2 g.) and dilute sulphuric acid (40 c.c., 2% w/v) was heated on the steam bath with vigorous stirring in an atmosphere of nitrogen for 30 minutes. After addition of mercuric sulphate (0·2 g.), heating and stirring were continued for a further 2—3 hours. Isolation as described above gave acetonylacetone (6·7 g.), b. p. 78—79°/16 mm., $n_{\mathrm{D}}^{15^\circ}$ 1·4289. The dioxime had m. p. 138°, undepressed on admixture with an authentic specimen.

Improved Preparation of Hex-3-*en*-5-*yn*-2-*ol* (XIII) (cf. Jones and McCombie, *J.*, 1943, 261).—A mixture of propenylethynylcarbinol (150 g.) and sulphuric acid (400 c.c., 1% w/v) was distilled with steam and the product was isolated by extraction of the distillate with ether after saturation with salt. This procedure yielded hex-3-en-5-yn-2-ol (120 g.), b. p. 79—81°/30 mm.,.$n_{\mathrm{D}}^{18 \cdot 5^\circ}$ 1·4842.

5-*Methyl*-3-*ethyl*-2-n-*propylfuran* (XIX).—When either 4-ethyloct-4-en-1-yn-3-ol (XVII) (Jones and McCombie, *J.*, 1942, 733) or 5-ethyloct-5-en-7-yn-4-ol (XVIII) (Jones and McCombie, *J.*, 1943, 261) was steam distilled in the presence of dilute sulphuric acid (1% w/v), in addition to (XVIII), a 20—25% yield of 5-*methyl*-3-*ethyl*-2-n-*propylfuran* was usually obtained. After distillation from sodium this had b. p. 64°/13 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4562 (Found : C, 79·1; H, 10·8. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). Light absorption in alcohol : Max. 2210 A.; ε = 9000. The *maleic anhydride adduct* was prepared by mixing equivalent quantities of the two reactants in ether at −10° and allowing to stand for several days at 0°. The solvent was removed under reduced pressure at −10° and the viscous product solidified after several days at 0° (cf. Butz, *J. Amer. Chem. Soc.*, 1935, **57**, 1314). Recrystallisation from a cooled mixture of ether and pentane gave small plates, m. p. 51·5—52·5° (Found : C, 67·1; H, 7·2. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·25%).

5-*Methyl*-3-*ethyl*-2-n-*propylfuran and* 4-*Ethyloctane*-2 : 5-*dione* (XX).—(*a*) A mixture of 4-ethyloct-4-en-1-yn-3-ol (10 g.), dilute sulphuric acid (100 c.c., 10% w/v) and mercuric sulphate (1·0 g.) was stirred vigorously on the steam bath for 5 hours. Isolation by means of ether gave the furan (2·9 g.), b. p. 68—70°/16 mm., $n_{\mathrm{D}}^{16^\circ}$ 1·4560, together with somewhat impure 4-ethyloctane-2 : 5-dione (4·7 g.), b. p. 110—112°/16 mm., $n_{\mathrm{D}}^{16^\circ}$ 1·4570. Repeated fractionation of a larger amount of the latter product gave pure 4-*ethyloctane*-2 : 5-*dione* as a very pale yellow oil, b. p. 110°/18 mm., $n_{\mathrm{D}}^{16^\circ}$ 1·4563 (Found : C, 70·3; H, 10·75. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·7%). Light absorption in alcohol : Maxima, 2280, 2750 and 2820 A.; ε = 3000, 320 and 340 respectively. With semicarbazide acetate in aqueous alcoholic solution the diketone formed a *monosemicarbazone*, m. p. 155·5°, after crystallisation from aqueous alcohol (Found : N, 18·3. $C_{11}H_{21}O_2N_3$ requires N, 18·5%). Light absorption in alcohol : Maximum 2280 A.; ε = 18,500.

(*b*) A mixture of 5-ethyloct-5-en-7-yn-4-ol (10 g.), alcohol (45 c.c.), dilute sulphuric acid (30 c.c., 1% w/v) and mercuric sulphate (0·2 g.) was refluxed for 5 hours. In some experiments (possibly due to variations in the order of mixing of the reagents) mercury was rapidly deposited and the addition of a further 0·2 g. of mercuric sulphate was necessary. Dilution with water and ether extraction gave the furan (6·4 g.), b. p. 68—70°/13 mm., $n_{\mathrm{D}}^{16^\circ}$ 1·4571, and the diketone (2·1 g.), b. p. 108—112°/13 mm., $n_{\mathrm{D}}^{16^\circ}$ 1·4570.

4-Ethyloct-4-en-1-yn-3-ol, similarly treated, gave the furan (5·0 g.), b. p. 68—72°/16 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4565, and the diketone (2·5 g.), b. p. 106—110°/16 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4590.

(*c*) A mixture of 5-ethyloct-5-en-7-yn-4-ol (10 g.), water (30 c.c.), alcohol (45 c.c.) and mercuric chloride (0·5 g.) was stirred on the steam-bath for 5—6 hours, during which time four portions, each of mercuric chloride (0·2 g.), were added. Dilution and ether extraction gave the furan (6·0 g.), b. p. 67—69°/13 mm., $n_{\mathrm{D}}^{14^\circ}$ 1·4580, and the diketone (1·0 g.), b. p. 103—106°/13 mm., $n_{\mathrm{D}}^{14^\circ}$ 1·4562.

Similarly 4-ethyloct-4-en-1-yn-3-ol gave the furan (4·7 g.), b. p. 68—72°/15 mm., $n_{\mathrm{D}}^{16^\circ}$ 1·4571, and diketone (2·7 g.), b. p. 108—110°/17 mm., $n_{\mathrm{D}}^{16^\circ}$ 1·4560.

2-*Methyl*-5-n-*amylfuran* (XXIII).—(*a*) When subjected to any of the treatments described above, dec-3-en-5-yn-2-ol (XXII) (Heilbron, Jones, and Raphael, *loc. cit.*) gave yields of the furan of the order of 10%, the carbinol being largely recovered unchanged. The pure 2-*methyl*-5-n-*amylfuran*, on distillation from sodium, had b. p. 88°/30 mm., $n_{\mathrm{D}}^{17^\circ}$ 1·4548 (Found : C, 79·0; H, 10·75. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). Light absorption in alcohol : Maximum, 2200 A.; ε = 8500. The maleic anhydride adduct dissociated too readily for it to be isolated in the pure state.

(*b*) Dec-3-en-5-yn-2-ol (30 g.) in methanol (80 c.c.) was added to the mercuric oxide–boron trifluoride–trichloroacetic acid catalyst (from 1 g. of mercuric oxide) in the usual manner. Stirring at 50—55° was continued for a further 3 hours after addition was complete (during which time two 1 g. portions of mercuric oxide and a further 0·4 c.c. of the boron trifluoride–ether complex were added) and finally at 20° for 15 hours. After pouring into water and extracting with ether, the residue was steam-distilled to separate the desired product from tarry material. Extraction of the distillate with ether yielded 2-methyl-5-*n*-amylfuran (10 g.), b. p. 64—68°/10 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4548, together with unchanged starting material (7·5 g.).

The authors thank the Rockefeller Foundation and I.C.I. Ltd., Dyestuffs Division, for financial assistance. They also thank Dr. J. T. McCombie for assistance in the early stages of the above work. Light absorption data were measured by Dr. E. A. Braude.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W. 7.

[*Received, September 27th,* 1945.]