was replaced with an acetone bath at room temperature, and 40 ml of ice-water was added very slowly, while the ammonia was evaporated under nitrogen. After most of the ammonia had been removed, the stirrer was stopped, and most of the alcohol was evaporated under vacuum at about 45°. Water (50 ml) was added to the residue to dissolve the salts, and the solution was acidified in the cold to pH 4.5 with a cooled 2 *N* hydrochloric acid solution. After stirring for 1 hr at ice-bath temperature, the crude acid was filtered and dried under high vacuum for 16 hr at 40° to give 0.99 g of crude acid XVIII. Recrystallization from acetone gave the analytical sample of XVIII: mp 141–142° dec; ν_{max}^{KBr} 3450 (hydroxyl group), 2500–2700 (associated OH of acid), 1710 (carboxyl carbonyl), 1680, and 1670 cm^{-1} (dihydroanisole).

Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.13; H, 7.88.

1,2,3,4,4aα,4bβ,5,6,7,9,10,10aβ-Dodecahydro-4β-hydroxy-7-oxo-2α-phenanthrenecarboxylic Acid (XIX).—The foregoing acid XVIII (560 mg) was refluxed under nitrogen for 1 hr in a mixture of 15 ml of tetrahydrofuran and 5 ml of 2 *N* hydrochloric acid. Distilled water (60 ml) was added to the cold mixture, and most of the THF was evaporated under vacuum. The crystalline precipitate was filtered and dried under high vacuum for 16 hr to give 528 mg of crude unsaturated ketohydroxy acid XIX. Recrystallization from acetone gave 450 mg (85%) analytically pure acid: mp 222.5–223°; λ_{max} 240 mμ (ϵ 16,700); ν_{max}^{KBr} 3350 (OH group), 2500–2700 (associated OH of acid), 1699 (carboxyl carbonyl), and 1660 cm^{-1} (α,β-unsaturated keto group).

Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.30; H, 8.01.

Acknowledgment.—The authors wish to express their thanks to Mr. C. Parios for his technical assistance in this investigation. Thanks are also due to Drs. E. Billeter and F. Vane for the nmr, to Dr. V. Toome for the ultraviolet, and to Mr. S. Traiman for the infrared spectroscopic data, and to Dr. A. Steyermark for the microanalyses.

Reactions of α,β-Unsaturated Acid Chlorides with Tertiary Amines

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Received November 2, 1965

Solvolysis of the acyl quaternary ammonium salt (II) formed from 3,3-dimethylacrylyl chloride and trimethylamine gave 3-hydroxy-2-isopropylidene-5-methyl-3,5-hexadienoic acid β-lactone (V) in 62% yield. In the presence of ethyl vinyl ether, the ketene intermediate(s) initially formed underwent cycloaddition to give unsaturated cyclobutanones (VI and VII). Several reactions of V are described.

The dehydrochlorination of an acid chloride through use of a tertiary amine is a classical method for the generation of a ketene.[1] Surprisingly, however, no

$$R_2CH{-}COCl + R_3'N \longrightarrow R_2C{=}C{=}O + R_3'N \cdot HCl$$

report in the chemical literature was found describing the reaction of α,β-unsaturated acid chlorides with tertiary amines.

It was anticipated that dehydrohalogenation might occur by removal of an α-hydrogen atom to yield an alkylidene ketene (A) or, just as likely, by 1,4 elimination to give an α,β-unsaturated ketene (B).

$$R_2CH{-}CH{=}CH{-}COCl \xrightarrow{R_3'N} \begin{array}{c} R_2CH{-}CH{=}C{=}C{=}O \\ \text{A} \\ \text{or} \\ R_2C{=}CH{-}CH{=}C{=}O \\ \text{B} \end{array}$$

Initial experiments were carried out with the readily available *trans*-crotonyl chloride. With tripropyl-, triethyl-, and trimethylamines under a variety of conditions, reaction occurred to give tertiary amine hydrochlorides. However, only a dark viscous polymeric product was obtained, and efforts to trap an unsaturated ketene intermediate with dihydropyran[2] were fruitless.

Substitution of 3,3-dimethylacrylyl chloride (3-methyl-2-butenoyl chloride, (I) for *trans*-crotonyl chloride led to the isolation of a pure product, but not until trimethylamine had been used in place of the unsatisfactory triethyl- and tripropylamines.

