was added before evaporation to take care of the newly formed amino group. The residual hydrochlorides were crystallized from polar–non-polar solvent mixtures, usually alcohol–ether. Except with reductions 4–7 and 16–17 (see Table II) the material as first obtained was substantially homogeneous; the melting point did not change significantly on further crystallization and the quantity obtained was approximately that to be expected.

With the reductions 4 and 5 the first product obtained was fairly pure methyl-*p*-anisylamine hydrochloride. The material in the mother liquors was, however, much lower melting and slow crystallization showed different crystal forms to be present. Fractional crystallization of mechanically separated portions resulted in the isolation of methyl-*o*-methoxybenzylamine hydrochloride and of methyl-*m*-methoxybenzylamine hydrochloride which were compared with synthetic specimens.

After the reductions 6 and 7 (which are substantially equivalent), evaporation was carried out at atmospheric pressure. A considerable fraction of *p*-cresol was separated and also a small neutral fraction. The hydrochlorides permitted separation into anisylamine hydrochloride and a small amount of phenolic base. The amount of the latter did not suffice for identification, and the difficulty in its isolation from the mixture was such as to permit no accurate estimation of the quantity originally present.

The reduction 16 furnished about the expected amount of hydrochloride which was obviously impure, but which analyzed correctly for $C_{12}H_{14}NCl$. Separation of a pure substance appeared hopeless so we can only say that both methyl menaphthylamines were present.

Reduction 17 also gave a non-homogeneous mixture of hydrochlorides from which methyl-4-phenylbenzylamine hydrochloride was separated readily. We believe methyl α-menaphthylamine to have been present but could not demonstrate it with the material available.

The authors are indebted to Mr. W. S. Ide for the many micro-analyses recorded here, and also for a number performed upon previously known substances (to confirm identification) and not included in the tables.

Summary

1. The effect of substituents on the stability of O-benzyl and N-benzyl bonds has been investigated through catalytic hydrogenolysis (debenzylation).

2. Alkyl groups in the α-position of benzyl alcohol stabilize the system somewhat, carboxyl and amino groups much more so. Aryl and cyano groups may labilize the system but at any rate do not stabilize it.

3. Substitution on the aromatic rings with —OMe, —OH, —NH_2, —Cl, —NR_3Cl and —CH_3 gives greater stability.

4. More extended aromatic systems as in menaphthyl and 4-phenylbenzyl are more labile than benzyl.

TUCKAHOE, N. Y. RECEIVED MAY 29, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Rearrangement of Allyl-Type Esters of β-Keto Acids

BY WALTER KIMEL AND ARTHUR C. COPE

Carroll reported recently that β,γ-unsaturated alcohols react with ethyl acetoacetate in the presence of alkaline catalysts to give unsaturated ketones.[1] The course of the reaction may be illustrated with cinnamyl alcohol and phenylvinylcarbinol, which yielded isomeric ketones.

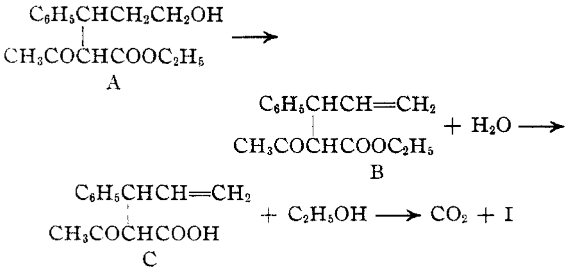
$$\text{(1)}\ CH_3COCH_2COOC_2H_5 + C_6H_5CH{=}CHCH_2OH \xrightarrow[170\text{-}240°]{NaOAc}$$

$$C_2H_5OH + CO_2 + \underset{\text{I}}{CH_3COCH_2CH(C_6H_5)CH{=}CH_2}\ (33\%)$$

$$\text{(2)}\ CH_3COCH_2COOC_2H_5 + C_6H_5CHOHCH{=}CH_2 \xrightarrow[220°]{KOAc}$$

$$C_2H_5OH + CO_2 + \underset{\text{II}}{CH_3COCH_2CH_2CH{=}CHC_6H_5}\ (75\%)$$

An addition mechanism was suggested for the reaction, bearing a formal resemblance to the Michael condensation. According to this interpretation, the intermediates in reaction (1) would be A, B and C.



$$\underset{\text{A}}{\begin{matrix} C_6H_5CHCH_2CH_2OH \\ | \\ CH_3COCHCOOC_2H_5 \end{matrix}} \longrightarrow \underset{\text{B}}{\begin{matrix} C_6H_5CHCH{=}CH_2 \\ | \\ CH_3COCHCOOC_2H_5 \end{matrix}} + H_2O \longrightarrow$$

$$\underset{\text{C}}{\begin{matrix} C_6H_5CHCH{=}CH_2 \\ | \\ CH_3COCHCOOH \end{matrix}} + C_2H_5OH \longrightarrow CO_2 + \text{I}$$

While this interpretation would account for the attachment of the $CH_3COCH_2^-$ group to the γ-carbon atom of the alcohol employed, objections may be raised to it. The mechanism requires that the hydroxymethyl group, —CH_2OH, shall activate the ethylenic double bond suffi-

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[1] Carroll, (a) *J. Chem. Soc.*, 704 (1940); (b) 1266 (1940); (c) 507 (1941).

