bonyl but the presence of nitrile (4.42 μ) and hydroxyl (2.95 μ) groups. The crude 3,ω-dihydroxynitrile was dissolved in 30 ml. of 15% ethanol containing 2.50 g. (0.045 mole) of analytical reagent potassium hydroxide, and the clear solution refluxed. After 20 hr. the solution was concentrated to half its original volume and extracted with two 20-ml. portions of ethyl acetate. The resulting aqueous solution was cooled in ice, acidified to pH 1 (hydrion paper) with 37% hydrochloric acid, and extracted with three 25-ml. portions of ethyl acetate. The ethyl acetate solution was dried and removal of the solvent gave the crude acid which was recrystallized from chloroform.

Preparation of *trans*-ω-Hydroxy-α,β-Unsaturated Acids (I).—*trans*-10-Hydroxy-2-decenoic acid (Ia), *trans*-9-hydroxy-2-nonenoic acid (Ib), and *trans*-8-hydroxy-2-octenoic acid (Ic) was prepared by the following method.

A mixture of 0.007 mole of the 3,ω-dihydroxy acid and 10 ml. of acetic anhydride was heated at 150° for 4 hr. Acetic acid was allowed to distil as it formed. The solvent was removed as thoroughly as possible, and the residual oil refluxed for 1 hr. with 50 ml. of 1 *N* alcoholic potassium hydroxide. Water was added, the bulk of the ethanol was removed, and the solution washed with ether and acidified. The aqueous phase was thoroughly extracted with ether, the ethereal phase was washed with water and dried, and the solvent was removed. The acids were recrystallized to constant melting point from diethyl ether–petroleum ether (b.p. 40–60°).

The infrared spectrum ($CHCl_3$) exhibited bands at 5.90, 6.06, and 10.2 μ. In the 60-Mc. n.m.r. spectrum (recorded on a Varian A-60 instrument) of the acids in $DCCl_3$, a doublet centered at δ 5.85 (p.p.m.)., with a *J* value of 18 c.p.s., was observed, indicating the *trans* configuration of the double bond.

Acknowledgment.—The authors wish to acknowledge the support of this project by the National Institutes of Health Grant EF-209, RG 9254, and the Wisconsin Alumina Research Foundation.

The Course of the Michael–Aldol Synthesis. I. The Formation of Cyclopentanediones[1]

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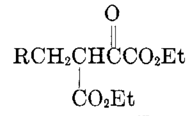
Received March 31, 1964

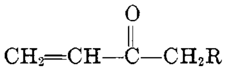
The reaction of ethyl α-ethoxalylpropionate with methyl vinyl ketone (or as reported with the corresponding Mannich base methiodide) in the presence of sodium ethoxide leads not to a cyclohexanedione or cyclohexenone but instead to an acetylcyclopentane-1,2-dione. The structure of this material and its hydrolysis product is discussed and the use of other unsaturated carbonyl compounds is illustrated.

In the course of a projected synthesis of ψ-santonin we wished to prepare the cyclohexenone carboxylic acid, **5a**. The obvious route to such a system appears to be the Michael addition of an enolate to an unsaturated ketone to yield a 1,5-diketone followed by an intramolecular aldol condensation to produce the cyclohexenone. In the case at hand the components of such a sequence would be ethyl α-ethoxalylpropionate (**1a**) and ethyl vinyl ketone (**2b**) or its equivalent. The expected stepwise path to the desired cyclic ketone should then be **1a** + **2b** → **3c** → **4a** → **5a**.



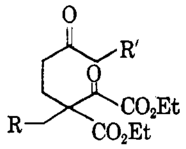
$$\mathrm{RCH_2\underset{\substack{|\\ CO_2Et}}{CH}\overset{\substack{O\\ \|}}{C}CO_2Et}$$

1a, R = H
b, R = CH_3

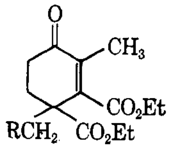


$$\mathrm{CH_2{=}CH{-}\overset{\substack{O\\ \|}}{C}{-}CH_2R}$$

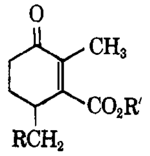
2a, R = H
b, R = CH_3



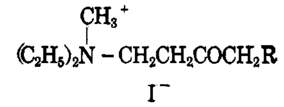
3a, R = R' = H
b, R = R' = CH_3
c, R = H; R' = CH_3