Under optimum conditions, a slight excess of dry trimethylamine gas was bubbled into a stirred solution of acid chloride in hexane. The acyl quaternary ammonium salt (II) thus formed precipitated in almost quantitative yield and was pumped free of excess amine and solvent.[3] It was then allowed to stir overnight at room temperature with dry acetone containing a catalytic amount of sodium iodide.[4] Filtration of trimethylamine hydrochloride, followed by concentration and recrystallization, gave a novel dimeric product, 3-hydroxy-2-isopropylidene-5-methyl-3,5-hexadienoic acid β-lactone (V), in 62% yield.

The β-lactone structure V was assigned on the basis of elemental, molecular weight, infrared, and nmr analyses (see Experimental Section). The last, in particular, was useful in distinguishing between V and the alternative β-lactone structures IVa and IVb expected from the dimerization of isopropylideneketene (IIIa) or isopropenylketene (IIIb) unaccompanied by allylic shifts into conjugation (see Chart I).

Lactone V may have been formed to a large extent, if not exclusively, by path b (1,4 elimination) rather than by path a (1,2 elimination), since an isopropenylketene intermediate (IIIb) could be trapped by ethyl vinyl ether to give the cycloaddition product, 3-ethoxy-2-isopropenylcyclobutanone (VI). The latter was isolated by fractional distillation as an approximately 1:1 mixture with its conjugated isomer, VII, to which it isomerized slowly at room temperature.[5] Attempts to isolate a pure sample of VI by glpc trapping were not

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[1] W. E. Hanford and J. C. Sauer, *Org. Reactions*, **3**, 108 (1946).

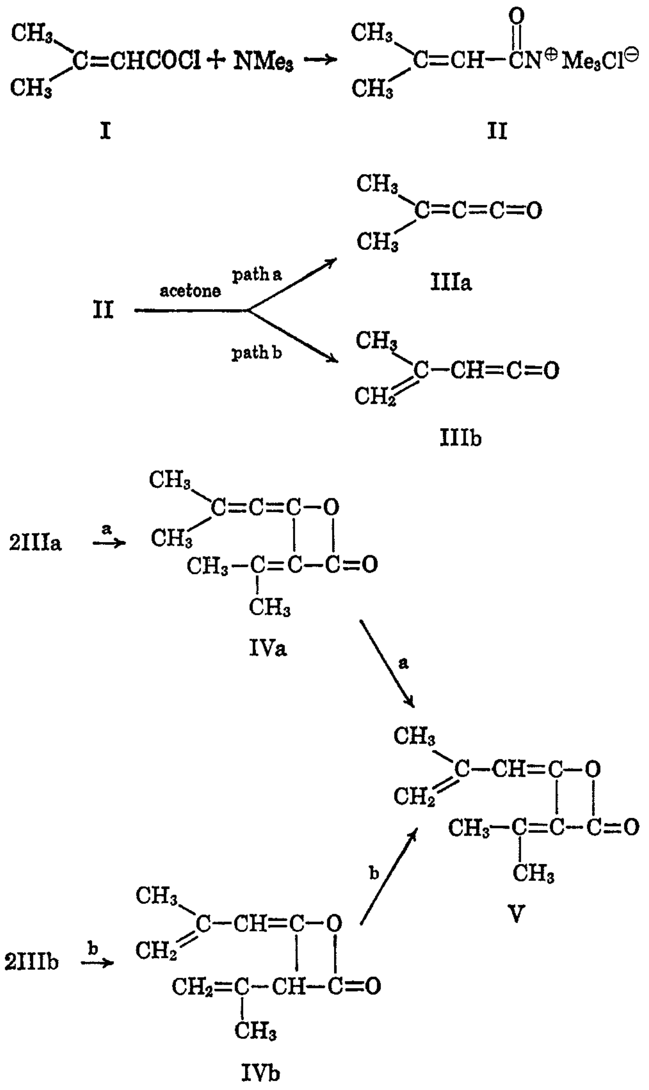
[2] Diphenyl- and dimethylketene react with dihydropyran to give cycloaddition products in high yields. See C. D. Hurd and R. D. Kimbrough, *J. Am. Chem. Soc.*, **82**, 1373 (1960); R. H. Hasek, P. G. Gott, and J. C. Martin, *J. Org. Chem.*, **29**, 1239 (1964).

