629. *Derivatives of Acetoacetic Acid. Part X.* The Condensation of Acetylenic Alcohols with α-Acyl Derivatives of Ethyl Acetoacetate and Diethyl Malonate.*

By R. N. LACEY.

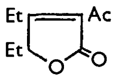
Ethyl diacetylacetate condenses with tertiary ethynylcarbinols to give 3-acetyl-2,5-dihydrofuran-2-one derivatives (III) (reaction B). But-3-yn-2-ol behaves similarly but affords a poor yield; propargyl alcohol simply gives the trans-esterification product. Ethyl diacetylacetate and ethyl α-propionylacetoacetate condense with 2-phenylbut-3-yn-2-ol to give dienediones (II; R^4 = COR) (reaction A).

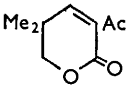
Diethyl acetylmalonate and 1-ethynylcyclohexanol give a dihydrofuranone-ester (IX) and 2-acetyl-5,6,7,8-tetrahydro-1-naphthol (reaction C). The propionyl and butyryl derivatives of malonic ester give the corresponding 2-acyl derivatives of 5,6,7,8-tetrahydro-1-naphthol. Diethyl acylmalonates condense with 2-methylbut-3-yn-2-ol and 3-methylpent-1-yn-3-ol to give 2,5-dihydrofuran-2-ones; but with 2-phenylbut-3-yn-2-ol the acylmalonates give 2-acyl-5-phenylphenol derivatives by reaction C.

THE action of heat on the acetoacetates of tertiary ethynylcarbinols $CH{:}C{\cdot}CRR'{\cdot}OH$, which gives conjugated dienones, was described in Part III of this series [1] and elsewhere.[2,3] In an important modification of this reaction, Naves [4] has shown that similar products are afforded by the pyrolysis of a mixture of ethyl acetoacetate and the ethynylcarbinol. In the present paper the reactions are studied between acetylenic alcohols and derivatives of acetoacetic ester such as ethyl diacetylacetate and various diethyl acylmalonates in the expectation that products such as (II; R^4 = COR or CO_2Et) might be formed.

$$\underset{\text{(I)}}{R^1CH_2{\cdot}CR^2(OH){\cdot}C{:}CH} + EtO_2C{\cdot}CHR^4{\cdot}COR^3 \longrightarrow \underset{\text{(II)}}{R^1CH_2{\cdot}CR^2{:}CH{\cdot}CH{:}CR^4{\cdot}COR^3} \qquad \textit{(Reaction A)}$$

When ethyl diacetylacetate and 1-ethynylcyclohexanol were heated together with continuous removal of low-boiling products, the temperature rapidly rose and predominantly ethanol and ethyl acetate distilled; carbon dioxide was evolved but in amount only 50% of that expected from the above equation. Isolation gave a crystalline, unsaturated acetyl-γ-lactone (III; $R^1R^2 = [CH_2]_4{>}$) in 37·5% yield. Spectroscopic comparison with the known lactone (IV) and with the δ-lactone (V) {representative of an alternative possible structure (VI; $R^1R^2 = [CH_2]_4{>}$)}, and, finally, independent synthesis from 1-acetylcyclohexyl acetoacetate by the method described in Part I [5] confirmed this structure (cf. Table 1).


(IV)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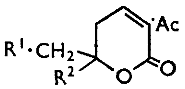
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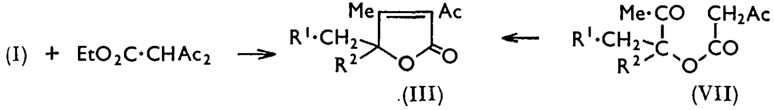

(Reaction B)

Carrying out the condensation in a high-boiling alcohol did not give higher yields. This suggested that the ethyl acetate evolved did not arise from the interaction of an

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* Part IX, *J.*, 1958, 2134.

[1] Lacey, *J.*, 1954, 827.

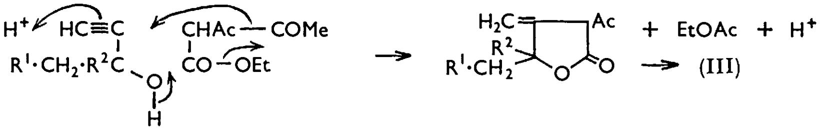
[2] Kimel and Sax, U.S.P. 2,661,368; Kimel, Surmatis, Weber, Chase, Sax, and Ofner, *J. Org. Chem.*, 1957, **22**, 1611.

[3] Preobrazhenski, Somokhvalov, and Miropol'skaya, *Doklady Akad. Nauk S.S.S.R.*, 1956, **107**, 103.

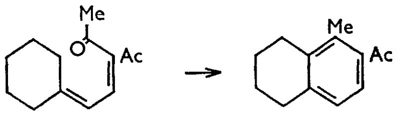
[4] Naves, *Compt. rend.*, 1955, **240**, 1437.

[5] Lacey, *J.*, 1954, 816.

intermediate with ethanol formed by transesterification but was formed as the result of an intermolecular reaction, tentatively formulated as shown.



