Derivatives of Acetoacetic Acid. Part III. The Pyrolysis of Acetoacetates of Ethynylcarbinols.*†

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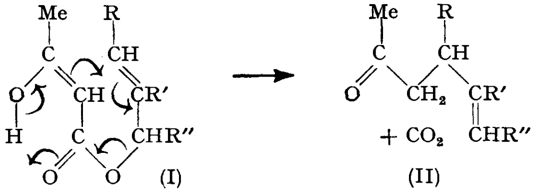
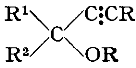
The acetoacetates of 3-methylbut-3-yn-2-ol, 3-methylpent-3-yn-2-ol, and 1-ethynyl*cyclo*hexanol were decarboxylated when heated in the presence of acids at 180—200°, giving 6-methylhepta-3 : 5-dien-2-one, 6-methylocta-3 : 5-dien-2-one, and 5-*cyclo*hexylidenepent-3-en-2-one, respectively. 1-Ethyl-1-methylhept-2-ynyl acetoacetate, an ester bearing a substituent in place of the ethynyl hydrogen atom, by contrast underwent the normal decarboxylation at 90—100° giving acetone and a vinylacetylene. 1 : 1-Dimethylprop-2-ynyl α-acetylbutyrate gave a low yield of dienone.

Until a few years ago, the only adequately described pyrolysis reaction of acetoacetic esters was the well-known formation of dehydroacetic acid and the parent alcohol (Arndt *et al.*, *Ber.*, 1924, **57**, 1489; 1936, **69**, 2377), a reaction which is observed when any acetoacetic ester is heated to about 150° or above, even when other reactions predominate. More recently, Kimel and Cope (*J. Amer. Chem. Soc.*, 1943, **65**, 1992), reinvestigating earlier observations by Caroll (*J.*, 1940, 704, 1266; 1941, 507), showed that allyl acetoacetate and its homologues (I) undergo decarboxylation when heated to about 200°, giving allylacetone and homologues (II). The nature of the products obtained from substituted allyl acetoacetates led the American authors to postulate a cyclic transition complex, the reaction being a further instance of the " allyl rearrangement " extensively studied by Cope and his collaborators. The pyrolysis of the acetoacetates of ethynylcarbinols (IV) forms the subject of the present paper, since it was considered possible that reactions analogous to those described for the esters of vinylcarbinols might take place, although it was realised that the resemblance might be only a formal one.



(I) (II)



(III; R = H)
(IV; R = CO·CH$_2$Ac)

There are no previous references to the preparation of acetoacetates of ethynyl carbinols, but it was shown that the general use of diketen in the presence of a catalytic quantity of triethylamine made these esters very readily available. Prop-2-ynyl acetoacetate (IV; $R^1 = R^2 = R^3 = H$) was stable at 200° for short periods. In the presence of toluene-*p*-sulphonic acid at 180—190° there was only a very slow evolution of carbon dioxide and acetylene; and, even after being heated overnight, 40% of the ester was recovered and 45% converted into dehydroacetic acid. Similar results were obtained on heating 1-methylprop-2-ynyl acetoacetate (IV; $R^1 = Me$, $R^2 = R^3 = H$), although in the presence of toluene-*p*-sulphonic acid, a moderately fast evolution of gas was observed. However, distillation afforded only acetone, but-3-yn-2-ol, and dehydroacetic acid, with no significant quantity of material boiling in the range expected for a C_7 ketone.

1 : 1-Dimethylprop-2-ynyl acetoacetate (IV; $R^1 = R^2 = Me$, $R^3 = H$) was also stable at 200° for short periods, but, in the presence of a trace of toluene-*p*-sulphonic acid, there was a brisk evolution of gas, containing 87—93% of carbon dioxide plus some acetylene. Distillation gave dehydroacetic acid, 2-methylbut-3-yn-2-ol, and a 54% yield of 6-methylhepta-3 : 5-dien-2-one, which exhibited a strong absorption maximum in the ultra-violet at 2890 Å, characteristic of the C:C·C:C·C:O chromophore with three alkyl substituents, was hydrogenated to the known 6-methylheptan-2-one, and had physical properties similar to those reported by Kuhn and Hoffer (*Ber.*, 1932, **65**, *B*, 651).

