ture was controlled by adjusting the rate of addition to the peracid. After a short time, a white precipitate of benzoic acid appeared. The reaction mixture was stirred overnight and then made basic with a 15% solution of sodium carbonate. The heavy organic layer was separated and distilled to yield 29 g. (>88%) of **1h**). The elemental analyses of **1g**, **1h**, and the new aziridines are given in footnotes to Table I.

1,2,3-Trialkylaziridines.—Treatment of the oxiranes with aqueous solutions of primary amines using appropriate modifications of the conditions described for the reaction of methylamine and **1f** gave amino alcohols in better than 60% yield. Reactions with **1a–d** were carried out at or below room temperature for 3–7 days; reactions with **1g** and **1h** were carried out in a manganese steel bomb at 100–110° for 48 hr. Each amino alcohol was converted to its corresponding aziridine *via* the sulfate ester as described for the preparation of **2f**[5] except that the sulfate ester was not heated above 140°. Yields exceeded 50%. The purity of the aziridines was assayed by g.l.p.c. with the same columns used to assay the oxiranes, and examination of their n.m.r. and infrared spectra showed further that contamination with amino alcohols or unsaturated isomers was insignificant.

Conversion of *threo*-3-Methylamino-2-butanol to 2a and 2b.—The amino alcohol, b.p. 151–155° (42 g., 0.41 mole), prepared from *cis*-2,3-dimethyloxirane (**1a**) and methylamine was treated with 2 equiv. of sulfuric acid. The mixture was heated gradually at water pump pressure to 190° and held at that temperature for 12 hr. The brown glass that resulted, which failed to crystallize at room temperature, was treated with excess 7 *N* sodium hydroxide. The reaction mixture was steam distilled until the head temperature reached 100°. The distillate was saturated with sodium hydroxide, and the ammoniacal organic phase was separated and dried with sodium hydroxide. Distillation gave two major fractions. The first fraction, b.p. 61–62°, weighed 16 g. (44%) and was 97.5% **2a**; the second fraction, b.p. 72–73°, weighed 7 g. (19%) and was 95% **2b**. The major contaminant in each fraction was the other isomer. When the sulfate ester prepared from the same amino alcohol was heated to <140° prior to treatment with base, the product contained less than 1.5% **2b**.

The stereospecificity of the conversion of the amino alcohol from **1c** and methylamine to **2c** was also destroyed by heating the sulfate ester to >170° for 8 hr.

Kinetics and Mechanism of Acid-Catalyzed Enol Ester Hydrolysis

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The acid-catalyzed hydrolysis rates of several enol esters have been measured in 50 wt. % aqueous dioxane. Relative rate at 65°, activation enthalpy (kilocalories per mole), and activation entropy (entropy units) are as follows: vinyl acetate, 1.00, 15.5, 0.7; vinyl propionate, 0.77, 13.2, −6.7; vinyl butyrate, 0.46, 14.8, −3.0; vinyl pivalate, 0.06, 22.7, 16.4; and isopropenyl acetate, 0.78, 16.8, 4.0. The mechanistic implications of the data are discussed.

In spite of the vast accumulation of data on free-radical reactions of enol esters, no studies have appeared on the mechanism of acid-catalyzed enol ester hydrolysis. Only recently has kinetic information been published on the basic hydrolysis of a few select enol esters and the results indicated no unusual features.[1]

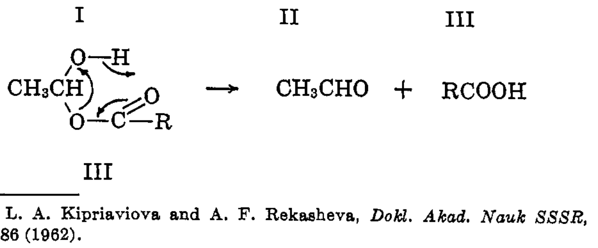
Our initial interest was focused on the mechanism of acid-catalyzed hydrolysis of cyclopropyl esters, since the possibility exists for a rate-determined ring opening of the cyclopropyl group followed by expulsion of acetaldehyde and an acyl carbonium ion.[2,4] Because many reactions of vinyl and cyclopropyl groups are similar[5,6] it was reasonable to suppose that enol esters might exhibit unique or unusual behavior during acid hydrolysis. Evidence will be presented which clearly eliminates either rapid reversible or rate-determined protonation of the olefin in the mechanistic sequence.