An oily by-product, which could not be purified, had an infrared spectrum characteristic of a substituted acetophenone. It is considered to have structure (VIII), having arisen by cyclisation of an intermediate (II; $R^1R^2 = [CH_2]_4{>}$, R^3 = Me, R^4 = Ac) formed by reaction A. Oxidation of this ketone (VIII) by sodium hypobromite gave an acid whose spectral properties were consistent with those of 5,6,7,8-tetrahydro-1-methyl-2-naphthoic acid.



(VIII)

The reaction of ethyl diacetylacetate with 2-methylbut-3-yn-2-ol (I; R^1 = H, R^2 = Me) and with 3-methylpent-1-yn-3-ol (I; $R^1 = R^2$ = Me) proceeded similarly, giving lactones of the type (III), the structures of which were confirmed by comparison with specimens prepared by the cyclisation of the acetoacetates (VII), but no acetophenone derivative was found. The formation of much high-boiling material may probably be ascribed to polymerisation of dienediones formed by reaction A; evolution of carbon dioxide and formation of ethanol are consistent with a substantial fraction of the total reaction being of this type.

There seemed to be no reason to expect that formation of 3-acyldihydrofuranones (III) would be confined to reactions involving tertiary ethynylcarbinols. But-3-yn-2-ol, on being heated with ethyl diacetylacetate, gave a small yield of a lactone (III; $R^1 = R^2$ = H), identified by conversion on treatment with acetic–hydrochloric acid into 2,4,5-trimethylfuran-3-carboxylic acid;[6] propargyl alcohol, however, gave only propargyl diacetylacetate under these conditions. It is suggested that greater success in the formation of lactones (III) is achieved with tertiary carbinols than with secondary or primary alcohols (which undergo alcoholysis), because of the smaller tendency of tertiary alcohols to undergo alcoholysis.

The reaction of ethyl diacetylacetate with 2-phenylbut-3-yn-2-ol (I; R^1 = H, R^2 = Ph) failed to follow path B but gave the crystalline dienedione (II; R^1 = H, R^2 = Ph, R^3 = Me, R^4 = Ac) in 25—30% yield, together with ethanol and carbon dioxide in good yield, according to reaction A. The analogous reaction with ethyl α-propionylacetoacetate proceeded similarly, and one of the possible stereoisomers of compound (II; R^1 = H, R^2 = Ph, R^3 = Et, R^4 = Ac) was obtained crystalline in small yield. Spectroscopic comparison with 3-acetyl-6-phenylhexa-3,5-dien-2-one confirmed the structures assigned (see Table 3).

Diethyl acetylmalonate and the alcohol (I; R^1 = H, R^2 = Me) at 100—200° gave ethyl acetate, ethanol, carbon dioxide, and the α-ethoxycarbonyl-γ-lactone (IX; R^1 = H, R^2 = Me), identified by comparison with a specimen prepared from diethyl malonate and 3-hydroxy-3-methylbutan-2-one (XI; R^1 = H, R^2 = Me) (cf. ref. 7) and by mild alkaline hydrolysis to a crystalline acid (X; R^1 = H, R^2 = Me). The formation of compounds of type (IX) is analogous (reaction B′) to the formation of 3-acetyl derivatives in the corresponding reactions of ethyl diacetylacetate. Similar reactions of the alcohol (I; R^1 = H, R^2 = Me) with the propionyl and benzoyl derivatives of malonic ester both

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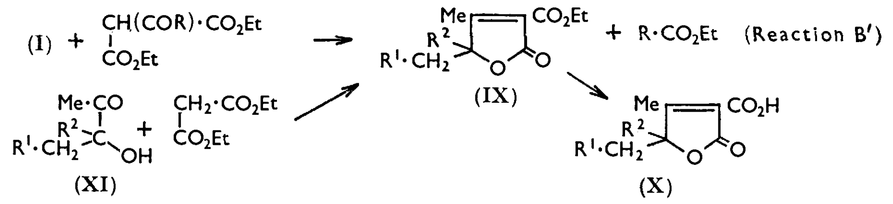
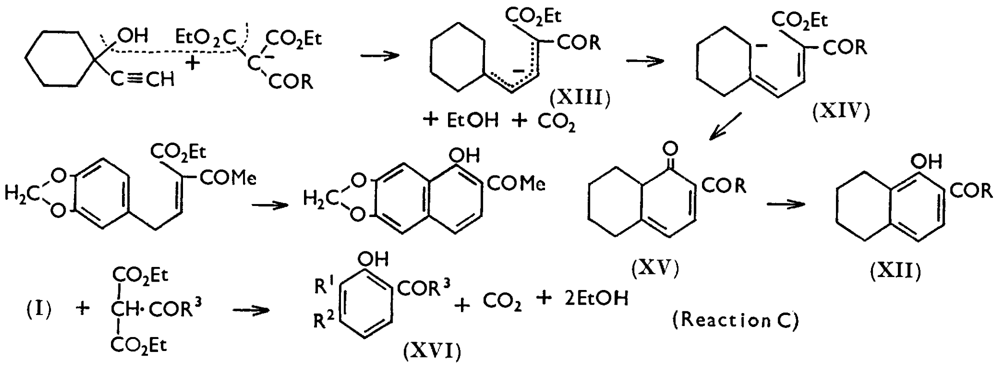
[6] Lacey, *J.*, 1954, 822.