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* Part II, preceding paper.

† Patent pending: B.P. Appln. 9355/1952.

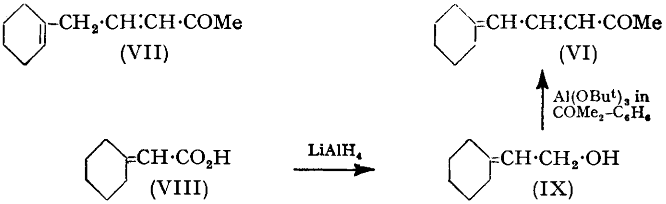
In the above reaction toluene-*p*-sulphonic acid can be replaced by sulphuric acid, phosphoric acid, or ferric chloride, and the pyrolysis can be carried out in the vapour phase at 320—340° by passing the ester through pumice granules impregnated with phosphoric acid.

1-Ethynyl-1-methylpropyl acetoacetate (IV; $R^1 = Me$, $R^2 = Et$, $R^3 = H$) was decarboxylated rapidly at 170—190° in the presence of toluene-*p*-sulphonic acid, giving a


(V)

50% yield of 6-methylocta-3 : 5-dien-2-one; this ketone exhibited a characteristic strong absorption band in the ultra-violet ($\lambda_{max.}$ 2880 Å), and when hydrogenated over Raney nickel previously washed with methanol containing 2% of acetic acid (cf. Weizmann, B.P. 574,446/1946) gave 6-methyloctan-2-one.

The acid-catalysed pyrolysis of 1-ethynyl*cyclo*hexyl acetoacetate at 180—200° afforded a 22·5% yield of 1-ethynyl*cyclo*hexanol and a 36% yield of a mixture of C_{11} ketones, boiling over a narrow range. Fractionation of this mixture gave material of widely varying refractive index, and examination of the ultra-violet absorption spectrum indicated that the product probably consisted of a mixture of the expected conjugated dienone (VI) and its isomer with an *endo*cyclic double bond (VII). Birch, Kon, and Norris (*J.*, 1923, 1361) showed that in the analogous case of *cyclo*hexenyl- and *cyclo*hexylidene-acetone, the two isomers were very rapidly converted into an equilibrium mixture in the presence of alkali and were obtained pure only by regeneration from pure crystalline derivatives. Solid derivatives of (VI) were obtained, and hydrolysis of the semi-carbazone by Kon's method (*J.*, 1930, 1616) gave pure 5-*cyclo*hexylidenepent-3-en-2-one, showing a single absorption maximum at 2900 Å.



An unambiguous synthesis of (VI) is outlined above. *cyclo*Hexylideneacetic acid (VIII) (cf. Schmid and Karrer, *Helv. Chim. Acta*, 1948, **31**, 1067) was reduced with lithium aluminium hydride to 2-*cyclo*hexylidene-ethanol (IX), previously prepared by the isomerisation of 1-vinyl*cyclo*hexanol (Dimroth, *Ber.*, 1938, **71**, *B*, 1333). (IX) was oxidised with aluminium *tert.*-butoxide in acetone–benzene and the product condensed with acetone to give (VI). Satisfactory analyses were not obtained for (VI) whether synthesised as above or as regenerated from the pure semicarbazone. Carbon and hydrogen figures were invariably low with all the compounds encountered of this type, probably owing to rapid auto-oxidation. Kuhn and Hoffer (*loc. cit.*) found that (V) rapidly resinified in air.

It was now of interest to examine whether the production of dienones by pyrolysis of *tert.*-ethynylcarbinols could be extended to esters in which the ethynyl hydrogen was replaced by alkyl. 1-Ethyl-1-methylhept-2-ynyl acetoacetate was prepared from diketen and the alcohol (III; $R^1 = Me$, $R^2 = Et$, $R^3 = Bu^n$) and, since on distillation at 1 mm. the product showed signs of decomposition, the crude ester was pyrolysed in the presence of toluene-*p*-sulphonic acid, without isolation. Gas evolution (95% carbon dioxide) was rapid at much lower temperatures (90—100°) than those employed in previous pyrolyses; distillation of the products afforded a 94% yield of acetone and a 64% yield of the substituted vinylacetylene, previously obtained by Thompson, Burr, and Shaw (*J. Amer. Chem. Soc.*, 1941, **63**, 186) by the vapour-phase dehydration of (III; $R^1 = Me$, $R^2 = Et$, $R^3 = Bu^n$).