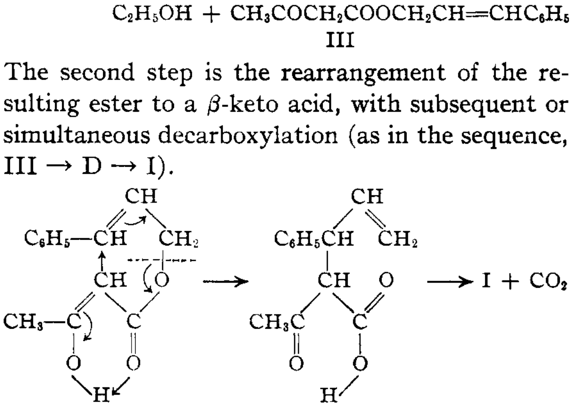
ciently to permit occurrence of the Michael condensation.[2] Other groups which are known to furnish sufficient activation to allow the Michael reaction to proceed are unsaturated.[3] Moreover, if ethyl acetoacetate can add to cinnamyl alcohol, dibenzoylmethane might be expected to add in a similar manner; actually, no such addition was observed.[1c] Also, an intermediate process according to this mechanism in the case of β,γ-unsaturated primary alcohols would be the dehydration of a primary alcohol, as in the conversion of A to B. Such a dehydration under the conditions of this reaction would be unusual.

We have found that the acetoacetates and benzoylacetates of several β,γ-unsaturated alcohols decompose on heating at temperatures of 170 to 250°, yielding γ,δ-unsaturated ketones and carbon dioxide. In some instances the ketones are obtained in high yield, and the reaction has merit in these cases as a synthetic method. The usual way of preparing the ketones which are obtained, would be to alkylate the sodium enolate of a β-ketonic ester with an allylic halide, and subject the resulting ester to ketonic hydrolysis. The pyrolytic method described in this paper has the advantage that it does not employ these halides, which may undergo an allylic shift in the course of preparation and consequently lead to impure products.[4]

From the results of this investigation, we would interpret Carroll's results in the following manner. The first step in the reactions which he studied is believed to be a re-esterification, which may be promoted by the alkaline catalyst; *i. e.*

$$\mathrm{CH_3COCH_2COOC_2H_5 + C_6H_5CH{=}CHCH_2OH \rightleftharpoons C_2H_5OH + \underset{\mathrm{III}}{CH_3COCH_2COOCH_2CH{=}CHC_6H_5}}$$

The second step is the rearrangement of the resulting ester to a β-keto acid, with subsequent or simultaneous decarboxylation (as in the sequence, III → D → I).



III D

The reaction is represented as occurring through the chelated enol form of the β-keto ester. The essential features of the mechanism are: (a) the cinnamyl group becomes detached from the ester oxygen to which it loses its electron pair; (b) the γ-carbon atom of the cinnamyl group becomes attached to the central methylene carbon atom of the β-keto ester (which acts as a donor center and contributes the electron pair for the union); (c) the double bond in the cinnamyl fragment shifts simultaneously in the manner indicated in formula D. Reasons for this interpretation of the behavior of allyl-type esters of β-keto acids on pyrolysis are indicated below, following a discussion of our experimental results.

Acetoacetic Ester Series.—Allyl acetoacetate was obtained easily by re-esterification of methyl acetoacetate with allyl alcohol, but re-esterification proved to be impractical with allyl-type alcohols of higher molecular weight. Presumably the point of equilibrium was unfavorable for the acetoacetates of the substituted allyl alcohols. However, the reaction of diketene with β,γ-unsaturated alcohols in the presence of approximately 0.01 molar equivalent of the corresponding sodium alkoxide at 0 to 25° provided an excellent method for preparing the acetoacetates. This method gave purer products and better yields than a procedure in which *p*-toluenesulfonic acid was used as the catalyst, although the latter conditions are reported to be advantageous for preparing acetoacetates from alcohols.[5] Chick and Wilsmore[6] have stated that sodium ethoxide reacts with diketene in alcohol solution to give the sodium enolate of ethyl acetoacetate.

Acetoacetates of the following alcohols were prepared from diketene: methallyl alcohol, crotyl alcohol, methylvinylcarbinol, cinnamyl alcohol, phenylvinylcarbinol, linalool and geraniol. It was necessary to obtain evidence that the geranyl acetoacetate prepared in this manner was structurally homogeneous, for although the product had a constant boiling point the refractive indices of successive fractions were different. After eliminating the possibility that these differences could be due to a variation in per cent. enol content of the fractions by allowing all of them to come to equilibrium, the discrepancy could be attributed to one of two causes. Either

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(2) Other β,γ-unsaturated alcohols employed by Carroll do not contain the phenyl group, which might influence the reactivity of the ethylenic linkage in cinnamyl alcohol and phenylvinylcarbinol.

(3) *Cf.* Connor and McClellan, *J. Org. Chem.*, **3**, 570 (1939).

(4) *Cf.* Young and Winstein, THIS JOURNAL, **57**, 2013 (1935), and later papers by Young.

(5) Boese (a) U. S. Patent 2,167,168 (July 25, 1939); (b) *Ind. Eng. Chem.*, **32**, 16 (1940).

(6) Chick and Wilsmore, *J. Chem. Soc.*, **93**, 946 (1908); **97**, 1978 (1910).