[7] Cologne and Dreux, *Compt. rend.*, 1956, **243**, 498.

gave the same lactone (IX; $R^1 = H$, $R^2 = Me$) with elimination of ethyl propionate and ethyl benzoate respectively; the 4-methyl group in the product must therefore originate from the ethynyl group in the alcohol (I; $R^1 = H$, $R^2 = Me$) and not from the acyl group of the substituted malonic ester, as could be supposed in the case involving diethyl acetylmalonate.



The alcohol (I; $R^1 = R^2 = Me$) with both the acetyl and the benzoyl derivative of malonic ester gave the lactone (IX; $R^1 = R^2 = Me$) which, however, was not obtained pure. The reactions of 1-ethynylcyclohexanol with α-acylmalonic esters were strikingly anomalous. The action of heat on a mixture of the alcohol (I; $R^1R^2 = [CH_2]_4>$) and diethyl acetylmalonate (1·25 mols.) gave carbon dioxide, a low-boiling distillate (70% ethanol, 30% ethyl acetate), and about 30% of a crystalline ketone with ultraviolet and infrared spectra (see Table 2) typical of an *o*-hydroxyacetophenone. Comparison with an authentic specimen showed that the solid product was 2-acetyl-5,6,7,8-tetrahydro-1-naphthol (XII; R = Me) (reaction C). The crude distilled product, before purification by crystallisation, showed infrared bands at 1767 and 1712 cm.$^{-1}$ which, coupled with the observed formation of ethyl acetate, showed that some δ-lactone (IX; $R^1R^2 = [CH_2]_4>$) (cf. Table 1) had also been formed (reaction B). In a second condensation, in which a 30% excess of the alcohol (I; $R^1R^2 = [CH_2]_4>$) was used, the lactone (IX) was the main product; it was obtained crystalline and gave a crystalline acid on hydrolysis. A sample was also prepared by condensing 1-acetylcyclohexanol with diethyl malonate. Diethyl butyrylmalonate and diethyl propionylmalonate condensed with the alcohol (I; $R^1R^2 = [CH_2]_4>$) according to path C, to give 2-butyryl and 2-propionyl derivatives (XII; R = Pr^n and R = Et) respectively; authentic specimens were prepared by Fries rearrangement of the appropriate 1-acyloxy-5,6,7,8-tetrahydronaphthalenes.



A suggested mechanism for these reactions is presented in formulæ. The first step involves the linkage of the ethynyl group to the anion derived from the acylmalonic ester in the way proposed[4] for the condensation of tertiary ethynylcarbinols and ethyl acetoacetate, with the elimination of carbon dioxide and ethanol to give the mesomeric anion (XIII). This could readily rearrange to (XIV), stabilised by conjugation through the diene system with the acyl group. Interaction of the ethoxycarbonyl group and the carbon atom bearing the negative charge would be sterically favoured and is analogous in

TABLE 1. *Spectra of lactones.*

Compound	Ultraviolet $\lambda_{max.}$ (Å)	Ultraviolet ε	Infrared (cm.$^{-1}$) lactone ring C:O (str.)	Infrared (cm.$^{-1}$) side-chain C:O (str.)	Infrared (cm.$^{-1}$) C:C (str.)	Infrared (cm.$^{-1}$) C–O–C
(IV)	2300	12,000	1770	1695	1630	~1050
	2250 (end abs.)	7,000[a]				
	3170	5,500				
(V)	2300	11,800	1736	1700	1618	—
(III; $R^1R^2 = [CH_2]_4>$)	2350	11,500	1770	1695	1635	~1030
	2530	12,500[a]				
	3070	11,500				
(III; $R^1 = H, R^2 = Me$)	2300	10,000	1770	1695	1635	~1030
	2525	11,000[a]				
	3065	12,000				
(III; $R^1 = R^2 = Me$)	2325	10,800	1760	1698	1630	1026
	2560	13,000[a]				
	3080	11,500				
(IX; $R^1 = H, R^2 = Me$)	2185	13,000	1776	1715	1656	~1050
(IX; $R^1 = R^2 = Me$)	—	—	1773	1713	1655	~1050
(IX; $R^1R^2 = [CH_2]_4>$)	2250	12,500	1770	1712	1658	1057

In 0·1N-sodium hydroxide in 9 : 1 ethanol–water.

TABLE 2. *Spectra of 2-acylphenols.*

	Ultraviolet $\lambda_{max.}$ (Å)	Ultraviolet ε	Infrared (cm.$^{-1}$) C:O (str.)	Infrared (cm.$^{-1}$) arom. bands	Infrared (cm.$^{-1}$) subst. arom. bands	Infrared (cm.$^{-1}$) OH
(XII; R = Me)	2220	25,500	1633	1585	1880	~800
	2680	15,000		1500		~2900
	3340	4,500				
(XII; R = Et)	2220	23,500	1633	1585	1880	~800
	2680	15,000		1500		~2900
	3300	4,600				
(XII; R = Pr^n)	2220	26,500	1633	1585	1880	~800
	2710	15,000		1500		~2900
	3340	4,500				
(XVI; $R^1 = H, R^2 = Ph, R^3 = Me$)	2860	23,000	1646	1626	813[a]	~790
	3340	7,000		1565	760[b]	~2900
				1497	693	
(XVI; $R^1 = H, R^2 = Ph, R^3 = Et$)	2860	22,500	1646	1626	802[a]	~785
	3330	7,500		1562	760[b]	~2900
				1493	694	

[a] 1,2,4-Substitution. [b] Monosubstituted benzene ring.

