liquor was chromatographed on 300 g of silica gel. Nonpolar material was eluted with 50% benzene–ether to give 1.04 g of **1b**, followed by mixed fractions and, finally, 2.68 g of 3β-(23*R*)-diacetoxy-(20*S*)-hydroxy-(22*R*,25*R*)-5α-spirostan-12-one (**2b**), eluted with 20% chloroform–ether. An analytical sample was recrystallized from methanol: mp 288–289°; $[\alpha]_D$ −21°; ir ν_{max} 3510 cm^{-1} (OH), λ_{max} 2.86 (OH), 5.77, 8.10 ($OCOCH_3$), 5.85 (C=O), spiroketal bands, 10.78 (s), 10.99 (s), 11.10 (w), and 11.41 μ (w); nmr τ 9.22 (d, *J* = 6 Hz, CH_3-27), 9.10 (CH_3-19), 8.80 (CH_3-18), 8.67 (CH_3-21), 8.02 ($OCOCH_3$-3), 7.92 ($OCOH_3$-23), and 5.08 (t, *J* = 2.2 Hz, H-23).

Anal. Calcd for $C_{31}H_{46}O_8$: C, 68.11; H, 8.48. Found: C, 68.49; H, 8.43.

3β-(23*R*)-Diacetoxy-(22*R*,25*R*)-5α-spirost-20(21)-en-12-one (4).—To a solution of 0.5 g of **2b** in 20 ml of pyridine at 0° was added 2.5 ml of thionyl chloride, dropwise with stirring. The mixture was allowed to stand at room temperature for 2 hr, poured over ice, extracted with ether, and washed with sodium bicarbonate and water. The residue was recrystallized from methanol to give 0.45 g of **4**: mp 281–283°; $[\alpha]_D$ −1.0°; ir λ_{max} 5.77, 8.10 ($OCOCH_3$), 5.85 (C=O), spiroketal bands, 10.81 (w), 10.91 (s), 11.02 (s), 11.14 (m), and 11.49 μ (m); nmr τ 9.20 (d, *J* = 6 Hz, CH_3-27), 9.09 (CH_3-19), 8.89 (CH_3-18), 8.01, ($OCOCH_3$-3), 7.92, ($OCOCH_3$-23), 5.08 (t, *J* = 2.2 Hz, H-23), and 4.58 (m, =CH_2-21).

Anal. Calcd for $C_{31}H_{44}O_7$: C, 70.43; H, 8.39. Found: C, 70.86; H, 8.58.

3β-Acetoxy-(22*R*,25*R*)-5α-spirost-20(21)-en-12-one (3).—The same procedure as the preparation of **4** was followed, using 0.5 g of **1b**, 20 ml of pyridine, and 2.5 ml of thionyl chloride. The residue was recrystallized from methanol to give 0.23 g of **3**: mp 229–232°; $[\alpha]_D$ +19°; ir λ_{max} 5.77, 8.10 ($OCOCH_3$), 5.85 (C=O), spiroketal bands, 10.22 (s), 10.95 (m), 10.87 (m), 11.04 (s) and 11.55 μ (m); nmr τ 9.20 (d, *J* = 6 Hz, CH_3-27), 9.09 (CH_3-19), 9.04 (CH_3-18), 8.00 ($OCOCH_3$-3), and 5.76 (m, =CH_2-21).

Anal. Calcd for $C_{29}H_{42}O_5$: C, 74.01; H, 8.99. Found: C, 73.79; H, 8.77.

Treatment of 3β-Acetoxy-(20*S*)-hydroxy-(22*R*,25*R*)-5α-spirostan-12-one with Peracid.—A solution of 0.4 g of **1a**, 0.4 g of *m*-chloroperbenzoic acid, and 0.4 g of *m*-chlorobenzoic acid in 50 ml of methylene chloride was stirred at room temperature, in the dark, for 5 days. The reaction was quenched by washing with a saturated sodium bisulfite solution, saturated sodium bicarbonate, and water. The residue (0.43 g) was acetylated in 2 ml of acetic anhydride and 10 ml of pyridine. The resulting acetate was recrystallized from methanol to afford 0.18 g of **1b**. The mother liquor was chromatographed on 15 g of silica gel. Upon elution with benzene–40% ether, 0.02 g of **1b** was obtained. Then 0.07 g of a mixed fraction was obtained, followed by 0.05 g of an unknown substance eluted with 20% chloroform–ether.