TABLE I

Acetoacetate	Pyrolysis Temp., °C.	Pyrolysis Time, hr.	Carbon dioxide yield, %	Ketone formed Name	Ketone formed Formula	Yield %
Allyl	185–200	92	55	Allylacetone	$CH_3COCH_2CH_2CH{=}CH_2$	31
Methallyl	200–215	25	40	Methallylacetone	$CH_3COCH_2CH_2C(CH_3){=}CH_2$	26
Crotyl	190–220	18	51	3-Methyl-1-hexene-5-one	$CH_3COCH_2CH(CH_3)CH{=}CH_2$	37
Methylvinylcarbinyl	185–200	12	84	5-Heptene-2-one	$CH_3COCH_2CH_2CH{=}CHCH_3$	80
Cinnamyl	250	1.2	95	3-Phenyl-1-hexene-5-one	$CH_3COCH_2CH(C_6H_5)CH{=}CH_2$	74
Phenylvinylcarbinyl	200–240	1	97	1-Phenyl-1-hexene-5-one	$CH_3COCH_2CH_2CH{=}CHC_6H_5$	88
Linalyl	170–235	1.2	97	Geranylacetone	$CH_3COCH_2CH_2CH{=}C(R)CH_3$[a]	78
Geranyl	220–230	8	66	Geranylacetone	$CH_3COCH_2CH_2CH{=}C(R)CH_3$[a]	23

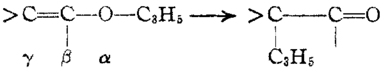
[a] R = $(CH_3)_2C{=}CHCH_2CH_2$—.

partial isomerization of geraniol to its geometric isomer, nerol, preceded esterification, or a partial allylic shift had produced some linalool which was converted to linalyl acetoacetate. The first of these possibilities was proved to be correct by subjecting two fractions of geranyl acetoacetate to catalytic hydrogenation, followed by hydrolysis and preparation of the allophanate of the saturated alcohol. The pure derivative which was obtained from each was the allophanate of tetrahydrogeraniol. The allophanate of tetrahydrolinalool may be obtained easily, in the same manner as the tetrahydrogeraniol derivative.

When allyl acetoacetate was refluxed in an atmosphere of nitrogen, carbon dioxide was evolved slowly and the reflux temperature gradually decreased. After heating for thirty-three hours, the chief products were found to be allyl alcohol, acetone and dehydroacetic acid. The yield of allylacetone was only 5.5%. Similar results were obtained on heating the ester in the presence of sodium acetate or sodium methoxide. However, pyrolysis of cinnamyl acetoacetate at 250° resulted in a rapid evolution of carbon dioxide and 3-phenyl-1-hexene-5-one (I) was formed in good yield. It appears that the refluxing temperature of allyl acetoacetate is too low to permit rapid reaction. Also, the small size of the ester alkyl group favors intermolecular reaction of the ester, which produces dehydroacetic acid. The same factors hold for the other allyl-type acetoacetates of low molecular weight. Diphenyl ether accordingly was used as a solvent in the pyrolysis of these esters, to increase the reflux temperature and depress the intermolecular side reaction by dilution. Results of pyrolysis of each of the esters are summarized in Table I. The first four esters were heated in the presence of an equal weight of diphenyl ether, while the others were heated without a solvent

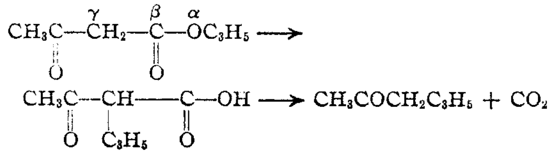
In all but two cases it was possible to identify the ketone formed simply by preparation of a known solid derivative. Methallylacetone was characterized as the semicarbazone, which was identical with an authentic specimen prepared by standard methods. The semicarbazone of 5-heptene-2-one melted at 104.5–105.5°, which deviates from the m. p. of 97° previously reported.[7] The structure of the ketone was consequently verified by ozonization and identification of the cleavage products as acetaldehyde and levulinic acid.

The ketone formed in the pyrolysis of each ester except geranyl acetoacetate is one in which inversion of the allylic group has occurred. The occurrence of inversion is explained by the mechanism postulated, as illustrated in the equation III → D → I above. The reaction is visualized as somewhat analogous to the Claisen rearrangement of allyl enol and phenol ethers.[8] It differs from the Claisen rearrangement, however, in that the three-atom system within which the allyl group migrates does not contain a double bond that undergoes a simultaneous shift. According to the views here expressed, this deficiency is overcome by the activation of the γ-atom by an adjacent acetyl group, which makes it a donor center and thus allows the reaction to proceed. The relation to the Claisen system may be shown by the skeletal formulas



$$>\underset{\gamma}{C}{=}\underset{\beta}{\underset{|}{C}}-\underset{\alpha}{O}-C_3H_5 \longrightarrow\ >\underset{C_3H_5}{\underset{|}{C}}-\underset{|}{C}{=}O$$

Claisen system



$$CH_3\underset{O}{\underset{\|}{C}}-\overset{\gamma}{CH_2}-\overset{\beta}{\underset{O}{\underset{\|}{C}}}-\overset{\alpha}{O}C_3H_5 \longrightarrow$$

$$CH_3\underset{O}{\underset{\|}{C}}-\underset{C_3H_5}{\underset{|}{CH}}-\underset{O}{\underset{\|}{C}}-OH \longrightarrow CH_3COCH_2C_3H_5 + CO_2$$

(Keto or enol form)

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[7] Braun and Gossel, *Ber.*, **57**, 373 (1924).