TABLE 3. *Spectra of dienones.*

	Ultraviolet $\lambda_{max.}$ (Å)	Ultraviolet ε	Infrared (cm.$^{-1}$) C:O (str.)	Infrared (cm.$^{-1}$) C:C	Infrared (cm.$^{-1}$) unsat. ester
(II; $R^1 = H, R^2 = Ph, R^3 = Me, R^4 = Ac$)	3300	30,500	1695	1610[a]	—
	2380	7,500	1664		
(II; $R^1 = H, R^2 = Ph, R^3 = Et, R^4 = Ac$)	3275	25,000	1695	1610[a]	—
	2390	8,400	1664		
Ph·CH:CH·CH:CAc$_2$	3320	34,000	1690	1613	—
	2380	10,000	1664		
(II; $R^1 = H, R^2 = Ph, R^3 = Et, R^4 = CO_2Et$)	3200	22,000	1715	1613[a]	1234
	2350	9,000	1690[b]		1280
			1780[c]		
Ph·CH:CH·CH:CAc·CO$_2$Et	3290	28,500	1715	1606	1230
	2355	8,600	1689		1285
Ph·CH:CH·CH:CH·CO$_2$Et	3090	36,500	1709	1630	1235
	2395	7,900		1000[d]	1265
	2325	10,000			
	2270[b]	9,000			

[a] In addition, these compounds showed typical "aromatic" and "monosubstituted aromatic" bands at 1583, 1497, 760, and 695 cm.$^{-1}$. [b] Shoulder. [c] Impurity, possibly (IX; $R^1 = H, R^2 = Ph$). [d] Typical of *trans-trans*-diene acids and esters.

mechanism to that for Claisen-type condensations; rearrangement of the diketone (XV) to (XII) completes the chain of reactions. An interesting, similar cyclisation of ethyl α-piperonylideneacetoacetate in pyridine–piperidine at 100°, due to Howell and Taylor,[8] is also illustrated above, as is the generalised reaction to give *o*-acylphenols.

The condensation of 2-phenylbut-3-yn-2-ol and diethyl acetylmalonate at 150—200° followed path C with elimination of ethanol and carbon dioxide, to give 2-acetyl-5-phenylphenol (XVI; $R^1 = H$, $R^2 = Ph$, $R^3 = Me$) in 27% yield. Similarly, the alcohol (I; $R^1 = H$, $R^2 = Ph$) and diethyl propionylmalonate gave a 10% yield of crystalline ketone (XVI; $R^1 = H$, $R^2 = Ph$, $R^3 = Et$), with a liquid by-product. Spectroscopic examination of the latter (see Table 3) and comparison with ethyl α-cinnamylideneacetoacetate suggested the structure (II; $R^1 = H$, $R^2 = Ph$, $R^3 = Et$, $R^4 = CO_2Et$) arising from reaction A. A small infrared C:O band at 1780 cm.$^{-1}$ suggested that the by-product also contained small amounts of the lactone ester (IX; $R^1 = H$, $R^2 = Ph$) formed by reaction B′. Diethyl butyrylmalonate and the alcohol (I; $R^1 = H$, $R^2 = Ph$) gave no solid product, but infrared spectra showed the presence of an unsaturated keto-ester, presumably (II; $R^1 = H$, $R^2 = Ph$, $R^3 = Pr^n$, $R^4 = CO_2Et$), and minor amounts of the lactone ester (IX; $R^1 = H$, $R^2 = Ph$) and acylphenol (XVI; $R^1 = H$, $R^2 = Ph$, $R^3 = Pr^n$), formed by reactions A, B′, and C respectively.

EXPERIMENTAL

M. p.s are corrected. Infrared and ultraviolet spectroscopic data refer to CCl_4 and EtOH solutions respectively.

Reactions of Ethynylcarbinols with Ethyl Diacetylacetate.—(a) *With* 1-*ethynylcyclohexanol.* Ethyl diacetylacetate (137·5 g., 0·8 mole) and 1-ethynylcyclohexanol (74·5 g., 0·6 mole) were heated together beneath a short distillation column fitted with a distillation head. During 3 hours' heating, the temperature rose from 140° to 190°; material of b. p. <80° (29 g.; ethanol, 42%; ethyl acetate 51%; acetone 5%) was removed at the head of the column during the reaction, and gas (7·5 l.), predominantly carbon dioxide, was evolved. Distillation gave a mixture of starting materials (29 g.) and an oil (75·1 g.), b. p. 130—150°/2 mm., which partially crystallised. The solid (47·0 g., 37·5%) was isolated by rubbing the whole with light petroleum (b. p. 60—80°), from which it crystallised to give 4-*acetyl*-2,5-*dihydro*-3-*methyl*-5-*oxofuran*-2-*spirocyclohexane* (III; $R^1R^2 = [CH_2]_4>$) as prisms, m. p. 101° (Found: C, 68·9; H, 7·7. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·75%). This gave a 2,4-*dinitrophenylhydrazone* as orange needles, m. p. 206° (decomp.), from ethyl acetate (Found: C, 55·35; H, 5·4; N, 14·7. $C_{18}H_{20}O_6N_4$ requires C, 55·65; H, 5·2; N, 14·45%).