[3] Since tertiary amines catalyze the polymerization of ketenes (see ref 1), it is important to remove excess amine prior to solvolysis of the salt.

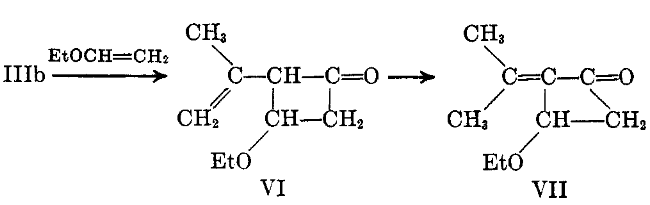
[4] While not essential, the use of sodium iodide shortened the reaction time and afforded somewhat higher yields of V.

[5] In a 3-day period, a 43:57 mixture of VI to VII had, by quantitative nmr analysis, changed to a 17:83 mixture.

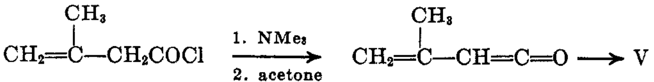
CHART I



successful owing to decomposition on the column. Analytically pure VII was readily secured by fractional distillation and its structure was determined by ultimate, infrared, and nmr analyses.



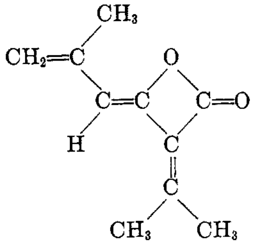
In an alternate synthesis of V, the acyl quaternary ammonium salt obtained from 3-methyl-3-butenoyl chloride (VIII) and trimethylamine was solvolyzed under optimum conditions to give the β-lactone in 20% yield.



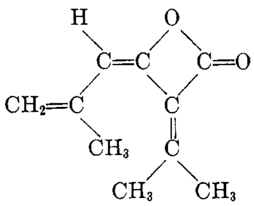
$$CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2COCl \xrightarrow[2.\ acetone]{1.\ NMe_3} CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}C{=}O \longrightarrow V$$

VIII IIIb

Molecular models indicate that the *trans* isomer (Va) would be favored over the *cis* (Vb) owing to the close proximity (in Vb) of the terminal isopropenyl group to one of the isopropylidene methyls.[6]



Va



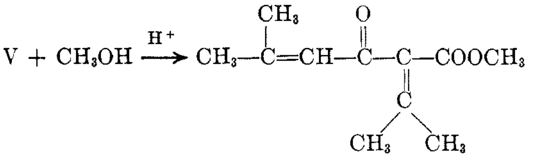
Vb

The dehydrohalogenation procedure used so successfully for the conversion of I to V was applied to a number of other α,β-unsaturated acid chlorides. In all cases, reaction occurred to give trimethylamine hydrochloride. In no instance, however, was a pure monomeric or dimeric ketene isolated. Those compounds investigated were *trans*-crotonyl, α,β,β-trimethylacrylyl, 2- and 3-butenoyl chlorides.

Lactone V was unstable at room temperature. A sample stored under vacuum underwent complete polymerization in less than 36 hr. The friable, pentane-insoluble material thus obtained melted indefinitely above 60° with decomposition. An infrared spectrum of the freshly prepared polymer showed a substantial band at 5.40 μ, thereby indicating residual β-lactone linkages. These gradually disappeared during several days exposure to atmospheric moisture.

When kept in the refrigerator (5°) for several days, the β-lactone suffered a lowering of melting point. It was therefore stored in a freezer at −35°. No change in the material was then observed over a 9-month period.

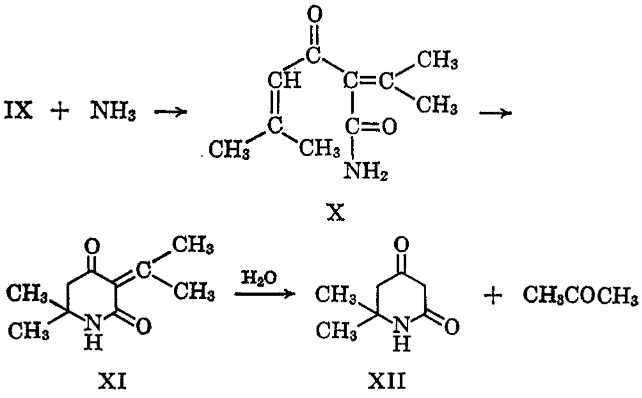
Reactions of β-Lactone V.—Methanolysis of V was best carried out at reflux using a trace of hydrochloric acid as catalyst. After 0.5 hr, distillation gave a 90% yield of methyl 2-isopropylidene-5-methyl-3-oxo-4-hexenoate (IX). In the absence of catalyst, the reaction was incomplete after 15 hr. The same product was formed with or without catalyst.