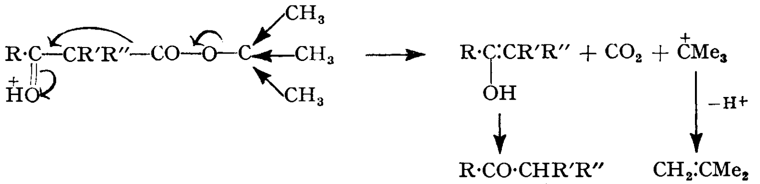
$$Et{\cdot}CMe(O{\cdot}CO{\cdot}CH_2Ac){\cdot}C⋮CBu^n \longrightarrow Me{\cdot}CH{:}CMe{\cdot}C⋮CBu^n + CO_2 + Me_2CO$$

Both the reaction conditions and the products are analogous to those met in the acid-catalysed pyrolysis of *tert.*-butyl esters of β-keto-acids (X) at 80—100° which gives *iso*butene, carbon dioxide, and a ketone (Yost and Hauser, *J. Amer. Chem. Soc.*, 1947, **69**, 2327; Renfrow and Walker, *ibid.*, 1948, **70**, 3957; Breslow, Baumgarten, and Hauser, *ibid.*, 1944, **66**, 1286; Fonken and Johnson, *ibid.*, 1952, **74**, 831; Libermann and Hengl, *Bull. Soc. chim.*, 1951, **18**, 974).

$$\mathrm{R{\cdot}CO{\cdot}CR'R''{\cdot}CO_2Bu^t} \xrightarrow{H^+} \mathrm{R{\cdot}CO{\cdot}CHR'R''} + \mathrm{CO_2} + \mathrm{CH_2{:}CMe_2}$$

(X) R = alkyl or aryl; R′ and R″ = H, alkyl, aryl, or CO_2R

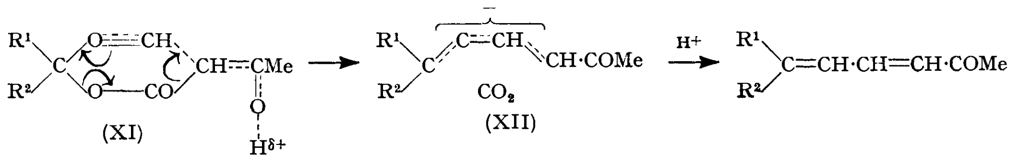
This reaction is confined to esters of *tert.*-alcohols and it must be supposed that the mechanism involves the addition of proton to the carbonyl oxygen, followed by electron migration towards this centre, the alkyl–oxygen ester linkage being loosened by the inductive effect of the three alkyl substituents.



That the acetoacetates of *tert.*-ethynylcarbinols possessing a free ethynyl hydrogen did not undergo this low-temperature decarboxylation must be attributed to the well-known electron-attracting influence of the ethynyl group, which would effectively prevent the postulated alkyl–oxygen fission. The retarding effect of the ethynyl group in three-carbon anionotropy as a result of its cationoid property has been well demonstrated by E. R. H. Jones, E. A. Braude, and their co-workers (cf. Braude, *Quart. Reviews*, 1950, **4**, 410). Substitution of the ethynyl hydrogen by alkyl would greatly reduce the electron-attracting influence of the group as a whole by virtue of the inductive effect of the substituent, thus enabling the normal low-temperature decarboxylation of an acetoacetate of a *tert.*-alcohol to take place.

When the α-ethyl derivative of 1 : 1-dimethylprop-2-ynyl acetoacetate was heated at 200—220° with toluene-*p*-sulphonic acid decarboxylation occurred only slowly and, even after 3 hr., only 0·74 mol. of carbon dioxide had been evolved. Distillation gave a product whose ultra-violet absorption spectrum indicated the expected dienone (estimated at about 25% yield), but it was contaminated with unchanged ester. Hydrogenation of the crude product gave 3-ethyl-6-methylheptan-2-one the structure of which was proved by independent synthesis.