[8] *Cf.* Tarbell, *Chem. Rev.*, **27**, 495 (1940).

The fact that the carbonyl group can shift from the enol form (in the acetoacetate) to the keto form in the ketone which is produced, and the possibility that hydrogen can be shifted from the enol hydroxyl to the ester carbonyl through the chelate ring of the enol, fit into the suggested mechanism in an attractive manner. There is no assurance that the possibility of these shifts is a necessary condition for the reaction, however.

The relative ease with which the reaction occurs with each isomeric pair of esters is in accord with this interpretation. The isomer which rearranges more rapidly is the one in which the γ-carbon atom of the allyl-type group is unsubstituted; consequently, there is less steric hindrance blocking the approach of this atom to the methylene carbon atom to which it becomes attached. The fact that inversion of the geranyl group does not occur may be rationalized, although it was unexpected, by the circumstance that its γ-carbon atom is disubstituted and consequently subject to very considerable steric hindrance.

Benzoylacetic Ester Series.—Benzoylacetates were prepared from crotyl alcohol and methylvinylcarbinol by re-esterification of ethyl benzoylacetate. Both esters evolved carbon dioxide rapidly on heating at 240 to 250°. Phenyl 2-methyl-3-butenyl ketone (V) was obtained from crotyl benzoylacetate (IV) in 76% yield, and phenyl 3-pentenyl ketone (VII) from the methylvinylcarbinyl ester (VI) in 83% yield.

$$\underset{\text{IV}}{C_6H_5COCH_2COOCH_2CH{=}CHCH_3} \xrightarrow{250^\circ}$$
$$CO_2 + \underset{\text{V}}{C_6H_5COCH_2CH(CH_3)CH{=}CH_2}$$

$$\underset{\text{VI}}{C_6H_5COCH_2COOCH(CH_3)CH{=}CH_2} \xrightarrow{240\text{–}250^\circ}$$
$$CO_2 + \underset{\text{VII}}{C_6H_5COCH_2CH_2CH{=}CHCH_3}$$

The fact that these benzoylacetic esters rearrange more readily than the corresponding acetoacetic esters is in accord with the proposed mechanism because the benzoyl group is a stronger activating group than the acetyl radical, which makes the central methylene carbon atom of the ester a more potent donor center.

The structure of V was proved by identification of formaldehyde as a cleavage product following ozonization, and by hydrogenation to the known ketone, phenyl 2-methylbutyl ketone, which was characterized as the semicarbazone. The structure of VII was verified by production of acetaldehyde on cleavage of the ozonide, and by hydrogenation to *n*-hexylbenzene.

Experimental Part[9]

Diketene was kindly furnished by the Carbide and Carbon Chemicals Corporation, and was used without purification. Phenylvinylcarbinol was prepared by the method described by Carroll,[1b] and had b. p. 72–73° (0.5 mm.); $n^{25}{}_D$ 1.5372. The other β,γ unsaturated alcohols were obtained from the Shell Development Company or the Eastman Kodak Company and purified by redistillation.

Reaction of Diketene with Allyl-type Alcohols.—The best yields of acetoacetates were obtained by employing the following procedure: Approximately 0.01 equivalent of sodium was dissolved in one molar equivalent of the alcohol in a three-necked flask equipped with a mercury-sealed stirrer, calcium chloride tube, dropping funnel and thermometer. The solution was cooled to 0° and diketene (1.5 molar equivalents) was added dropwise, with stirring, at such rate that the temperature did not rise above 5°. The reaction mixture was allowed to stand at 0° until the odor of diketene could no longer be detected (one to two days). The excess diketene is converted to dehydroacetic acid, so the solution was acid at this point. It was diluted with ether and extracted with sufficient 5% sodium carbonate solution to remove the acid present. The ether solution was washed with water, dried over sodium sulfate and concentrated *in vacuo*. The ester was purified by distillation at a pressure low enough so that no decomposition occurred. When the esters were fractionated slowly, the distillate contained a preponderance of the enol form. This was indicated by the fact that the refractive indices of the freshly distilled esters changed slowly on the refractometer from high values indicating a large per cent. of enol to lower equilibrium values.

Rearrangement of Allyl-type Esters.—The esters were placed in a two-necked flask attached by a ground glass joint to a reflux condenser. A thermometer was immersed in the liquid. The top of the condenser was connected by pressure tubing to a large gas buret or gasometer filled with saturated salt solution. The system, which was gastight, was swept with nitrogen, after which the flask was heated in a Wood's metal bath either to the boiling point or to a temperature at which carbon dioxide was evolved rapidly. The progress of the reaction was followed by measuring the carbon dioxide evolved. When its evolution ceased, the mixture was cooled to room temperature and the gas sample was made homogeneous by allowing it to stand and raising and lowering the leveling bulb of the gas buret. The volume of the gas was measured and its composition determined by the usual procedure of gas analysis. In each case, the gas evolved proved to be pure carbon dioxide. The liquid in the flask was fractionated, either through a Widmer column with a 16-cm. spiral, or through an adiabatic, total-reflux variable take off type column with a 30 × 1.2 cm. section packed with glass helices.