$$V + CH_3OH \xrightarrow{H^+} CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}\overset{O}{\overset{\|}{C}}{-}\underset{\underset{CH_3\quad CH_3}{C}}{\underset{\|}{C}}{-}COOCH_3$$

IX

Since no pure product was isolated from the reaction of V with aqueous ammonium hydroxide, keto ester IX was shaken with that reagent at 25°. This



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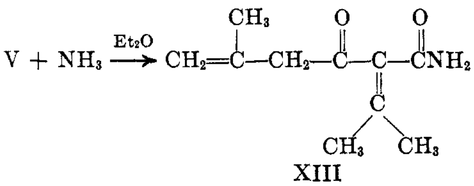
[6] A recent dipole moment study of methylketene β-lactone dimer showed it to have a *trans* configuration. See J. E. Baldwin, *J. Org. Chem.*, **29**, 1882 (1964).

gave 6,6-dimethyl-2,4-piperidinedione (XII) in 53% yield. The formation of XII may have occurred by cyclization of an initially formed keto amide (X), followed by loss of acetone from XI *via* a "retro-Knoevenagel" reaction. As with IX, structure XII was assigned on the basis of elemental, infrared, and nmr analyses (see Experimental Section).

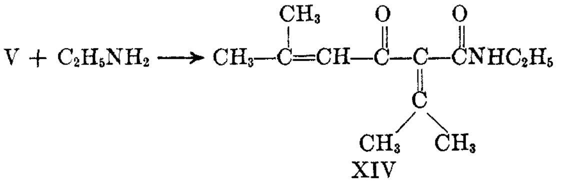
Reaction of V with 1.1 molar equiv of ammonia in ether at 0–5° gave 2-isopropylidene-5-methyl-3-oxo-5-hexenamide (XIII) in 35% yield. Nmr analysis showed the presence of two vinyl protons as a doublet centered at δ 4.8; this ruled out the conjugated isomer (4-hexenamide) as an alternate structure.



$$\mathrm{V + NH_3 \xrightarrow{Et_2O} CH_2{=}C(CH_3){-}CH_2{-}C({=}O){-}C({=}C(CH_3)_2){-}C({=}O)NH_2}$$

XIII

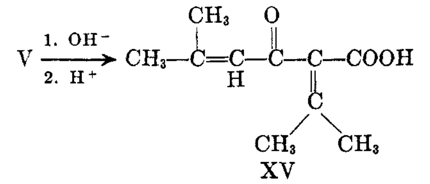
Treatment of V with 1 equiv of ethereal ethylamine at 5–25° afforded N-ethyl-2-isopropylidene-5-methyl-3-oxo-4-hexenamide (XIV) in 80% yield. This shift of the 5,6 double bond into 4,5 conjugation was probably promoted by residual ethylamine. In the above reaction of V with ammonia, a low temperature was maintained until removal of excess amine was complete. This procedure apparently prevented isomerization of the XIII initially formed.



$$\mathrm{V + C_2H_5NH_2 \longrightarrow CH_3{-}C(CH_3){=}CH{-}C({=}O){-}C({=}C(CH_3)_2){-}C({=}O)NHC_2H_5}$$

XIV

Saponification of the β-lactone was effected by shaking a sample with 1 equiv of 2 *N* aqueous sodium hydroxide for 3 hr. Careful acidification liberated an oily solid in 85% yield. Recrystallization resulted in a large loss, but gave a product (37% yield) with analyses in support of 2-isopropylidene-5-methyl-3-oxo-4-hexenoic acid (XV) as the correct structure.



$$\mathrm{V \xrightarrow[2.\ H^+]{1.\ OH^-} CH_3{-}C(CH_3){=}CH{-}C({=}O){-}C({=}C(CH_3)_2){-}COOH}$$

XV

Experimental Section

All melting points were taken with a Thomas–Hoover apparatus using a calibrated thermometer. Nmr spectra were measured with a Varian A-60 instrument, using tetramethylsilane as an internal standard.