It is suggested that the mechanism of the decarboxylation of *tert.*-alkynyl acetoacetates to give dienones involves first the acid-catalysed enolisation of the ester, followed by the ionisation of the enolic hydrogen and the formation of a partial bond between the ethynyl group and the α-carbon atom of the acetoacetic acid residue. The sharing of the electrons made available by the ionisation will reduce the electron-attracting properties of the ethynyl group, thus permitting the influences that caused the normal type of decarboxylation of *tert.*-alkyl acetoacetates to come into effect. Further, sharing of the electrons comprising the triple bond will permit the formation of a cyclic transition complex (XI),



(XI) (XII)

thus further facilitating the formation of the anion (XII) which, on addition of proton, gives the dienone. The slow and incomplete reaction of the ester bearing an α-alkyl substituent would result from the lower enolisation tendency of such substituted esters.

Attention is drawn to the similarity between this reaction and the condensation of ethynylcarbinols with phenols (blocked in the *para*-position) to give chromens (Späth and co-workers, *Ber.*, 1939, **72**, 963, 2093; 1941, **74**, 193; Karrer, Legler, and Schwab, *Helv. Chim. Acta*, 1940, **23**, 1132). In both cases the reactions are acid catalysed, are confined to *tert.*-ethynyl derivatives, and involve the linkage of an ethynyl group to the carbon atom α- to an enolic (or phenolic) hydroxyl.

EXPERIMENTAL

M. p.s were determined on a Kofler block and are corrected. Light-absorption determinations were carried out in ethanol.

Preparation of Acetoacetates.—The acetoacetates were prepared by the dropwise addition of diketen (97—98%) to the agitated carbinol containing catalytic quantities of triethylamine. The results are tabulated below.

		Et_3N,	Yield,				Found, %		Reqd., %	
No.	Temp.	%	%	B. p./mm.	n_D^{20}	Formula	C	H	C	H
1	60—70°	0·13	83·5	97—100°/11	1·4551	$C_7H_8O_3$	60·15	5·85	60·0	5·75
2 [1]	60—70	0·17	82	95—98/12	1·4441	—	—	—	—	—
3 [2]	70	0·2	98·5	96—99/12	1·4462	$C_9H_{12}O_3$	64·35	7·3	64·25	7·2
4	70	0·2	83·5	110—116/14	1·4518	$C_{10}H_{14}O_3$	65·75	7·9	65·9	7·75
5	60—70	0·35	87	108/1	1·4796	$C_{12}H_{16}O_3$	69·5	7·95	69·2	7·75
6	70	0·15	—	—	—	—	—	—	—	—

1. III; $R^1 = R^2 = R^3 = H$. 2. III; $R^1 = Me$, $R^2 = R^3 = H$. 3. III; $R^1 = R^2 = Me$, $R^3 = H$. 4. III; $R^1 = Me$, $R^2 = Et$, $R^3 = H$. 5. III; $R^1R^2 = [CH_2]_5>$, $R^3 = H$. 6. III; $R^1 = Me$, $R^2 = Et$, $R^3 = Bu^n$.

[1] Previously described in Part I of this series.

[2] Subsequently solidified, plates, m. p. 49—49·5°, from light petroleum (b. p. 60—80°).

Pyrolysis of 1 : 1-*Dimethylprop*-2-*ynyl Acetoacetate.*—The ester (IV; $R^1 = R^2 = Me$, $R^3 = H$) (17 g.) and toluene-*p*-sulphonic acid (0·05 g.) were heated, by means of an oil bath at 170—180°, in a small flask fitted with a short air condenser. A rapid evolution of gas was observed, and, after 2·5 hr., 2·10 l. (at 18° and 758 mm.) of carbon dioxide (93% purity by analysis) were collected. Distillation of the liquid products, after the addition of anhydrous sodium acetate (0·1 g.), gave the following fractions: (*a*) (III; $R^1 = R^2 = Me$, $R^3 = H$), b. p. 100—110°/758 mm., 1·1 g., n_D^{20} 1·4210, (*b*) b. p. 85—90°/12 mm., 6·0 g., n_D^{20} 1·5184, and (*c*) b. p. 90—94°/12 mm., 0·7 g., n_D^{20} 1·5018. The yield of material, b. p. 85—94°/12 mm., was 54% (as $C_8H_{12}O$); redistillation gave 6-methylhepta-3 : 5-dien-2-one (V), b. p. 87—89°/12 mm., n_D^{20} 1·5265 (Kuhn and Hoffer, *loc. cit.*, give b. p. 86—90°/15 mm., n_D^{19} 1·5292) (Found: C, 76·9; H, 9·65. Calc. for $C_8H_{12}O$: C, 77·3; H, 9·75%). The oxime formed needles, m. p. 114—115°, from ethanol (Found: C, 68·75; H, 9·4. Calc. for $C_8H_{13}ON$: C, 69·0; H, 9·4%) [Kuhn and Hoffer, *loc. cit.*, give m. p. 108—109° (corr.)]. Light absorption of (V): max., 2890 Å; ε, 29,500.