The mother-liquor was washed several times with warm 10% sodium hydroxide solution and distilled, to give an oil supposed to be mainly 6-*acetyl*-1,2,3,4-*tetrahydro*-5-*methylnaphthalene* (VIII), b. p. 110—114°/0·6 mm., n_D^{20} 1·5500. Spectroscopic examination showed the product to contain about 5% of the spiran (III); bands attributed to the ketone (VIII) were 1687 (C:O str.), 1595 (aromatic ring in conjugation with carbonyl group), 806 (δ-CH aromatic), and 1895 cm.$^{-1}$ (1,2,3,4-aromatic substitution). The oil (1·0 g.) was stirred with aqueous potassium hypobromite (from 3 g. of bromine and 4 g. of potassium hydroxide in 20 ml. of water) at room temperature for 3 hr. The excess of reagent was destroyed with sodium sulphite solution; the whole was filtered and acidified to give a precipitate (0·6 g.) which on crystallisation from aqueous ethanol gave 5,6,7,8-*tetrahydro*-1-*methyl*-2-*naphthoic acid* as plates, m. p. 167° (Found: C, 75·55; H, 7·9. $C_{12}H_{14}O_2$ requires C, 75·75; H, 7·4%), $\lambda_{max.}$ 2395 (ε 10,600), 2825 Å (ε 1350) [cf. 5,6,7,8-tetrahydro-2-naphthoic acid,[9] $\lambda_{max.}$ 2420 (ε 12,000), 2780 (ε 1200), 2880 Å (ε 1000)].

The spiran (III) was also prepared (cf. ref. 5) by adding diketen (29 g.) to a boiling solution of 1-acetylcyclohexanol (47 g.) in toluene (100 ml.) containing triethylamine (2 ml.) during 0·5 hr.; water was eliminated by means of a trap. After 1 hour's refluxing, the solvent was evaporated and the residue crystallised from light petroleum (b. p. 60—80°), to give the spiran (49 g., 71%), m. p. and mixed m. p. 101°.

(b) *With* 2-*methylbut*-3-*yn*-2-*ol*. Ethyl diacetylacetate (60 g., 0·35 mole) and 2-methylbut-3-yn-2-ol (42 g., 0·5 mole) were condensed as described above. The temperature rose from 135°

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[8] Howell and Taylor, *J.*, 1956, 4252.

[9] Dauben, Hiskey, and Markhart, *J. Amer. Chem. Soc.*, 1951, **73**, 1395.

to 180° during 4 hr.; distillate (14·5 g.; ethanol, 50%; ethyl acetate, 40%) was collected and carbon dioxide (3·3 l.) was evolved. The product was distilled to give an oil (26·2 g.), b. p. 130—135°/13 mm., which solidified. Crystallisation from light petroleum (b. p. 60—80°) gave 3-acetyl-2,5-dihydro-4,5,5-trimethylfuran-2-one (III; $R^1 = H$, $R^2 = Me$) as needles, m. p. 50·5° (lit.,[7] m. p. 50°).

(c) *With 3-methylpent-1-yn-3-ol.* Ethyl diacetylacetate (50 g., 0·27 mole) and 3-methylpent-1-yn-3-ol (29·5 g., 0·3 mole) were condensed as above. The temperature rose to 230° during 2·5 hr., distillate (13·5 g.), b. p. 70—75°, was removed, and carbon dioxide (2·0 l.) was evolved. Distillation gave *3-acetyl-5-ethyl-2,5-dihydro-4,5-dimethylfuran-2-one* (8·1 g.) (III; $R^1 = R^2 =$ Me), b. p. 135—140°/13 mm., n_D^{20} 1·4859 (Found: C, 65·9; H, 7·85. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·75%), which gave a *semicarbazone*, needles, m. p. 215—216° (from ethanol) (Found: C, 55·35; H, 7·0; N, 17·65. $C_{11}H_{17}O_3N_3$ requires C, 55·2; H, 7·2; N, 17·55%).

The lactone (21·5 g.) was also prepared from 3-hydroxy-3-methylpentan-2-one (23·2 g.) and diketen (17·5 g.) by the general method,[5] then having b. p. 147—149°/17 mm., n_D^{20} 1·4823 (semicarbazone, m. p. and mixed m. p. 215°).