3-Methyl-2-butenoyl Chloride (I).—To 300 g (3.0 moles) of 3,3-dimethylacrylic acid (Aldrich) in a dry 2-l., round-bottom flask was added 500 g (4.2 moles) of thionyl chloride. After gas evolution slowed, the mixture was heated under reflux until the internal temperature reached 95°. Removal of excess thionyl chloride at the water pump, followed by fractional distillation, gave 316 g (88% yield) of 3-methyl-2-butenoyl chloride, bp 71–72° (50 mm), $n^{20}\mathrm{D}$ 1.4675.[7]

3-Methyl-2-butenoyltrimethylammonium Chloride (II).—To a dry 1-l., three-neck, round-bottom flask equipped with stirrer, thermometer, drying tube, and a gas-inlet tube were charged 119 g (1.0 mole) of 3-methyl-2-butenoyl chloride and 625 ml of benzene. This mixture was stirred at 10–15° as 65 g (1.1 moles) of trimethylamine was allowed to evaporate from 10 g of potassium hydroxide pellets and flow as a gas through the inlet tube.

After completion of the addition, the mixture was stirred 0.5 hr longer. The precipitated white salt was collected by filtration (rubber dam) and washed with benzene. The yield of vacuum-dried 3-methyl-2-butenoyltrimethylammonium chloride was 167 g (94%), mp 175–200° dec.

Anal. Calcd for $C_8H_{16}ClNO$: C, 54.1; H, 9.1; Cl, 20.0; N, 7.9. Found: C, 53.7; H, 9.2; Cl, 20.7; N, 8.0.

3-Hydroxy-2-isopropylidene-5-methyl-3,5-hexadienoic Acid β-Lactone (V). Method A.—To a dry round-bottom flask were charged 500 ml of dry acetone (dried successively over Drierite and then over Linde Molecular Sieve 4A) and 7.5 g (0.050 mole) of sodium iodide. After solution of the iodide, 89 g (0.50 mole) of II was added in one portion. The mixture was stirred 15 hr at 25° prior to filtration to remove 55.2 g (100% yield) of insoluble salts.

Vacuum concentration of the filtrate at 25° gave 38 g of residue, all but 4.5 g of which was pentane soluble. Crystallization at −30° of the concentrated pentane solution gave 16.1 g (39% yield) of relatively pure product, mp 40–46°. Recrystallization gave 13.0 g with mp 46–48°. A final crystallization afforded pure 3-hydroxy-2-isopropylidene-5-methyl-3,5-hexadienoic acid β-lactone, mp 48–49°.

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.1; H, 7.4; mol wt, 164. Found: C, 72.8; H, 7.4; mol wt, 167 ± 5 (cryoscopic in benzene).

Infrared analysis showed β-lactone carbonyl absorption at 5.40 μ with a shoulder at 5.32 μ. Other significant bands were located at 5.81, 6.00, 6.89, 7.29, 7.58, 7.78, 9.12, 9.45, 9.80, 10.21, 11.37, 11.78, 12.34, and 12.75 μ.

The nmr spectrum (in CCl_4) showed single peaks at δ 1.98 (CH_3, 6 H), 2.16 (CH_3, 3 H), and 5.53 (C=CH, 1 H), and a poorly resolved multiplet centered at δ 4.94 ($C{=}CH_2$, 2 H).

Method B.—To a solution of 60 g (0.50 mole) of 3-methyl-2-butenoyl chloride in 350 ml of dry hexane at 10–12° was added as a dry gas 33 g (0.55 mole) of trimethylamine. After completion of the addition, the suspended salt was stirred 20 min longer at 10°. The gas-inlet tube was replaced by a spray trap and excess amine and solvent were pumped under vacuum into a large Dry Ice cooled trap. To the resulting dry solid was added a solution of 7.5 g of sodium iodide in 400 ml of dry acetone.

After stirring 15 hr at 25°, the mixture was processed as in method A to give 2.0 g of pentane-insoluble material and 23.8 g of β-lactone, mp 40–42°. Claisen distillation of the filtrate gave 7.5 g of fraction A, bp 84–89° (1 mm), 1.7 g of fraction B, bp 110–115° (1 mm), and 5.1 g of residue.