Registry No.—**2b**, 23405-42-7; **3**, 23405-43-8; **4**, 23405-44-9.

Thermal Decomposition of β-Hydroxy Esters. Ethyl-3-hydroxy-3-methylbutanoate

B. L. Yates and J. Quijano

Departamento de Química, Universidad del Valle, Cali, Colombia

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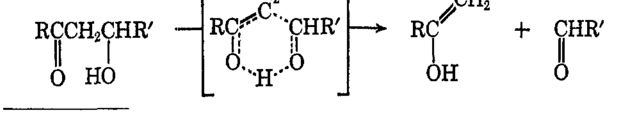
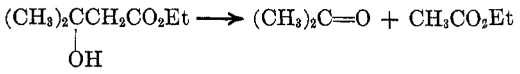
From recent studies[1] on the mechanism of the thermal decomposition of β-hydroxy ketones, it has been proposed that the reaction involves a cyclic six-membered transition state.



An obvious extension to this work would be to examine the thermal decomposition of β-hydroxy esters to see if they decompose by a similar mechanism. If such is the case, it would be predicted that the β-hydroxy ester ethyl 3-hydroxy-3-methylbutanoate would pyrolyze to acetone and ethyl acetate.



$$(CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}CH_2CO_2Et \longrightarrow (CH_3)_2C{=}O + CH_3CO_2Et$$

A literature search has indicated that, as far as can be ascertained, the thermal decomposition of β-hydroxy esters has not previously been studied. Accordingly, a study has been carried out on the thermal decomposition of ethyl 3-hydroxy-3-methylbutanoate, which was prepared by a Reformatsky reaction between ethyl bromoacetate and acetone.[2] The pyrolyses were carried out in xylene solution in sealed glass tubes that had been carefully washed to remove all traces of acid or base, and the products of the reaction were analysed by gas chromatography, using a 5-ft column of SE-30 on Chromosorb W.

It was found that in xylene solution ethyl 3-hydroxy-3-methylbutanoate did indeed decompose at temperatures of 180–250° to give acetone and ethyl acetate in yields of 90–95%. The products of the reaction were characterized both by their glpc retention times and in the case of acetone by the formation of a 2,4-dinitrophenylhydrazone, mp 127–8° (after crystallization), from the products of pyrolysis. (The reported melting point of the 2,4-dinitrophenylhydrazone of acetone is 128°.[3]) In the gas chromatography of the products of pyrolysis apart from the solvent peak (xylene) only peaks due to acetone and ethyl acetate were observed. The yields were calculated using glpc by comparison of the peak areas of the products of pyrolysis with those of a known mixture of ethyl acetate and acetone in xylene using benzene as an internal standard. In tubes that were not carefully washed some dehydration occurred as evidenced by the appearance of a new peak due to water in the gas chromatograph of the pyrolysis products.

The kinetics of the decomposition were followed by the methods used in the earlier study.[1a] The reaction was followed to at least two half-lives at 217.8 and 206.0° and one half-life at 191.4 and 179.4°. Good first-order kinetics were observed, the first-order plots being linear for all the periods during which the reaction was followed. The rate constants obtained are listed in Table I, and were found to be reproducible to within ±5%. Equal rate constants were obtained when the reaction was followed by the rate of appearance of the

TABLE I

RATE CONSTANTS FOR THE PYROLYSIS OF ETHYL 3-HYDROXY-3-METHYLBUTANOATE

	Temperature, °C			
	179.4	191.4	206.0	217.8
$k \times 10^6$, sec^{-1}	0.269	0.812	2.76	6.88

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[1] (a) B. L. Yates and J. Quijano, *J. Org. Chem.*, **34**, 2506 (1969); (b) G. G. Smith and B. L. Yates, *ibid.*, **30**, 2067 (1965).