The ketone (V) (6·2 g.) in methanol (20 c.c.) was agitated in hydrogen in the presence of Raney nickel (0·5 g. paste; washed with methanol containing 2% acetic acid) at 16°. 2·26 l. at 16°/760 mm. (theory, 2·37 l.) of gas were absorbed in 3 hr. Distillation gave 6-methylheptan-2-one, b. p. 164·5°, n_D^{20} 1·4162 (Hey and Morris, *J.*, 1948, 48, give b. p. 164—164·5°, n_D^{20} 1·4144). The m. p.s of the 2 : 4-dinitrophenylhydrazone, m. p. 74—75° (lit. m. p. 77°), and the semicarbazone, m. p. 152—153° (lit. m. p. 154—155°), were undepressed in admixtures with authentic specimens.

Replacement of toluene-*p*-sulphonic acid with (*a*) sulphuric acid (0·035 g.), gave a 46% yield (b. p. 87—95°/11 mm., n_D^{20} 1·4995) and 2·3 l. of gas (91% CO_2) in 3 hr., (*b*) phosphoric acid (0·05 g., 90%), gave a 55% yield (b. p. 83—85°/11 mm., n_D^{20} 1·5199) and 2·1 l. of gas (90% CO_2) in 3 hr., and (*c*) anhydrous ferric chloride (0·05 g.), gave a 12% yield (b. p. 86—90°/12 mm., n_D^{20} 1·5150) and 1·6 l. of gas (93% CO_2) in 4 hr.

Pyrolysis of 1 : 1-*Dimethylbut*-2-*ynyl Acetoacetate.*—The ester (IV; $R^1 = Me$, $R^2 = Et$, $R^3 = H$) (18·2 g.) and toluene-*p*-sulphonic acid (0·05 g.) were heated at 180—190°; 2·19 l. (at 18°/761 mm.) of carbon dioxide (96% pure) were collected in 70 min. Distillation of the product (12·75 g.), after addition of sodium acetate (0·1 g.), gave 2-methylpent-3-yn-2-ol (0·95 g.), b. p. 38—42°/14 mm., n_D^{20} 1·4400, and a main fraction (6·88 g., 50% yield) which, on redistillation, gave 6-*methylocta*-3 : 5-*dien*-2-*one*, b. p. 93—98°/14 mm., n_D^{20} 1·5212. Satisfactory analyses were not obtained (Found: C, 76·55; H, 9·95. $C_9H_{14}O$ requires C, 78·2; H, 10·2%). Light absorption: max., 2880 Å; ε, 21,000. The 2 : 4-*dinitrophenylhydrazone* formed red needles, m. p. 183—185°, from acetic acid (Found: C, 56·35; H, 5·7; N, 17·4. $C_{15}H_{18}O_4N_4$ requires C, 56·6; H, 5·7; N, 17·6%).

6-Methylocta-3 : 5-dien-2-one (5·19 g.) and Raney nickel (0·5 g.; washed as previously described) in ethanol (20 c.c.) were agitated in hydrogen at 30—40° for 4·5 hr.; 1·735 l. (at 20°/750 mm.) had then been absorbed (theory 1·83 l.). Distillation of the product gave 6-*methyloctan*-2-*one* (3·67 g., 70·5%), b. p. 77—78°/16 mm., n_D^{20} 1·4265 (Found: C, 75·95; H, 12·55. $C_9H_{18}O$ requires C, 76·0; H, 12·75%). A 2 : 4-*dinitrophenylhydrazone* crystallised as yellow needles, m. p. 58°, from aqueous methanol (Found: C, 55·55; H, 6·8; N, 17·1. $C_{15}H_{22}O_4N_4$ requires C, 55·8; H, 6·85; N, 17·4%).