Carbon and hydrogen and infrared analysis of fraction A indicated a 75:25 mixture of β-lactone and 3-methyl-2-butenoic anhydride (*Anal.* Calcd: C, 71.3; H, 7.5. Found: C, 71.3; H, 7.6. Additional carbonyl absorption at 5.63 and 5.85 μ.). Storage of fraction A at 0° gave 1.8 g of β-lactone, mp *ca.* 40°; the total yield of relatively pure β-lactone was therefore 25.6 g (62%).

Recrystallization of 20.0 g of the product from pentane at −30° gave 17.3 g, mp 43–48°, which was pure enough for further reaction.

3-Methyl-3-butenoyl Chloride (VIII).—A solution of 32 g (0.32 mole) of 3-methyl-3-butenoic acid[8] in 65 ml of benzene was treated with 100 g (0.79 mole) of oxalyl chloride. After completion of gassing, the mixture was heated under reflux on the steam bath for 2 hr. Concentration at the water pump followed by fractional distillation gave 21.1 g (55% yield) of 3-methyl-3-butenoyl chloride, bp 60–61° (100 mm).

When the reaction was carried out using excess thionyl chloride at 25° for 15 hr followed by a 15-min reflux, a 32% yield of VI was obtained along with a large dark residue.

Reaction of 3-Methyl-3-butenoyl Chloride with Trimethylamine.—The reaction was carried out as above (method B) using 21.1 g (0.178 mole) of 3-methyl-3-butenoyl chloride, 160 ml of *n*-hexane and 14.2 g (0.24 mole) of trimethylamine. After

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[7] L. I. Smith and V. A. Engelhardt [*J. Am. Chem. Soc.*, **71**, 2671 (1949)] reported bp 59–61° (30 mm).

[8] R. B. Wagner, *ibid.*, **71**, 3214 (1949).

removal of excess amine and solvent under vacuum, the yellow-orange salt was stirred for 15 hr with a solution of 3.0 g of sodium iodide in 200 ml of dry acetone.

Work-up as above gave 21 g of amine salt, 2.5 g of pentane-insoluble material, and a pentane concentrate that gave 2.9 g (20% yield) of product on cooling at −30°. Recrystallization afforded 1.9 g of material, mp 47–48°. This was shown to be identical with the β-lactone prepared from I by mixture melting point (47.5–49°) and superimposable infrared spectra.

3-Ethoxy-2-isopropylidenecyclobutanone (VII).—The quaternary salt prepared as a in method B was allowed to stir at 25° for 3 days with a mixture of 200 ml of dry acetone, 200 ml of dry ethyl vinyl ether, and 5 g of sodium iodide. After filtration to remove amine salt, the filtrate was concentrated under vacuum to a residue. This was shaken with pentane to leave 5 g of insoluble material. Concentration and Claisen distillation of the pentane solution at 0.5 mm gave fraction A, bp 53–79° (31.8 g); fraction B, bp 80–103° (19.2 g); and 3.9 g of residue.

Fraction B represents a 47% yield of product calculated as the β-lactone. An attempt to establish purity by gas chromatography was unsuccessful; the presence of β-lactone was confirmed by recrystallization from pentane to give that product, mp 45–47°.

Redistillation of fraction A through a 0.7 × 50 cm glass spiral-packed column at 5 mm gave fraction C, bp 75–80° (2.7 g, $n^{25}\text{D}$ 1.4649); fraction D, bp 80–81° (5.2 g, $n^{25}\text{D}$ 1.4704); fraction E, bp 81–82° (17.7 g, $n^{25}\text{D}$ 1.4747); and 7.0 g of residue. Fraction E was assigned the structure 3-ethoxy-2-isopropylidenecyclobutanone (23% yield).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.1; H, 9.2; mol wt, 154. Found: C, 70.1; H, 9.2; mol wt, 154.

The infrared spectrum of E showed carbonyl absorption at 5.77 μ and a C=C band at 6.02 μ.[9] The nmr spectrum (in $CDCl_3$) showed a triplet at δ 1.17 ($-OC-CH_3$, 3 H), singlets at δ 1.84 and 2.04 (CH_3, 6 H), a quartet at δ 2.72 ($-CH_2-\overset{|}{C}=O$, 2 H), a quartet at δ 3.48 ($-OCH_2-$, 2 H), and a multiplet centered at δ 4.61 ($O-\overset{|}{\underset{|}{C}}-H$, 1 H).