Allyl Acetoacetate.—Methyl acetoacetate (500 g., 4.3 moles) and allyl alcohol (400 g., 6.9 moles) were refluxed

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[9] Boiling and melting points are uncorrected.

in a 2-liter flask attached to a total-reflux variable take off type column with a 70 × 1.2 cm. section packed with glass helices. Methanol (127 g., b. p. 65°) was distilled from the reaction mixture during six hours. The mixture was then fractionated through the column *in vacuo;* the yield of allyl acetoacetate was 435 g. (71%); b. p. 66.5° (14 mm.); n^{25}_{D} 1.4380; d^{25}_{25} 1.0366; M_{D} calcd. (keto form) 35.73, (enol form) 36.77, found 36.09. Boese (ref. 5a) reports b. p. 194° for this ester, but records no other properties.

Anal. Calcd. for $C_7H_{10}O_3$: C, 59.12; H, 7.09. Found: C, 59.18; H, 7.11.

Allylacetone.—Allyl acetoacetate (100 g.) dissolved in 100 g. of diphenyl ether was pyrolyzed by the procedure described above. After refluxing for thirty-five hours the rate of gas evolution had diminished considerably. All material boiling up to 130° was removed by distillation, and the residue was reheated and the process described above was repeated at intervals of fifteen hours. A total of 8790 cc. (55%) of carbon dioxide was evolved in ninety-two hours. The low-boiling distillates were combined and redistilled, yielding 21.4 g. (31%) of allylacetone, b. p. 127–128°, n^{25}_{D} 1.4174. The ketone was identified by preparation of its 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. with a known sample[10] 107–108°.

Methylallyl Acetoacetate.—Sodium (0.2 g.) was dissolved in 20 g. of methallyl alcohol. Diketene (33.6 g.) was added and the mixture was allowed to stand at 0–5° for forty-eight hours. By the general procedure outlined above, 36.8 g. (85%) of methallyl acetoacetate was obtained, b. p. 95–97° (18 mm.); n^{25}_{D} 1.4411; d^{25}_{25} 1.0128; M_{D} calcd. (keto form) 40.35, (enol form) 41.40, found 40.85.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.32; H, 7.66.

Methallylacetone.—Methallyl acetoacetate (78.8 g.) dissolved in 80 g. of diphenyl ether was heated at 200–215° as described above; 4522 cc. (40%) of carbon dioxide was evolved in twenty-five hours. Distillation of the residue through a Widmer column yielded 14.5 g. (26%) of methallylacetone, b. p. 147–149°; n^{25}_{D} 1.4285. The semicarbazone of this ketone, prepared in the usual manner and recrystallized from 30% alcohol, had m. p. 136.5–137.5°.

A known sample of methallylacetone was prepared by the standard acetoacetic ester synthesis from methallyl chloride and ethyl acetoacetate. The substituted acetoacetic ester, without purification, was subjected to ketonic hydrolysis by refluxing for eight hours with 10% potassium hydroxide. Methallylacetone was obtained in 51% yield, b. p. 148–149°; n^{25}_{D} 1.4279; d^{25}_{26} 0.8475; M_{D} calcd. 34.08, found 34.15.

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.79. Found: C, 75.24; H, 10.87.

The semicarbazone, prepared in the usual manner and recrystallized from 30% alcohol, melted at 136.5–137.5°.

Anal. Calcd. for $C_8H_{15}ON_3$: C, 56.77; H, 8.93. Found: C, 56.80; H, 9.00.

Mixed m. p. with the semicarbazone of the methallylacetone prepared by pyrolysis showed no depression.

Crotyl Acetoacetate.—The product obtained by reaction of a solution of 0.2 g. of sodium in 20 g. of crotyl alcohol with 33.6 g. of diketene at 0 to 5° for forty-eight hours was distilled through a Widmer column. The yield of crotyl acetoacetate was 35.7 g. (83%); b. p. 100–102° (16 mm.); n^{25}_{D} 1.4449; d^{25}_{25} 1.0186; M_{D} calcd. (keto form) 40.35, (enol form) 41.40, found 41.25.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.38; H, 7.71.

3-Methyl-1-hexene-5-one.—Crotyl acetoacetate (49 g.) dissolved in 49 g. of diphenyl ether was heated at 190–220° for eighteen hours. The yield of carbon dioxide was 3850 cc. (51%). The product was distilled through the small total-reflux type column, yielding 13 g. (37%) of 3-methyl-1-hexene-5-one, b. p. 137–138.5°; n^{25}_{D} 1.4197. These physical constants are in good agreement with properties reported recently for this ketone.[10] The semicarbazone of the ketone had m. p. of 111.5–112.5° and showed no depression on mixture with a known sample.[10]

Methylvinylcarbinyl Acetoacetate.—This ester was obtained in yield of 76.6 g. (89%) by reaction of 67.2 g. of diketene with a solution of 0.4 g. of sodium in 40 g. of methylvinylcarbinol at 0–5° during thirty-two hours. Its properties were: b. p. 92–93° (18 mm.); n^{25}_{D} 1.4342; d^{25}_{25} 1.0005; M_{D} calcd. (keto form) 40.35, (enol form) 41.40, found 40.60.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.66; H, 7.77.