4a, R = H
b, R = CH_3

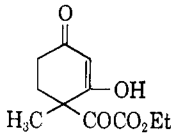


5a, R = R' = H
b, R = CH_3; R' = H
c, R = H; R' = CH_3CH_2



$$\mathrm{(C_2H_5)_2\overset{\substack{CH_3^{\,+}\\ |}}{N}-CH_2CH_2COCH_2R\quad I^-}$$

6a, R = H
b, R = CH_3



7

This general type of synthesis is well documented[3] and in this case two closely similar sequences have been carried out. Martin and Robinson[4] reported the reaction of the sodium salt of **1a** with the Mannich base methiodide **6a**. They isolated in unspecified yield an acidic material for which they suggested the cyclohexanedione **7**. In an almost totally analogous sequence, Büchi and Warnhoff[5a,b] obtained the expected keto acid **5b**, from the homologous starting materials **1b** and **6b**. Neglecting for the moment the validity of the structural assignments of these compounds the following points may be noted. The experimental procedures for the two cases are similar. In each, a sodium alkoxide in benzene–alcohol solution (ethanol in the first example and methanol in the second) is used for the initial condensation. Although **3b** was isolated in a crude form and converted to the cyclic product (**5b**) by treatment with aqueous base, Martin and Robinson effected cyclization of their intermediate by adding a second mole of sodium ethoxide to the solution presumably containing **3a**. Despite these apparently small differences in procedure, the products in the two cases are very different structurally. Elemental analysis alone

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[1] The authors gratefully acknowledge the support of this research by the National Institutes of Health, Grant No. GM 10509-01.

[2] Taken in part from the Ph.D. Thesis of J. A. Hartman, Wayne State University, 1963.

[3] For a review of this subject, see E. D. Ginsburg and R. Pappo, *Org. Reactions*, **10**, 179 (1959).

[4] R. H. Martin and R. Robinson, *J. Chem. Soc.*, 1866 (1949).

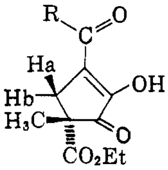
[5] (a) G. Büchi and E. W. Warnhoff, *J. Am. Chem. Soc.*, **81**, 4443 (1959); (b) the authors have kindly supplied us with the details of their experimental procedures.

serves to indicate the difference, since the keto acid **5b** must formally result from the hydrolysis of a cyclization product **4b** that differs from the starting materials (**1b** and **2b**) by the elements of water and methyldiethylamine. In contrast the compound for which **7** is the suggested structure differs from its progenitors by the elements of the trialkylamine and ethanol. With regard to the structures proposed for these materials, the assignment of **5b** is unquestionably correct. For example, the ultraviolet spectrum of **5b** ($\lambda_{\max}^{\text{EtOH}}$ 244 mμ) best fits a cyclohexenone of this substitution pattern. Little experimental evidence is available, however, to support **7**. The material yields a monosemicarbazone and gives a positive ferric chloride test. Although the latter reaction is suggestive of an enolic system (as in **7**) considerations of possible pathways for the sequence lend little credence to the suggested structure. This formulation, for example, requires the condensation of the methyl group of the intermediate **3a** with an unactivated tertiary carbethoxyl. It appears more likely that this condensation would occur with the reactive α-dicarbonyl system.

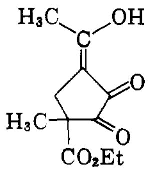
Since we required a method for the preparation of **5a** as a synthetic intermediate, we reinvestigated these reaction sequences to determine the actual structure of the product obtained by Martin and Robinson and to investigate the effect of changes in reaction conditions on the structures of the products. At the outset of this work we utilized the vinyl ketones, **2a** and **2b**, on the basis of their presumed[6] equivalence to the methiodides **6a** and **6b**. The results of these investigations are reported in the present communication.