Pyrolysis of 1-*Ethynyl*cyclo*hexyl Acetoacetate.*—The acetoacetate (15 g.) and toluene-*p*-sulphonic acid (0·4 g.) were heated at 180—200° for 2 hr., 1·43 l. of gas (67% carbon dioxide) being evolved. After the addition of sodium acetate (0·2 g.), the product was distilled giving the following fractions: (*a*) 1-ethynyl*cyclo*hexanol, b. p. 77—80°/12 mm., n_D^{20} 1·4826 (2·01 g.); (*b*) b. p. 130—133°/12 mm., n_D^{20} 1·4169 (0·81 g.); (*c*) b. p. 133—135°/12 mm., n_D^{20} 1·4259 (1·97 g.); (*d*) b. p. 135—137°/12 mm., n_D^{20} 1·5381 (1·45 g.); and a residue of dehydroacetic acid. Light absorption: (*c*), max., 2330 and 2900 Å; ε, 15,400 and 12,000, respectively; (*d*), max., 2330 and 2900 Å; ε, 8400 and 13,000, respectively. The yield of material, b. p. 130—137°/12 mm., was 36%.

Fraction (*d*) gave a *semicarbazone* [plates, m. p. 204°, from aqueous ethanol (Found: C, 65·2; H, 8·2; N, 18·8. $C_{12}H_{19}ON_3$ requires C, 65·15; H, 8·65; N, 19·0%)] and a 2 : 4-*dinitrophenylhydrazone* [a dark red solid, m. p. 194° (decomp.), from aqueous acetic acid (Found: N, 16·5. $C_{17}H_{20}O_4N_4$ requires N, 16·3%)]. The semicarbazone (1·1 g.) was hydrolysed by aqueous sulphuric acid (20 c.c.; 0·5N) in boiling light petroleum (b. p. 60—80°) for 5 hr. with vigorous agitation, a clear solution being obtained. 5-cyclo*Hexylidenepent*-3-*en*-2-*one* (VI) (0·53 g.) had b. p. 94—95°/0·5 mm., n_D^{20} 1·5557. Unsatisfactory microanalyses were obtained (Found: C, 78·35, 78·7; H, 9·4, 9·45. $C_{11}H_{16}O$ requires C, 80·4; H, 9·8%). Light absorption: max. 2900 Å; ε, 27,800.

5-cyclo*Hexylidenepent*-3-*en*-2-*one.*—1-Hydroxy*cyclo*hexylacetic acid was prepared by the standard Reformatsky procedure ("Organic Reactions," Wiley, Vol. I, p. 17) followed by hydrolysis with aqueous alkali. It was converted into *cyclo*hexylideneacetic acid (VIII) as described by Schmid and Karrer (*loc. cit.*), but with a poorer yield (28%; lit. 42·2%).

*cyclo*Hexylideneacetic acid (23 g.) was added, in dry ether solution (350 c.c.), to an agitated, cooled solution of lithium aluminium hydride (9·3 g.) in dry ether (300 c.c.) during 0·5 hr. After a further 10 min., the excess of reagent was decomposed with ethyl acetate (50 g.), and the complex hydrolysed with saturated ammonium chloride solution (100 c.c.). After filtration, the product was isolated with ether, giving 2-*cyclo*hexylidene-ethanol (IX) (13·7 g., 66·7%), b. p. 101—106°/15 mm., n_D^{20} 1·4930 (Dimroth, *loc. cit.*, gives b. p. 95—96°/13·5 mm.). The 3 : 5-dinitrobenzoate had m. p. 90—91° (lit. m. p. 90—91°).