5-Heptene-2-one.—Methylvinylcarbinyl acetoacetate (47.8 g.) in 45 g. of diphenyl ether was heated at 185–200° for twelve hours. The yield of carbon dioxide was 5780 cc. (84%). Distillation through a Widmer column yielded 27.5 g. (80%) of 5-heptene-2-one, b. p. 151–153°, n^{25}_{D} 1.4272. The semicarbazone of the ketone had m. p. 104.5–105.5°. Constants reported by Braun and Gossel[7] for this ketone are: b. p. 152–155°, n^{20}_{D} 1.4292; semicarbazone, m. p. 97°.

A solution of 3 g. of the ketone in 100 cc. of pentane was ozonized at −5°. When the ozonization was complete (three hours), the pentane was removed *in vacuo* and the ozonide was warmed on a steam-bath with 50 cc. of 3% hydrogen peroxide. A small amount of the solution was distilled and a semicarbazone was prepared from the distillate; m. p. and mixed m. p. with acetaldehyde semicarbazone 161–163°. An oxime was prepared from the residue after evaporation to a volume of 15 cc.; m. p. and mixed m. p. with a known sample of levulinic acid oxime, 93–95°.

Cinnamyl Acetoacetate (III).—A solution of sodium (0.4 g.) in cinnamyl alcohol (50 g.) and diketene (42 g.) were allowed to react for twenty-four hours at 20–30°. In order to prevent rearrangement, it was necessary to distil the product at low pressure. The yield of III was 56.2 g. (69%); b. p. 101–104° (0.025 mm.); n^{25}_{D} 1.5422; d^{25}_{25} 1.1029; M_{D} calcd. (keto form) 59.84, (enol form) 60.88, found 62.47, exaltation 1.59 to 2.63.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.44; H, 6.42.

3-Phenyl-1-hexene-5-one (I).—III (47.3 g.) was heated at 250° for seventy minutes, during which time 4625 cc. (95%) of carbon dioxide was evolved. Distillation gave 27.8 g. (74%) of I, b. p. 85–86° (1 mm.); n^{25}_{D} 1.5193; d^{25}_{25} 0.9877; M_{D} calcd. 53.57, found 53.72.

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(10) Cope, Hofmann and Hardy, THIS JOURNAL, **63**, 1856 (1941).

Anal.[11] Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.87; H, 8.12.

The 2,4-dinitrophenylhydrazone of this ketone, after recrystallization from a mixture of alcohol and ethyl acetate (2:1), melted at 102–103°. Carroll[1b] reported the b. p. of an impure preparation of this ketone as 99–103° (2 mm.), and the m. p. of its 2,4-dinitrophenylhydrazone as 101–102°.

Anal.[11] of the 2,4-dinitrophenylhydrazone. Calcd. for $C_{18}H_{18}O_4N_4$: C, 61.01; H, 5.12. Found: C, 61.10; H, 5.25.

Phenylvinylcarbinyl Acetoacetate.—This ester was prepared by reaction of a solution of 0.2 g. of sodium in 21 g. of phenylvinylcarbinol with 17.6 g. of diketene at 20–30° for twenty-four hours. Distillation of the product gave 24 g. (70%) of phenylvinylcarbinyl acetoacetate, b. p. 77° (0.002 mm.); $n^{25}\mathrm{D}$ 1.5130; $d^{25}{}_{25}$ 1.0826; $M\mathrm{D}$ calcd. (keto form) 59.84, (enol form) 60.88, found, 60.77.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.82; H, 6.49.

1-Phenyl-1-hexene-5-one (II).—Phenylvinylcarbinyl acetoacetate (18.1 g.) on pyrolysis for one hour at 200–240° gave 1802 cc. (97%) of carbon dioxide. Vigorous evolution of carbon dioxide commenced at 170°, and the reaction was exothermic. On distillation, 12.7 g. (88%) of II was obtained, b. p. 97–99° (0.30 mm.); $n^{25}\mathrm{D}$ 1.5458; $d^{25}{}_{25}$ 0.9997; $M\mathrm{D}$ calcd. 53.57, found 55.33, exaltation 1.76.

Anal.[11] Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.41; H, 7.81.

The 2,4-dinitrophenylhydrazone of II, recrystallized from alcohol and ethyl acetate (2:1), had m. p. 143.5–145°; the semicarbazone, recrystallized from 50% alcohol, melted at 130.5–131°. The constants reported by Carroll[1b] for this ketone are: b. p. 125–130° (4 mm.); $n^{20}\mathrm{D}$ 1.5475; 2,4-dinitrophenylhydrazone, m. p. 145–146.5°. Also, Fischer, Wiedemann and Robertson[12] report the semicarbazone of II, m. p. 132°.

Anal.[11] of the 2,4-dinitrophenylhydrazone. Calcd. for $C_{18}H_{18}O_4N_4$: C, 61.01; H, 5.12. Found: C, 60.98; H, 5.23.

Linalyl Acetoacetate.—A solution of 0.2 g. of sodium in 25 g. of linalool was treated in the usual fashion with 18 g. of diketene at 20–30°, and allowed to stand overnight. By the general procedure given above, 23.5 g. (61%) of linalyl acetoacetate was obtained, b. p. 71–74° (0.006 mm.); $n^{25}\mathrm{D}$ 1.4626; $d^{25}{}_{25}$ 0.9654; $M\mathrm{D}$ calcd. (keto form) 67.60, (enol form) 68.64, found 68.14.