The sodium salt of ethyl α-ethoxalylpropionate was treated with methyl vinyl ketone in benzene–ethanol solution according to the procedure of Martin and Robinson. Distillation of the crude oily product afforded a crystalline ketonic material, m.p. 52–53.5°, 81% yield. The identity of this solid substance with the liquid one obtained by the previous workers from the reaction of **1a** and **6a** was indicated by the similarity of the melting points of the corresponding semicarbazones. The elemental analyses of the 52–53.5° compound, $C_{11}H_{14}O_5$, and of the above derivative also fit the empirical formulae previously reported, and the crystalline material shows the expected acidic and enolic properties. Examination of the ultraviolet spectrum of the solid ketone demonstrated, however, that **7** could not be the correct structure. The compound exhibits a maximum in ethanol solution at 293 mμ (ε 13,200). Basification of the solution produces a shift to 360 mμ. An enolic system is clearly responsible for this behavior, but these data are incompatible with **7**. A system analogous to the suggested one, cyclohexane-1,3-dione[7] displays a maximum at 255 mμ shifting to 280 mμ in base. We shall show from the following spectral evidence that the condensation product is in fact, the acetylcyclopentane-1,2-dione **8a**.

The infrared spectrum of **8a** in chloroform supports the suggested functionality of the five oxygen atoms. Three carbonyl groups, a nonconjugated ester, a conjugated ketone in a five-membered ring, and an unsaturated methyl ketone are indicated by bands at 1751, 1724, and 1670 cm.$^{-1}$. The remaining oxygen is part of an hydroxyl group giving rise to broadened absorption in the C–H region (2800–3300 cm.$^{-1}$), and the peak for the double bond of the enol system is found at 1600 cm.$^{-1}$. Confirmation of structure **8a** is obtained from consideration of the n.m.r. spectrum. The ethyl ester is found as a typical triplet (τ 8.73), quartet (τ 5.77) pattern. The quaternary ring methyl and the acetyl methyl appear as singlets at τ 8.55 and 7.56. A broad singlet at τ 0.8 is found for the hydroxyl proton. The two remaining protons give rise to an AB quartet at τ 6.79 and 7.48 (J = 18 c.p.s.) and are clearly geminal protons in chemically different environments. One hydrogen (Hb) lies *cis* to the polar carbethoxyl and is presumably responsible for the deshielded low-field pair of the AB quartet. The other "sees" only the ring methyl and the observed pattern is typical of such systems.[8] It is noteworthy that **8a** is a unique structure for the condensation product. Neither the alternative enol **9** nor the triketo form **10** is present in detectable amount. As described above the n.m.r. spectrum is compatible only with **8a**. This conclusion is also supported by the fact that the infrared spectrum of the triketo ester in the solid state (KBr) is identical with the spectrum in solution. Clearly, a tautomeric equilibrium does not occur here. In contrast 2-acetylcyclopentanone displays the spectral properties[9] of both **11** and the enol **12**. The explanation for the unique enol structure of **8a** lies in the fact that both of the alternatives are cyclopentane-1,2-diones. The rigidity of the five-membered ring in cases like these forces the carbonyl dipoles to be coplanar.[10] This unfavorable interaction is overcome only in **8a**.[11]



8a, R = CH_3-
b, R = CH_3CH_2-
c, R = CH_3CH_2O-
d, R = H



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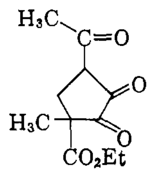

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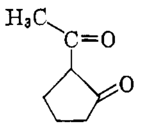

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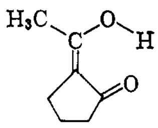

12

Although spectral evidence establishes the structure of the condensation product, we sought corrobrative chemical information. Degradation of **8a** *via* base cleavage proved fruitless since the compound is either converted to its enolate salt or in time destroyed. Concentrated hydrochloric acid at room temperature, however, effects a ready conversion of the keto ester to a new material, m.p. 138–139°. The elemental analysis

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(6) T. A. Spencer, K. K. Schmiegel, and K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 3785 (1963); W. S. Johnson, J. J. Korst, R. A. Clement, and J. Dutta, *ibid.*, **82**, 4623 (1961); J. H. Brewster and E. L. Eliel, *Org. Reactions*, **7**, 99 (1953).

(7) E. R. Blount, V. W. Eager, and D. C. Silverman, *J. Am. Chem. Soc.*, **68**, 566 (1946).

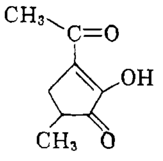
(8) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 89.

(9) A. W. Allen and R. P. A. Sneeden, *Tetrahedron*, **18**, 821 (1962).

(10) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1959, p. 379.