A mixture of 2-*cyclo*hexylidene-ethanol (10 g.), acetone (100 c.c.), aluminium *tert.*-butoxide (20 g.), and benzene (250 c.c.) was refluxed in an atmosphere of nitrogen for 48 hr. The product was cooled, shaken with water, and filtered. After being washed, the solvent layer was evaporated and the residue distilled, giving 5-*cyclo*hexylidenepent-3-en-2-one (5·26 g.), b. p. 102—106°/1 mm., n_D^{20} 1·5540, in addition to recovered *cyclo*hexylidene-ethanol (1·16 g.; b. p. 66—68°/1 mm.), and an intermediate fraction (1·19 g.; b. p. 68—102°/1 mm.). The semicarbazone had m. p. 204°, alone or in admixture with that derived from the ketone obtained in pyrolysis experiments.

Pyrolysis of 1 : 1-*Dimethylprop*-2-*ynyl* α-*Acetylbutyrate.*—1 : 1-Dimethylprop-2-ynyl acetoacetate (50·5 g.) was refluxed with ethyl iodide (51·5 g.) in a solution of potassium *tert.*-butoxide (from 11·7 g. of potassium in 180 c.c. of *tert.*-butanol). Titration of samples indicated that the reaction was substantially complete after 0·5 hr., and after 1 hr. the bulk of the solvent was evaporated, water added, and the product isolated with ether. Distillation gave 1 : 1-*dimethylprop*-2-*ynyl* α-*acetylbutyrate* (36·9 g., 62·5%), b. p. 105—110°/13 mm., n_D^{20} 1·4430 (Found: C, 67·65; H, 8·5. $C_{11}H_{16}O_3$ requires C, 67·3; H, 8·2%). Unexpectedly, the ester was insoluble in aqueous sodium hydroxide, gave no colour with ferric chloride, but gave a white precipitate with ammoniacal silver nitrate. The 2 : 4-*dinitrophenylhydrazone* formed pale orange microcrystals, m. p. 140°, from ethanol (Found: C, 54·5; H, 5·4; N, 14·9. $C_{17}H_{20}O_6N_4$ requires C, 54·25; H, 5·35; N, 14·9%).

The acetylbutyrate (11·8 g.) was heated with toluene-*p*-sulphonic acid (0·05 g.) at 200—220°: after 3 hr. 1·01 l. of gas (93% carbon dioxide) had been evolved. Distillation of the residue (8·8 g.) gave fractions (*a*) b. p. 96—102°/10 mm., n_D^{20} 1·4715 (4·8 g.), (*b*) b. p. 102—105°/10 mm., n_D^{20} 1·4600 (2·5 g.), and high-boiling material. Fraction (*b*) consisted substantially of unchanged ester, while (*a*) comprised ester with 40—50% of a dienone, as indicated by the light absorption : max., 2910 Å; ε, 10,000.

The mixed products, b. p. 96—105°/10 mm., were hydrogenated in methanol in the presence of "acid-washed" Raney nickel until absorption ceased. Distillation gave a fraction (31% of total), b. p. 72—78°/10 mm., n_D^{20} 1·4255, which gave a *semicarbazone* (from aqueous methanol), m. p. 87° (Found : C, 62·1; H, 10·55; N, 19·7. $C_{11}H_{23}ON_3$ requires C, 61·95; H, 10·85; N, 19·7%). This did not depress the m. p. of the derivative of authentic 3-ethyl-6-methylheptan-2-one.

3-*Ethyl*-6-*methylheptan*-2-*one*.—Ethyl α-acetylbutyrate (79 g.) was refluxed with *iso*pentyl bromide (83 g.) in the presence of potassium *tert.*-butoxide (from 19·5 g. of potassium in 250 c.c. of *tert.*-butanol) for 3 hr. Isolation gave *ethyl* 3-*acetyl*-6-*methylheptane*-3-*carboxylate* (62·8 g., 55%), b. p. 123—128°/12 mm., n_D^{20} 1·4375 (Found : C, 68·35; H, 10·75. $C_{13}H_{24}O_3$ requires C, 68·4; H, 10·6%).

The ester was hydrolysed by the method employed by Renfrow (*J. Amer. Chem. Soc.*, 1944, **66**, 146) for the "ketonic" hydrolysis of disubstituted acetoacetic esters, giving 3-*ethyl*-6-*methylheptan*-2-*one* (54% yield), b. p. 70—72°/11 mm., n_D^{20} 1·4230 (Found : C, 76·9; H, 13·0. $C_{10}H_{20}O$ requires C, 76·85; H, 12·9%). The semicarbazone (see above) had m. p. 87°.

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