(d) *With but-3-yn-2-ol.* Ethyl diacetylacetate (50 g.) and but-3-yn-2-ol (21 g.) were condensed as above. The temperature rose to 230° during 2·5 hr.; distillate (10·5 g.), b. p. 70—75°, was collected; carbon dioxide (2·0 l.) was evolved. Distillation of the residue gave 3-acetyl-2,5-dihydro-4,5-dimethylfuran-2-one (6·4 g.) (III; $R^1 = R^2 = H$), b. p. 136—142°/15 mm., n_D^{20} 1·4868 (lit.,[5] b. p. 134—138°/12 mm., n_D^{20} 1·4915). After the lactone (1·0 g.) had been heated in acetic acid (10 ml.) and concentrated hydrochloric acid (5 ml.) [6] at 100° for 1 hr., addition of water and crystallisation of the precipitate from aqueous methanol gave 2,4,5-trimethylfuran-3-carboxylic acid, m. p. and mixed m. p. 131° (lit.,[10] 131—132°).

(e) *With propargyl alcohol.* Ethyl diacetylacetate (50 g.) and propargyl alcohol (19 g.) were heated together. In 5 hr. ethanol (13 ml.) distilled and the temperature rose to 180°. Distillation of the product gave *propargyl diacetylacetate* (8 g.), b. p. 119—124°/15 mm., which crystallised as plates, m. p. 39° [from light petroleum (b. p. 40—60°)] (Found: C, 59·35; H, 5·55. $C_9H_{10}O_4$ requires C, 59·15; H, 5·5%), $\lambda_{max.}$ 2760 Å (ε 9700), end absorption 2100 Å (ε 8500), $\nu_{max.}$ 3260 (CH str. in ⋮CH), 2120 (C≡C str.), 1718 (C=O str.), and 1540 cm.$^{-1}$ (broad " enol " band).

(f) *With 2-phenylbut-3-yn-2-ol.* Ethyl diacetylacetate (39 g., 0·22 mole) and 2-phenylbut-3-yn-2-ol (29·2 g., 0·2 mole) were condensed as above. The temperature was allowed to rise to 170° during 3 hr. Material (8 g.; b. p. 75—78°; consisting of ethanol 89%, ethyl acetate 7%, and acetone 4%) distilled, and carbon dioxide (5·2 l.) was evolved. The residue was distilled to give an oil (18·2 g.), b. p. 140—160°/0·8 mm., which, on crystallisation from light petroleum (b. p. 40—60°), gave *3-acetyl-6-phenylhepta-3,5-dien-2-one* (II; $R^1 = H$, $R^2 = Ph$, $R^3 = Me$, $R^4 = Ac$) (11·0 g.) as pale yellow needles, m. p. 73·5° (Found: C, 81·1, 79·85; H, 7·45, 7·45. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·05%). The product formed a *semicarbazone*, needles, m. p. 206·5° (from ethanol) (Found: C, 66·9; H, 6·75; N, 14·65. $C_{16}H_{19}O_2N_3$ requires C, 67·35; H, 6·7; N, 14·8%), a dark red *2,4-dinitrophenylhydrazone*, powder, m. p. 207° [from toluene–light petroleum (b. p. 60—80°)] (Found: C, 61·35; H, 4·85; N, 14·2. $C_{21}H_{20}O_5N_4$ requires C, 61·75; H, 4·95; N, 13·75%), and a pink colour with aqueous ferric chloride.

2-Phenylbut-3-yn-2-ol (29·2 g.) and ethyl α-propionylacetoacetate (41 g.) were heated at 160—200° for 2 hr. as above. Distillate (8·0 g.) and carbon dioxide (4·0 l.) were obtained. Isolation gave *4-acetyl-7-phenylocta-4,6-dien-3-one* (3·7 g.), b. p. 164—171°/1 mm., which crystallised from light petroleum as needles, m. p. 82—83° (Found: C, 79·2; H, 7·65. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·5%).

Reactions of Ethynylcarbinols with Acylmalonic Esters.—(a) *With 2-methylbut-3-yn-2-ol.* (i) Diethyl acetylmalonate (50·5 g., 0·25 mole) and 2-methylbut-3-yn-2-ol (21 g.) were caused to react as above. The temperature rose from 112° to 223° during 2 hr.; carbon dioxide (2·0 l.) was evolved; distillate, b. p. 70—78° (11 g., ethanol, 40%; ethyl acetate, 50%), was collected. The residue was distilled, to give ethyl 2,5-dihydro-4,5,5-trimethyl-2-oxofuran-3-carboxylate (IX; $R^1 = H$, $R^2 = Me$) (10·2 g.), b. p. 170—175°/15 mm., n_D^{20} 1·4862, which crystallised. Recrystallisation from light petroleum (b. p. 40—60°) gave the ester as needles, m. p. and mixed m. p. 34° (lit.,[7] m. p. 36°, b. p. 168°/16 mm.).

Hydrolysis of the ester (IX; $R^1 = H$, $R^2 = Me$) (0·5 g.) by shaking it at 50° with 10% aqueous sodium hydroxide (10 ml.) for 0·5 hr., acidification with hydrochloric acid, and isolation with ether gave *2,5-dihydro-4,5,5-trimethyl-2-oxofuran-3-carboxylic acid* (0·4 g.) (X; $R^1 = H$,

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[10] Reichstein, Zschokhe, and Syz, *Helv. Chim. Acta*, 1932, **15**, 1112.