(11) There is still an interaction between two positive carbonyl carbons in **8** as it is a "vinylogous" α-diketone. Since the acyl group may rotate, however, the dipoles need not be coplanar.

of this compound, $C_8H_{10}O_3$, indicates that the net change is the loss of the carbethoxyl function. The resulting triketone is capable of enolization in a number of ways. Excluding all forms which contain an unenolized α-dicarbonyl system we must still consider four possible tautomers, **13**–**16**, for the structure of the hydrolysis product. In fact this substance, in contrast to **8a**, does not exist as a single enol (except in the crystal) and spectral evidence suggests strongly that **14a** and **15** are the favored isomers. The n.m.r. spectrum of the mixture in deuteriochloroform shows no significant resonances at higher field than τ 8.1. This clearly eliminates **13** since the ring methyl in this structure would be expected to give rise to a high-field doublet. The presence of **14a** is demonstrated by the appearance of two multiplets at τ 8.05 and 7.15. The first results from the vinylic ring methyl singlet superimposed on the absorption of the enolized acetyl methyl and this latter band is split by coupling with the ring methylene protons.[12] Since all the substituents lie in the plane of the five-membered ring in **14a**, the methylene hydrogens are in identical chemical environments in contrast to the precursor **8a**. The resonance lines for this group display the usual change[8] in going from two protons of similar chemical shift to protons of identical shift. In addition to these peaks, however, there is present the typical methyl ketone absorption at τ 7.65 and a series of low-intensity bands between τ 6 and 8. This pattern must arise from the presence of **15** and/or **16**. Although **16** cannot be excluded with certainty from consideration of the n.m.r. spectrum, both infrared and ultraviolet data indicate that the singly enolized form **15** is the other component of the tautomeric mixture. The infrared spectrum of the hydrolysis product in chloroform is different from that in the solid state (KBr). The latter shows a single carbonyl band at 1665 cm.$^{-1}$. In solution, however, a second carbonyl appears at higher frequency. The position of this peak, 1724 cm.$^{-1}$, is compatible with the formation of an unenolized acetyl group as in **15**. The presence of **14** and **15** in solution is also reflected in the ultraviolet. In ethanol solution the maximum lies at 270 mμ (ϵ 7850) with a shoulder at 300 mμ (ϵ 5240). As might be expected, the spectrum is roughly equivalent to the combination of the chromophores of **17**[13] (λ_{max}^{EtOH} 259 mμ) and **12** (λ_{max}^{EtOH} 286 mμ). In base, however, the enol mixture is converted to a single anion which absorbs at 357 mμ. It is also noteworthy that the ultraviolet spectrum of a freshly prepared chloroform solution of **14a** shows only a single maximum at 298 mμ. Although we have not followed the change quantitatively, when the solution is allowed to stand for several days the spectrum shifts to the one obtained in ethanol. Again the shift is in the direction of increasing amounts of **15** rather than the more highly conjugated enol **16**, and the low rate of the process is a reflection of the lack of ease of a prototrophic shift in a nonhydroxylic medium. The same process can be observed in the infrared, since the ratio of the two carbonyl peaks again change in the direction of increasing amounts of **15**.



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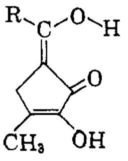
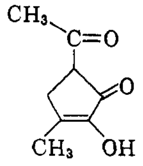


14a, R = CH$_3$
b, R = CH$_3$CH$_2$



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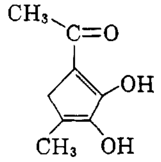

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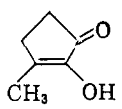

17

To test the generality of the condensation reaction leading to the 1,2-cyclopentandione described above, we investigated the reaction of **1a** with a number of unsaturated carbonyl compounds. Ethyl vinyl ketone, ethyl acrylate, and acrolein reacted readily while with mesityl oxide only starting material was recovered. The products obtained from the first three were all similar in properties to **8a** and are assigned structures **8b**, **c**, and **d**, respectively.[14] The n.m.r. spectra of these materials are in excellent agreement with that of **8a**. In particular, the AB quartet characteristic of the ring methylene group is observed, and in each case only a single enolic form is present. Although the formyl keto ester **8d** was resinified by acid treatment, **8b** was decarbethoxylated by acid hydrolysis to yield a triketone **14b**. The latter as expected closely resembles **14a** and again appears to be a mixture of tautomers. Finally with the diester **8c** we have rigorous confirmation of the cyclopentandione structure since our material proved identical with the same substance prepared by previous workers, by an alternative route.[15a,b] In addition, acid hydrolysis of this compound according to the reported method produced the known 3-methylcyclopentane-1,2-dione (**17**).[15a,b]

The reaction of diethyl α-ethoxalylpropionate with unsaturated carbonyl compounds appears to be a reasonably general method for the synthesis of acylcyclopentandiones and we are studying variations of the reactions described here. The factors which govern the formation of this system *vis a vis* a substituted cyclohexenone will be discussed in the following publication.