The infrared spectrum of fraction D showed an additional band at 5.63 μ, indicating the presence of the nonconjugated 3-ethoxy-2-isopropylcyclobutanone as an impurity.[9]

When the experiment was repeated exactly as above except for a decrease in reaction time to 20 hr, the fractional distillation gave fraction C, bp 68–75° (3.0 g, $n^{25}\text{D}$ 1.4577); fraction D, bp 75–81° (4.4 g, $n^{25}\text{D}$ 1.4688); fraction E, bp 81–82° (11.3 g, $n^{25}\text{D}$ 1.4762), and 7 g of residue. After 1 day, fractions C and D were combined and a 5.2-g sample was Claisen distilled at 1 mm and a bath temperature of 60–65° to give a 5.1-g sample (F) with $n^{25}\text{D}$ 1.4645. Infrared analysis showed carbonyl bands of nearly equal intensity at 5.63 and 5.76 μ.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.1; H, 9.2. Found: C, 69.8; H, 9.2.

Nmr analysis ($CDCl_3$) showed a triplet at δ 1.7 ($-OC-CH_3$, 3 H), singlets at δ 1.79, 1.90, and 2.08 ($CH_3C=C$, 4.7 H), multiplets at δ 2.7–3.2 [$-C(=O)CH_2-$, 2 H], 3.3–3.9 ($-OCH_2-$, $-O-CH<$, 2.5 H), and 4.1–4.8 ($C=C-CH-C=O$, $C=C-CH-O-$, 1 H) as well as a peak at δ 4.9 ($H_2C=C-$, 0.5 H). This analysis was in agreement for a mixture containing 57% of 3-ethoxy-2-isopropylidenecyclobutanone (VII) and 43% of 3-ethoxy-2-isopropenylcyclobutanone (VI).

Sample F was allowed to stand at 25° under nitrogen for 3 days in the presence of a trace of hydroquinone. It then showed $n^{25}\text{D}$ 1.4713 and had a greatly decreased carbonyl band at 5.63 μ. A 1.827-g sample was flash-distilled into a Dry Ice cooled trap at 60–70° (bath) and 0.5 mm leaving a residue of only 0.005 g. Nmr analysis of the distillate showed it to contain 83% of VII and 17% of VI.

Methyl 2-Isopropylidene-5-methyl-3-oxo-4-hexenoate (IX).—A solution of 34 g (0.21 mole) of V (mp 38–45°) in 250 ml of methanol containing 1 ml of concentrated hydrochloric acid was heated under reflux for 1 hr. Claisen distillation gave 36.5 g (90% yield) of methyl 2-isopropylidene-5-methyl-3-oxo-4-hexenoate, bp 75–76° (0.5 mm), $n^{25}\text{D}$ 1.4932.

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.3; H, 8.2; carbonyl value, 0.509 equiv/100 g. Found: C, 67.0; H, 8.2; carbonyl value, 0.478 equiv/100 g.

The infrared spectrum showed carbonyl absorption at 5.84 and 6.00 μ (conjugated ester and ketone, respectively) and other significant bands at 6.21, 6.98, 7.27, 7.86, 8.2, 9.08, 9.30, and 9.84 μ.

The nmr spectrum (in CCl_4) showed four singlets at δ 1.8–2.2 (CH_3, 12 H), a singlet at δ 3.66 ($-OCH_3$, 3 H), and a band at δ 6.03 ($-C=CH-$, 1 H).

6,6-Dimethyl-2,4-piperidinedione (XII).—A 5.0-g (0.025-mole) sample of IX was shaken at 25° for 3 hr with 25 ml of concentrated ammonium hydroxide. After filtration to remove a trace of insoluble material, the filtrate was concentrated at the water pump at 40°. Crystallization of the residue from water gave 1.9 g (53% yield) of 6,6-dimethyl-2,4-piperidinedione, mp 178–179°. Recrystallization gave 1.4 g, mp 179–180°.

Anal. Calcd for $C_7H_{11}NO_2$: C, 59.6; H, 7.9; N, 9.9; mol wt, 141. Found: C, 59.7; H, 7.9; N, 10.1; mol wt, 145 ± 5 (ebullioscopic in dichloroethane).