R^2 = Me), needles, m. p. 115·5—116·5° [from benzene–light petroleum (b. p. 60—80°)] (Found: C, 56·8; H, 6·05%; equiv., 168. $C_8H_{10}O_4$ requires C, 56·45; H, 5·9%; equiv., 170), end absorption, 2100 Å (ε 12,000).

(ii) Diethyl propionylmalonate (21·6 g.) and 2-methylbut-3-yn-2-ol (8·5 g.) were refluxed together for 4 hr.; the temperature rose from 126 to 230°; no distillate was removed; there was only a small evolution of gas. Distillation of the residue gave the ester (IX; R^1 = H, R^2 = Me) (8·8 g.), b. p. 126—132°/1·5 mm., which solidified. Crystallisation of a portion from light petroleum (b. p. 40—60°) gave the pure product as needles, m. p. and mixed m. p. 33—34°.

(iii) Diethyl benzoylmalonate (26·4 g.) and 2-methylbut-3-yn-2-ol (9·0 g.) were heated together under reflux. The temperature rose from 128° to 202° during 12 hr.; there was substantially no gas evolution. The residue was distilled, to give ethyl benzoate (infrared analysis indicated *ca.* 75% purity) (7·0 g.), b. p. 88°/12 mm., and the ester (IX; R^1 = H, R^2 = Me) (9·4 g.), b. p. 167—170°/12 mm., m. p. and mixed m. p. 33—34°.

(b) *With 3-methylpent-1-yn-3-ol.* (i) Diethyl acetylmalonate (50 g.) and 3-methylpent-1-yn-3-ol (25 g.) were heated together for 4 hr., during which the temperature rose to 235°, 3 l. of gas were evolved, and a mixture (12 g.), b. p. 70—78°, of ethanol and ethyl acetate was removed. Distillation of the residue gave an oil (19·3 g.), b. p. 122—130°/1·0 mm., n_D^{20} 1·4828.

(ii) Diethyl benzoylmalonate (79 g.) and 3-methylpent-1-yn-3-ol (30 g.) were heated under reflux for 20 hr.; the final temperature was 200°. Distillation gave ethanol (3·4 g.), ethyl benzoate (32 g.), and an oil (12·6 g.), b. p. 135—140°/1·5 mm., n_D^{20} 1·4970.

Infrared examination of the products and comparison with the spectrum of the lactone (IX; R^1 = H, R^2 = Me) indicated that the products from the two experiments above consisted of ethyl 5-ethyl-2,5-dihydro-4,5-dimethyl-2-oxofuran-3-carboxylate (IX; R^1 = R^2 = Me) and were approximately 90% pure; no satisfactory analyses were obtained.

(c) *With 1-ethynylcyclohexanol.* (i) Diethyl acetylmalonate (124·5 g., 0·62 mole) and 1-ethynylcyclohexanol (62·0 g., 0·5 mole) were heated together for 5 hr. The temperature rose from 155° to 180°, carbon dioxide (9·0 l.) was evolved; distillate, b. p. 73—75° (23·6 g.; ethanol 70%, ethyl acetate 30%), was removed. Distillation of the residue gave an oil (29·5 g.), b. p. 131—141°/2 mm., which solidified. Recrystallisation from aqueous methanol gave 2-acetyl-5,6,7,8-tetrahydro-1-naphthol (XII; R = Me), m. p. and mixed m. p. 47—48° (lit.,[11] m. p. 46·5—47°) (Found: C, 75·25; H, 7·35. Calc. for $C_{12}H_{14}O_2$: C, 75·75; H, 7·4%). An oxime gave needles, m. p. 154·5—155°, from light petroleum (b. p. 60—80°) (lit.,[11] m. p. 154·5—156°). A red 2,4-*dinitrophenylhydrazone* had m. p. 247—248° (from butan-1-ol) (Found: C, 58·8; H, 5·05; N, 15·1. $C_{18}H_{18}O_5N_4$ requires C, 58·4; H, 4·9; N, 15·1%).

In a second experiment diethyl acetylmalonate (25 g.) was heated with 1-ethynylcyclohexanol (20 g., 30% excess). The final temperature was 265°, gas (2·45 l.) was evolved, and distillate (10 g.; 70% of ethyl acetate) was collected. Distillation gave an oil (5·0 g.), b. p. 152—163°/0·8 mm., which solidified. Crystallisation from light petroleum (b. p. 60—80°) gave 4-*ethoxycarbonyl*-2,5-*dihydro*-3-*methyl*-5-*oxofuran*-2-*spirocyclohexane* (IX; R^1R^2 = $[CH_2]_4>$) as plates, m. p. 65·5—66·5° (Found: C, 65·8; H, 7·83. $C_{13}H_{18}O_4$ requires C, 65·5; H, 7·6%).

Diethyl malonate (32 g.) and 1-acetylcyclohexanol (28·4 g.) were heated at 220° for 4 hr.; ethanol (18 g.) distilled. Distillation of the residue followed by crystallisation as above gave the spiran (5·0 g.), m. p. and mixed m. p. 66°.

This spiran (0·5 g.) was heated at 60° for 15 min. with ethanol (5 ml.) and 10% aqueous sodium hydroxide (5 ml.). It afforded the *spiran acid*, plates, m. p. 146°, from benzene–light petroleum (b. p. 60—80°) (Found: C, 63·35; H, 7·05. $C_{11}H_{14}O_4$ requires C, 62·85; H, 6·7%).