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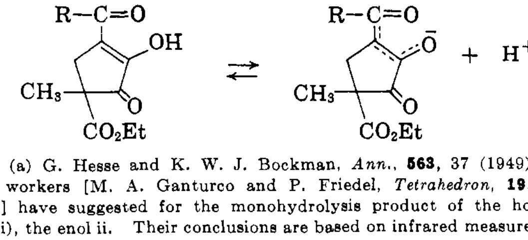
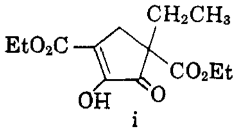
(12) It has been suggested by a referee that the multiplicity of these bands may be a result of having both the *cis* and *trans* forms of **14a** present in solution.

(13) J. Enkvist, B. Alfredsson, M. Merikallio, P. Paakkonen, and O. Jarvella, *Acta Chem. Scand.*, **8**, 51 (1954).

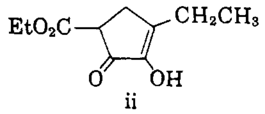
(14) All of these materials show a low-intensity ultraviolet absorption band in neutral 95% ethanol which corresponds to the dissociated anion and which indicates the following equilibrium. Rough estimations from the spectra give K-values $\simeq 10^{-6}$–10^{-7}.



(15) (a) G. Hesse and K. W. J. Bockman, *Ann.*, **563**, 37 (1949). (b) Other workers [M. A. Ganturco and P. Friedel, *Tetrahedron*, **19**, 2039 (1963)] have suggested for the monohydrolysis product of the homolog of **8c** (i), the enol ii. Their conclusions are based on infrared measurements and are in agreement with ours concerning the direction of enolization of the ring carbonyl groups of this system.



i



ii

Experimental

Analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind. Melting points and boiling points are uncorrected. Infrared measurements were made on a Perkin-Elmer Model 137-B Infracord spectrophotometer and ultraviolet measurements on a Cary Model 14 spectrophotometer. N.m.r. spectra were obtained with either a Varian DP 60 or A-60 spectrometer in deuteriochloroform solution with tetramethylsilane as internal standard and resonance positions are given in τ-values.

2-Hydroxy-3-acetyl-5-methyl-5-carbethoxycyclopent-2-enone (8a).—To a chilled solution of 2.3 g. of sodium (0.1 g.-atom) in 50 ml. of absolute ethanol, 20.2 g. (0.1 mole) of ethyl α-ethoxalylpropionate[16] in 25 ml. of dry benzene was added over 20 min. Freshly distilled methyl vinyl ketone (7.1 g., 0.1 mole) was then added dropwise and the solution stirred for 2 hr. at room temperature. After heating at reflux for an additional hour the mixture was left to stand at room temperature overnight. The reaction mixture was then poured onto ice, acidified with 10% hydrochloric acid, and extracted with ether. After washing with water and drying over sodium sulfate, the ether solution was concentrated to give 23.8 g. of an amber oil, b.p. 142–143° (0.7 mm.) [lit.[4] b.p. 138–140° (0.5 mm.)]. Distillation of the material through a small Vigreux column afforded 18.3 g. (81%) of an oil which solidified on standing. Crystallization from ether–hexane gave soft plates: m.p. 52–53.5°; $\lambda_{\max}^{\mathrm{EtOH}}$ 293 mμ (ϵ 13,200), 360 (1200), 360 (13,800) (base); $\nu_{\max}^{\mathrm{CHCl_3}}$ 3448, 1754, 1724, 1667, 1600 cm.$^{-1}$; n.m.r., see Discussion.

Anal. Calcd. for $C_{11}H_{14}O_5$: C, 58.40; H, 6.24. Found: C, 58.68; H, 6.42.

The semicarbazone prepared in the usual manner was recrystallized from ethanol to give colorless prisms, m.p. 204–205° dec. (lit.[4] m.p. 198–201° dec.).