Anal. Calcd. for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.74; H, 9.45.

Geranylacetone.—Linalyl acetoacetate (16.0 g.) was heated at 170–235° for seventy minutes, giving 1465 cc. (97%) of carbon dioxide. The vigorous evolution of gas started at 140°. The product, geranylacetone, was purified by distillation, yield 10.2 g. (78%); b. p. 101–103° (2.5 mm.); $n^{25}\mathrm{D}$ 1.4660; semicarbazone, m. p. 94.5–95°. Constants reported by Carroll[1a] for this ketone are: b. p. 101–102° (3 mm.); $n^{20}\mathrm{D}$ 1.4683; semicarbazone, m. p. 96°.

Anal.[11] of the semicarbazone. Calcd. for $C_{14}H_{25}ON_3$: C, 66.89; H, 10.02. Found: C, 67.20; H, 10.06.

Geranyl Acetoacetate.—Sodium (0.2 g.) was dissolved in 25 g. of geraniol, and the solution was allowed to react with 18 g. of diketene at 0 to 5° for eighteen hours. The product was purified as outlined above and distilled, giving 29.8 g. (77%) of geranyl acetoacetate, b. p. 79–80° (0.006 mm.); $n^{25}\mathrm{D}$ 1.4670; $d^{25}{}_{25}$ 0.9625; $M\mathrm{D}$ calcd. (keto form) 67.60, (enol form) 68.64, found 68.59.

Anal. Calcd. for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.20; H, 9.46.

Successive fractions of this ester with constant b. p. had different refractive indices. On redistillation of the compound, three fractions of equal weight had the following refractive indices: (1) $n^{25}\mathrm{D}$ 1.4645; (2) $n^{25}\mathrm{D}$ 1.4672; (3) $n^{25}\mathrm{D}$ 1.4702. However, the structural homogeneity of the ester was proved as follows: three g. of fraction (1) was hydrogenated quantitatively in the presence of 1 g. of palladinized charcoal[13] in alcohol solution and the reduced ester was hydrolyzed directly by adding 5 g. of potassium hydroxide to the alcohol solution and refluxing for four hours. On distillation, 1 g. of tetrahydrogeraniol, b. p. 98–100° (7 mm.), $n^{25}\mathrm{D}$ 1.4368, was obtained. The allophanate of this alcohol, recrystallized from 50% alcohol, had m. p. 117–118°. In the same manner, 3 g. of fraction (2) was catalytically hydrogenated and hydrolyzed, yielding 1.2 g. of tetrahydrogeraniol, b. p. 101° (8 mm.); $n^{25}\mathrm{D}$ 1.4372; allophanate, m. p. 117–118°. Both of these allophanates were identical in m. p. and mixed m. p. with the derivative of a sample of tetrahydrogeraniol prepared by catalytic hydrogenation of geraniol.

Anal. of the allophanate. Calcd. for $C_{12}H_{24}O_3N_2$: C, 58.99; H, 9.90. Found: C, 59.09; H, 9.93.

An allophanate was prepared readily from tetrahydrolinalool (made by hydrogenation of linalool) in the same manner as the tetrahydrogeraniol derivative. It melted at 108–109°.[14]

Rearrangement of Geranyl Acetoacetate.—Geranyl acetoacetate (99.9 g.) was heated in two portions at 220–230° for eight hours. A total of 6605 cc. (66%) of carbon dioxide was collected. Evolution of gas did not begin until the temperature of the liquid was 220°. After pyrolysis, the liquid was fractionally distilled, and yielded 19.0 g. (23%) of geranylacetone, b. p. 101.5–103° (2.2 mm.); $n^{25}\mathrm{D}$ 1.4656; semicarbazone, m. p. 94.5–95.5°. The mixed m. p. of this semicarbazone with the derivative of geranylacetone prepared from linalyl acetoacetate was not depressed.

Crotyl Benzoylacetate (IV).—A solution of 0.3 g. of sodium in crotyl alcohol (1.0 mole) was allowed to react with ethyl benzoylacetate (0.5 mole) in a flask attached to a small total-reflux type column by refluxing at a pressure of 100 mm. Ethyl alcohol was distilled from the reaction mixture during six hours at a temperature of 34°. Ether was added to the residue, and the solution was washed with dilute hydrochloric acid, dried over sodium sulfate and concentrated *in vacuo*. On distillation, there was obtained 33.8 g. (31%) of IV, a light yellow liquid; b. p.

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[11] This compound has been prepared by Carroll (ref. 1b). It was analyzed because no analysis was reported in the previous work.

[12] Fischer, Wiedemann and Robertson, *Ann.*, **520**, 52–70 (1935).

[13] Hartung, THIS JOURNAL, **50**, 3372 (1928).

[14] Barbier and Locquin, *Ann. Chim.*, [9] **2**, 398 (1914), give m. p. 110–111° for tetrahydrolinalool allophanate.

112–114° (0.20 mm.); n^{25}_{D} 1.5347; d^{25}_{25} 1.0942; M_{D} calcd. (keto form) 59.84, (enol form) 60.88, found 62.25, exaltation 1.37 to 2.41.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.24; H, 6.33.