(ii) Diethyl propionylmalonate (54 g.) and 1-ethynylcyclohexanol (31 g.) were heated together as above for 2 hr. The final temperature was 233°; 10·2 l. of carbon dioxide were evolved; distillate, principally ethanol (16·2 g.), b. p. 75—78°, was collected. Distillation of the residue gave several fractions, b. p. 130—180°/1·5 mm. (35·6 g.), which solidified. Recrystallisation from aqueous methanol gave 2-propionyl-5,6,7,8-tetrahydro-1-naphthol (21·8 g.) as needles, m. p. and mixed m. p. 88—89° (lit.,[11] m. p. 87·5—88·5°).

(iii) Diethyl butyrylmalonate (23 g.) and 1-ethynylcyclohexanol (13·6 g.) were heated together as above for 1·25 hr.; 2·75 l. of carbon dioxide were evolved; the final temperature was 230°; distillate (5 g.), principally ethanol, b. p. 75—78°, was collected. Distillation of the residue gave 2-butyryl-5,6,7,8-tetrahydro-1-naphthol (9·0 g.), b. p. 125—141°/0·9 mm., which crystallised from methanol as needles, m. p. and mixed m. p. 41·5—42° (lit.,[11] m. p. 43·5—44°).

[11] Sergievskaya and Morozovskaya, *J. Gen. Chem.* (*U.S.S.R.*), 1944, **14**, 1107.

(d) *With* 2-*phenylbut*-3-*yn*-2-*ol*.—(i) Diethyl acetylmalonate (44·5 g.) and 2-phenylbut-3-yn-2-ol (29 g.) were heated together for 3 hr.; a temperature of 200° was reached; distillate (11 g.), mostly ethanol, was collected; carbon dioxide (5·15 l.) was evolved. Distillation of the residue gave an oil (15·7 g.), b. p. 156—167°/1·5 mm., which crystallised. Recrystallisation from light petroleum (b. p. 40—60°) gave 4-acetyl-3-hydroxybiphenyl (XVI; R^1 = H, R^2 = Ph, R^3 = Me) (12 g.) as plates, m. p. and mixed m. p. 91—92° (Found: C, 79·8; H, 5·8. Calc. for $C_{14}H_{12}O_2$: C, 80·0; H, 5·75%) (lit.,[12] m. p. 90·5—91·5°). The phenol gave a pink colour with aqueous ferric chloride, a sparingly soluble sodium salt with aqueous sodium hydroxide solution, and a 2,4-*dinitrophenylhydrazone*, which crystallised as needles, m. p. 260°, from benzene (Found: C, 61·25; H, 4·3; N, 13·85. $C_{20}H_{16}O_5N_4$ requires C, 61·2; H, 4·1; N, 14·3%).

(ii) Diethyl propionylmalonate (47·5 g.) and 2-phenylbut-3-yn-2-ol (29 g.) were heated together for 1·5 hr.; the final temperature was 230°. Carbon dioxide (5·0 l.) was evolved; distillate (10 g.; ethanol 80%, ethyl propionate 10—12%,) was collected. Distillation of the residue gave an oil (20·5 g.), b. p. 154—170°/0·8 mm., which on being rubbed with light petroleum (b. p. 40—60°) gave a pale yellow solid (4·8 g.), m. p. 108—109°, and a mother-liquor (see below). Recrystallisation from ethanol gave 3-hydroxy-4-propionylbiphenyl (XVI; R^1 = H, R^2 = Ph, R^3 = Et) as plates, m. p. 113—113·5° (lit.,[12] m. p. 109—110·5°) (Found: C, 79·7; H, 6·35. Calc. for $C_{15}H_{14}O_2$: C, 79·6; H, 6·25%).

The mother-liquors were distilled to give an oil (13 g.), b. p. 162—164°/1 mm., n_D^{20} 1·5910, presumed to be substantially *ethyl* 5-*phenyl*-2-*propionylhexa*-2,4-*dienoate* (II; R^1 = H, R^2 = Ph, R^3 = Et, R^4 = CO_2Et) (Found: C, 75·0; H, 7·45. $C_{17}H_{20}O_3$ requires C, 74·95; H, 7·4%) (light absorption, see Table 3).

(iii) Diethyl butyrylmalonate (50·5 g.) and 2-phenylbut-3-yn-2-ol (29 g.) were heated together at 150—230° for 1·25 hr.; 4·25 l. of carbon dioxide were evolved and distillate (6·1 g., mainly ethanol) was collected. Distillation gave an oil (22·7 g.), b. p. 156—170°/0·9 mm., n_D^{20} 1·5904, shown by infrared examination to contain 35—45% of phenol (XVI; R^1 = H, R^2 = Ph, R^3 = Pr^n), 55—45% of keto-ester (II; R^1 = H, R^2 = Ph, R^3 = Pr^n, R^4 = CO_2Et), and about 10% of furanone (III; R^1 = H, R^2 = Ph).

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[12] Bradsher, Brown, and Porter, *J. Amer. Chem. Soc.*, 1954, **76**, 2359.