Anal. Calcd. for $C_{12}H_{17}N_3O_5$: C, 50.88; H, 6.05; N, 14.83. Found: C, 50.84; H, 5.94; N, 14.62.

2-Hydroxy-3-propionyl-5-methyl-5-carbethoxycyclopent-2-enone (8b).—Substitution of 8.4 g. (0.1 mole) of ethyl vinyl ketone for the methyl compound in the above procedure led, after distillation, to a pale yellow oil: b.p. 143–145° (0.1 mm.); 14.3 g. (59%); $\lambda_{\max}^{\mathrm{EtOH}}$ 293 mμ (ϵ 11,600), 360 (515), 360 (13,700) (base); $\nu_{\max}^{\mathrm{CHCl_3}}$ 3509, 1754, 1724, 1672, 1600 cm.$^{-1}$; n.m.r., 8.79 (triplet, J = 7 c.p.s.) $\mathrm{CH_3CH_2{-}C{=}O}$, 8.69 (triplet, J = 7 c.p.s.) $\mathrm{CH_3CH_2{-}O{-}}$, 8.53 (singlet) $\mathrm{CH_3{-}C{-}}$, 7.45 and 6.74 (AB quartet, J = 15 c.p.s.) $\overset{\mathrm{H}}{\underset{\mathrm{H}}{>}}\mathrm{C}<$, 7.10 (quartet, J = 7 c.p.s.) $\mathrm{CH_3}\mathit{CH}_2\mathrm{{-}C{-}}$, 5.73 (quartet, J = 7 c.p.s.) $\mathrm{CH_3}\mathit{CH}_2\mathrm{{-}O{-}}$.

The compound was analyzed as its semicarbazone; microcrystals, m.p. 181–181.5°, were obtained from ethanol.

Anal. Calcd. for $C_{13}H_{19}N_3O_5$: C, 52.52; H, 6.44; N, 14.14. Found: C, 52.74; H, 6.68; N, 14.38.

2-Hydroxy-3,5-dicarbethoxy-5-methylcyclopent-2-enone (8c).—The oxalyl ester (**1a**, 20.2 g., 0.1 mole) was added dropwise over 30 min. to a stirred suspension of 2.5 g. (0.102 mole) of granular sodium hydride in 200 ml. of dry benzene. Additional benzene (50 ml.) was then added to disperse the gelatinous precipitate and the mixture was allowed to stand for 3 hr. at room temperature to ensure complete salt formation. The flask was then immersed in an ice bath and 10.1 g. (0.1 mole) of freshly distilled ethyl acrylate in 25 ml. of dry benzene was added. After coming to room temperature and standing overnight, the reaction mixture was heated for 2 hr. on the steam bath. The solvent was removed by distillation and the residual oil was neutralized with acetic acid. After pouring into water acidified with hydrochloric acid, the crude product was extracted with methylene chloride. After drying over sodium sulfate, the solvent was evaporated and the residue (21.3 g.) was distilled over a short path to give 4.29 g. (21%) of **1a** and 10.7 g. (42%) of **8c**, b.p. 125–142° (1 mm.) [lit.[14] b.p. 142° (0.002 mm.)]. The monosodium salt was crystallized from ethanol to give fine needles: m.p. 180–181° dec. (lit.[14] m.p. 179° dec.); $\lambda_{\max}^{\mathrm{EtOH}}$ 282 mμ (ϵ 8950), 343 (2080), 343 (9450) (base); $\nu_{\max}^{\mathrm{CHCl_3}}$ 3390, 1724, 1695, 1661, 1587 cm.$^{-1}$; n.m.r., 8.93 and 8.68 (two triplets, J = 7 c.p.s.) $\mathit{CH}_3\mathrm{CH_2{-}O{-}}$, 8.67 (singlet) $\mathrm{CH_3{-}C{-}}$, 7.71 and 7.06 (AB quartet, J = 15 c.p.s.) $\overset{\mathrm{H}}{\underset{\mathrm{H}}{>}}\mathrm{C}<$; 5.94 and 5.71 (two quartets, J = 7 c.p.s.) $\mathrm{CH_3}\mathit{CH}_2\mathrm{{-}O{-}}$. Hydrolysis of 1.01 g. of the diester by the reported procedure gave 0.26 g. (58%) of 3-methylcyclopentane-1,2-dione, m.p. 101–105°. Crystallization from carbon tetrachloride gave fine needles: m.p. 104–106° (lit.[14] m.p. 106°); $\lambda_{\max}^{\mathrm{EtOH}}$ 259 mμ (ϵ 11,630), 299 (8400) (base); $\nu_{\max}^{\mathrm{CHCl_3}}$ 3390, 3311, 1709, 1658 cm.$^{-1}$; n.m.r.,[17] 8.04 (singlet) $\mathit{CH}_3\mathrm{{-}C{=}C{-}OH}$, 7.66 (singlet) $\mathrm{{-}CH_2{-}CH_2{-}}$, 3.38 (singlet) $\mathrm{{-}C{=}C{-}O{-}}\mathit{H}$.