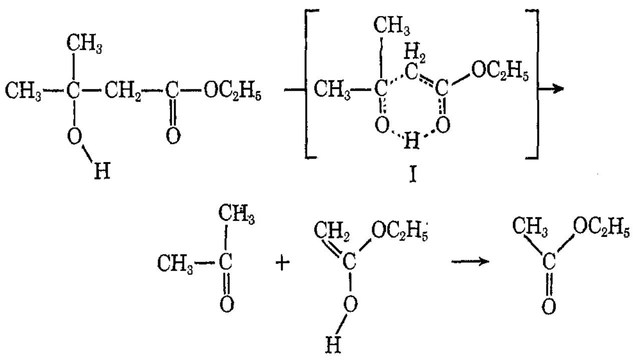
[2] V. Hartmeann and H. Buenger, *Justus Liebigs Ann. Chem.*, **667**, 35 (1963).

[3] A. I. Vogel "Practical Organic Chemistry," Longmans, Green and Co., London, 1957, p 346.

acetone and of the ethyl acetate as well as by the rate of disappearance of the β-hydroxy ester. In the gas chromatography of the products of the reaction no peak due to ethylene was observed indicating that a possible side reaction, the pyrolysis of the ester involving the OC_2H_5 group, takes place to a negligible degree at the temperature of the reaction.

Varying the initial ester concentration over 1, 2, 4, and 8% by volume did not affect the velocity of the pyrolysis as evidenced by observed rate constants at 206.0° of 2.65, 2.80, 2.76, and 2.62 $\times 10^{-6}$ sec^{-1}. Packing the reaction tubes with glass wool which increased the surface area by a factor of at least 15 gave a rate constant of 2.60 $\times 10^{-6}$ at 206.0°, compared to 2.76 $\times 10^{-6}$ sec^{-1} in an unpacked vessel.

These results indicate that the reaction is homogeneous and of first-order. This taken together with the products of the reaction and the negative entropy of activation, which is typical of those reactions that are thought to involve cyclic transition states,[4] suggests that the pyrolysis of ethyl 3-hydroxy-3-methylbutanoate involves the cyclic six-membered transition state I.



Furthermore, the fact that the pyrolysis of ethyl 3-hydroxy-3-methylbutanoate has proved to follow the course predicted from the results obtained from the work on the β-hydroxy ketones strongly suggests that a similar mechanism is involved in the pyrolysis of both types of compounds. A comparison of the rate of pyrolysis in xylene solution of ethyl 3-hydroxy-3-methylbutanoate with that of the analogously substituted β-hydroxy ketone, 4-hydroxy-4-methyl-2-pentanone, reveals however that the β-hydroxy ester tends to pyrolyze more slowly than the β-hydroxy ketone, the respective rates at 206.0° being 2.76 $\times 10^{-6}$ and 1.00 $\times$ 10^{-3} sec^{-1}. This could perhaps reflect the greater difficulty of formation of the enol form of ethyl acetate than that of acetone.[5] It is interesting that in the analogous case of ester pyrolysis, in which reaction an intermediate enol form is not required, carbonates ($ROCOOCH_2CH_2R$) tend to pyrolyze more rapidly than the corresponding ester ($RCOOCH_2CH_2R$).[6]

The results of the present study would thus seem to indicate that the pyrolysis of β-hydroxy esters involves a cyclic six-membered transition state similar to those proposed for various other thermal decomposition reactions, for example, the pyrolysis of esters,[4] β-hydroxy olefins,[7] β,γ-unsaturated acids,[8] and β-hydroxy ketones.[4]

Registry No.—Ethyl 3-hydroxy-3-methylbutanoate, 18267-36-2.

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(6) G. G. Smith and B. L. Yates, *J. Org. Chem.*, **30**, 434 (1965); G. L. O'Conner and H. R. Nace, *J. Amer. Chem. Soc.*, **75**, 2118 (1953).

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(8) G. G. Smith and S. E. Blau, *J. Phys. Chem.*, **68**, 1231 (1964).