Phenyl 2-Methyl-3-butenyl Ketone (V).—When IV (22.3 g.) was heated for two hours at 250°, 2060 cc. (90%) of carbon dioxide was evolved. Distillation of the residue gave 13.6 g. (76%) of V, b. p. 98–100° (2.1 mm.); n^{25}_{D} 1.5223; d^{25}_{25} 0.9799; M_{D} calcd. 53.57, found 55.94, exaltation 2.37.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.70; H, 7.96.

The semicarbazone of V, recrystallized from alcohol, had m. p. 176–177.5°.

Anal. Calcd. for $C_{13}H_{17}ON_3$: C, 67.50; H, 7.41. Found: C, 67.80; H, 7.53.

A solution of 3 g. of V in 100 cc. of pentane was ozonized for four hours at −5°. The solvent was removed *in vacuo* and the ozonide was decomposed by warming on a steam-bath with 100 cc. of water, 1 g. of zinc dust and traces of hydroquinone and silver nitrate. A portion of the solution was distilled and a methone derivative was prepared from the distillate according to the method of Weinberger[15]; m. p. and mixed m. p. with formaldehyde methone 187–188°.

V (2.7 g.) was quantitatively hydrogenated in alcohol solution in the presence of palladinized charcoal. The reduction was stopped when one molar equivalent of hydrogen had been absorbed. On distillation, 2.4 g. of the saturated ketone, phenyl 2-methylbutyl ketone, was obtained; b. p. 135° (14 mm.); n^{25}_{D} 1.5100. The semicarbazone of this ketone, recrystallized from 50% alcohol, melted at 178–179.5°, in agreement with one recorded m. p.[16]

Methylvinylcarbinyl Benzoylacetate (VI).—This ester was prepared in the same manner as the crotyl ester from 0.3 g. of sodium, 2.5 moles of methylvinyl carbinol and 0.5 mole of ethyl benzoylacetate except that ethyl alcohol was removed at atmospheric pressure during forty hours. The product was purified in the same way as IV and distilled. The yield of VI was 71 g. (65%); b. p. 110° (0.5 mm.); n^{25}_{D} 1.5254; d^{25}_{25} 1.0858; M_{D} calcd. (keto form) 59.84, (enol form) 60.88, found 61.81, exaltation 0.93 to 1.97.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.20; H, 6.50.

Phenyl 3-pentenyl ketone (VII).—VI (50 g.) was heated at 240–250° for two hours, during which time 4840 cc. (94%) of carbon dioxide was collected. The yield of VII was 33.2 g. (83%); m. p. 23°; b. p. 96–97° (1 mm.); n^{25}_{D} 1.5270; d^{25}_{25} 0.9612; M_{D} calcd. 53.57, found 55.90, exaltation 2.33.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.58; H, 7.99.

The semicarbazone, prepared and recrystallized from alcohol in the usual way, had m. p. 129–130°.

Anal. Calcd. for $C_{13}H_{17}ON_3$: C, 67.50; H, 7.41. Found: C, 67.75; H, 7.49.

VII (2.1 g.) was subjected to ozonization in the manner described for V. Acetaldehyde was identified as a cleavage product by preparation of a methone derivative, m. p. and mixed m. p. with acetaldehyde methone 138–140°.

An alcoholic solution of VII (3.4 g.) was quantitatively hydrogenated in the presence of palladinized charcoal. Three molar equivalents of hydrogen were absorbed. The reduction product, b. p. 98° (9 mm.), n^{25}_{D} 1.4842, was proved to be *n*-hexylbenzene by preparing a 2,4-diacetamino derivative,[17] whose m. p. and mixed m. p. with a known sample[18] was 197–199°.

We are indebted to Mr. Saul Gottlieb for all microanalyses reported in this paper.

Summary

Allyl acetoacetate and the acetoacetates of seven other β,γ-unsaturated alcohols have been prepared. The reaction of diketene with the alcohols in the presence of a small amount of the sodium alkoxide affords a satisfactory method for the synthesis of these esters. On heating at temperatures of 170 to 250°, the esters evolved carbon dioxide and produced γ,δ-unsaturated ketones in yields of 23 to 88%. In every case except one the substituted allyl group was inverted, indicating that the reaction proceeds by a cyclic mechanism somewhat analogous to the Claisen rearrangement.

Two β,γ-unsaturated esters of benzoylacetic acid also yielded carbon dioxide and γ,δ-unsaturated ketones on heating, indicating that the reaction may be quite general for allyl-type esters of β-keto acids. The reaction has merit as a synthetic method for certain γ,δ-unsaturated ketones.

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[15] Weinberger, *Ind. Eng. Chem., Anal. Ed.*, **3**, 365 (1931).

[16] Stenzyl and Fichter, *Helv. Chim. Acta*, **20**, 846 (1937). Davies, Dixon and Jones, *J. Chem. Soc.*, 468 (1930) give the m. p. as 160°.

[17] *Cf.* Ipatieff and Schmerling, THIS JOURNAL, **59**, 1056 (1937), for preparation of 2,4-diacetamino derivatives of alkylbenzenes.

[18] This derivative was prepared by Mr. Harold Levy in connection with work to be published later.