2-Hydroxy-3-formyl-5-methyl-5-carbethoxycyclopent-2-enone (8d).—The addition of acrolein (5.6 g., 0.1 mole) to the sodium salt of **1a** was carried out as according to the method described for **8a**. The crude product was dissolved in ether and the product (12.3 g., 58%) was precipitated by the addition of hexane. A second crop (3.4 g., 14%) was obtained by crystallization of the material from the mother liquors. Recrystallization from chloroform–hexane afforded colorless prisms: m.p. 102–103°; $\lambda_{\max}^{\mathrm{EtOH}}$ 300 mμ (ϵ 8060), 367 (1690), 3.67 (12,600) (base); $\nu_{\max}^{\mathrm{CHCl_3}}$ 3390, 2850, 1742, 1718, 1681, and 1597 cm.$^{-1}$; n.m.r., 8.74 (triplet, J = 7 c.p.s.) $\mathit{CH}_3\mathrm{CH_2{-}O}$, 8.45 (singlet) $\mathrm{CH_3{-}C{-}}$, 7.40 and 6.62 (AB quartet, J = 17 c.p.s.) $\overset{\mathrm{H}}{\underset{\mathrm{H}}{>}}\mathrm{C}<$, 5.76 (quartet, J = 7 c.p.s.) $\mathrm{CH_3}\mathit{CH}_2\mathrm{{-}OC}$, −0.7 (singlet) $\mathrm{{-}\overset{H}{C}{=}O}$.

Anal. Calcd. for $C_{10}H_{12}O_5$: C, 56.59; H, 5.71. Found: C, 56.63; H, 5.73.

When treated with concentrated or dilute hydrochloric acid, **8d** was converted to a red intractable gum.

2-Hydroxy-3-acetyl-5-methylcyclopentent-2-enone (14a).—The keto ester **8a** (8.9 g.) was dissolved in 250 ml. of concentrated hydrochloric acid and stirred at room temperature overnight. Gas evolution was observed. The red solution was first extracted with methylene chloride, then diluted, partially neutralized with sodium hydroxide, and again extracted with methylene chloride. The combined extracts were dried over sodium sulfate and the solvent was removed to give 4.0 g. of a pale orange solid. Crystallization from chloroform–hexane gave 3.1 g. (51%) of material, m.p. 133–138°. The analytical sample crystallized from methylene chloride as colorless needles: m.p. 138–139°; $\lambda_{\max}^{\mathrm{EtOH\ or\ CHCl_3}}$ 270 mμ (ϵ 7850), 305 (5100), 357 (12,640) (basic EtOH); $\nu_{\max}^{\mathrm{CHCl_3}}$ 3509, 3333, 1724, 1669, 1613 cm.$^{-1}$; n.m.r., see Discussion.

Anal. Calcd. for $C_8H_{10}O_3$: C, 62.39; H, 6.54. Found: C, 62140; H, 6.60.

2-Hydroxy-3-propionyl-5-methylcyclopent-2-enone (14b).—Treatment of 1 g. of the propionyl compound **8b** by the above procedure yielded 0.35 g. (50%) of tannish plates, m.p. 118–124°. Crystallization from chloroform–hexane gave colorless short needles: m.p. 124–125°; $\lambda_{\max}^{\mathrm{EtOH}}$ 268 mμ (ϵ 6730), 305 (340), 355 (10,900) (base); $\nu_{\max}^{\mathrm{CHCl_3}}$ 3521, 3333, 1715, 1667, 1605 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.33; H, 7.23.

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[16] R. F. B. Cox and S. M. McElvain, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 272.

[17] "N.m.r. Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 129.