Nmr analysis (in $CDCl_3$) showed three sharp singlets at δ 1.33 (CH_3, 6 H), 2.56 ($-CH_2\overset{|}{C}=O$, 2 H), and 3.20 ($O=\overset{|}{C}-CH_2-\overset{|}{C}=O$, 2 H), and broad NH absorption beyond δ 7.5.

2-Isopropylidene-5-methyl-3-oxo-5-hexenamide (XIII).—To a stirred solution of 4.9 g (0.030 mole) of V in 25 ml of ether at 0–5° was added dropwise 124 ml (0.032 mole) of 0.26 *N* ethereal ammonia. After 1 hr longer at 0°5°, the mixture was filtered to remove 0.4 g of insoluble material. The filtrate was concentrated under vacuum in the cold and the resulting oil was crystallized from chloroform–hexane to give 1.9 g (35% yield) of amide, mp 81–84°. Another crystallization gave 1.4 g, mp 85–87°.

Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.2; H, 8.3; N, 7.7. Found: C, 65.8; H, 8.1; N, 7.7.

An infrared spectrum showed NH_2 band at 2.88 and 2.96 μ and carbonyl absorption at 6.02 μ. The nmr spectrum (in $CDCl_3$, formic acid added) showed peaks at δ 1.74 ($C=C-CH_3$, 3 H) 1.97 [$C=C(CH_3)_2$, 6 H], 3.32 ($-CH_2-\overset{|}{C}=O$, 2 H), 4.83 ($-C=CH_2$, 2 H), and 6.2–7.2 ($O=\overset{|}{C}-NH_2$, 2 H).

N-Ethyl-2-isopropylidene-5-methyl-3-oxo-4-hexenamide (XIV).—To a stirred solution of 1.46 g (8.9 mmoles) of V in 25 ml of ether at 0–5° was added dropwise 3 ml of 2.96 *N* ethereal ethylamine (8.9 mmoles). After 1 hr longer at 25°, the mixture was concentrated on the steam bath and micro Claisen distilled to give 1.5 g (80% yield) of yellow liquid, bp 100° (<1 mm, bath temperature of 125–130°), $n^{25}\text{D}$ 1.5119.

Anal. Calcd for $C_{12}H_{19}NO_2$: C, 68.9; H, 9.2; N, 6.7. Found: C, 68.5; H, 9.1; N, 6.8.

The infrared spectrum showed on N–H peak at 2.93 μ and C=O and C=C bands at 6.03 and 6.22 μ, respectively.

The nmr spectrum (in CCl_4) showed multiplets at δ 0.9–1.3 ($N-C-CH_3$, 3 H), 1.8–2.2 [$C=C(CH_3)_2$, 12 H], and 3.0–3.5 ($-N-CH_2-$, 2 H); also present were peaks at δ 6.23 ($-C=CH-$, 1 H) and 7.5–7.9 ($O=\overset{|}{C}-NH-$, 1 H).

2-Isopropylidene-5-methyl-3-oxo-4-hexenoic Acid (XV).—To a 125-ml glass-stoppered erlenmeyer flask was charged a solution of 2.0 g (0.050 mole) of sodium hydroxide in 25 ml of water and 8.2 g (0.050 mole) of V. After shaking mechanically for 3 hr, the bulk of the solid was in solution. The mixture was then stirred overnight magnetically and filtered to remove a trace of oily material.

Dropwise treatment of the stirred filtrate with 4 *N* hydrochloric acid just until congo red paper turned blue gave 7.7 g (85% yield) of oily solid. Recrystallization from ether–pentane gave 3.3 g, mp 70–80°. This melting point was not sharpened by further treatment; so the once-recrystallized acid was analyzed.

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.9; H, 7.7; neut equiv, 182. Found: C, 65.4; H, 7.7; neut equiv, 184.

The nmr spectrum (in $CDCl_3$) showed singlets at δ 1.94 and 2.21 [$C=C(CH_3)_2$, 12 H], a peak at δ 6.26 ($-C=CH-$, 1 H), and a singlet at δ 11.90 ($-COOH$, 1 H).

Acknowledgment.—The assistance of Mr. J. W. Forbes in interpreting the nmr spectra is gratefully acknowledged.

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[9] J. Conia and J. Sandré [*Bull. Soc. Chim. France*, 744 (1963)] reported bands at 5.73 and 5.95 μ for 2-isopropylidenecyclobutanone and carbonyl absorption at 5.62 μ for 2-isopropenylcyclobutanone.