Results

The rate constants for acid-catalyzed hydrolysis of several vinyl esters were determined by acid titration of aliquots from sealed ampoules (see Experimental) and are tabulated in Table I. The rate law is pseudo first order and exhibited no sign of reversibility. The data for vinyl acetate at 65° clearly indicate that the reaction is first order in hydronium ion. The relative rates at 65° are tabulated in Table II and a summary of the activation parameters appears in Table III.

Discussion

The finding that the sulfuric acid catalyzed hydrolysis of vinyl acetate in aqueous dioxane containing O^{18}-enriched water produced no isotopic enrichment in the product acid clearly indicates that the hydrolysis mechanism involves exclusive vinyl–oxygen cleavage.[7] Although protonation of the ether oxygen atom with subsequent cleavage to a vinyl carbonium ion is a formal possibility, the well-known inertness of vinyl and phenyl halides toward solvolysis[8] would preclude this path in favor of an initial hydration of the double bond followed by a sequence of steps outlined below without any specific implications about the details of the conversion of I to II, *vide infra*. The kinetic in-



$$H_2C{=}CHOC(=O)R \xrightarrow{H_3O^+} CH_3CH(\overset{+}{O}H_2)OC(=O)R \rightleftarrows CH_3CH(OH)OC(=O)R$$

I II III

$$CH_3CH(OH)OC(=O)R \longrightarrow CH_3CHO + RCOOH$$

III

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[1] C. H. DePuy and L. R. Mahoney, *J. Am. Chem. Soc.*, **86**, 2653 (1964).

[2] The first step of such a mechanism has an analogy in the ring-opening reactions of cyclopropanols in the presence of acids.[3]

[3] C. H. DePuy and F. W. Breitbeil, *J. Am. Chem. Soc.*, **85**, 2176 (1963).

[4] The mechanism of acid-catalyzed cyclopropyl ester hydrolysis will be the subject of a separate paper.

[5] C. A. Coulson and W. F. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

[6] A. O. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

[7] L. A. Kipriaviova and A. F. Rekasheva, *Dokl. Akad. Nauk SSSR*, **144**, 386 (1962).

[8] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 153.

TABLE I

RATE DATA FOR ACID HYDROLYSIS OF ENOL ESTERS IN 50 WT. % AQUEOUS DIOXANE

Compd.	Temp., °C.[a]	$[H^+]_{initial}$	k_1, sec.$^{-1}$[b]	k_2, l./mole sec.[b,c]
Vinyl acetate	40	0.1313	3.99×10^{-5}	3.04×10^{-4}[d]
Vinyl acetate	55	0.1055	1.025×10^{-4}	9.72×10^{-4}
Vinyl acetate	65	0.1313	2.63×10^{-4}	2.00×10^{-3}
Vinyl acetate	65	0.0699	1.44×10^{-4}	2.06×10^{-3}
Vinyl acetate	65	0.0439	8.56×10^{-5}	1.95×10^{-3}
Vinyl propionate	55	0.1055	8.64×10^{-5}	8.19×10^{-4}
Vinyl propionate	65	0.1313	2.02×10^{-4}	1.54×10^{-3}
Vinyl butyrate	55	0.1313	5.98×10^{-5}	4.55×10^{-4}[e]
Vinyl butyrate	65	0.1313	1.20×10^{-4}	9.12×10^{-4}[d]
Vinyl pivalate	55	0.1313	7.43×10^{-6}	5.66×10^{-5}
Vinyl pivalate	65	0.1313	1.59×10^{-5}	1.21×10^{-4}
Vinyl pivalate	75	0.1313	4.61×10^{-5}	3.51×10^{-4}[f]
Isopropenyl acetate	55	0.1055	7.48×10^{-5}	7.09×10^{-4}
Isopropenyl acetate	65	0.1313	2.04×10^{-4}	1.55×10^{-3}

[a] Variation in temperature was ≤±0.05°. [b] All rate constants were determined by the method of least squares. [c] Least-squares probable error is ≤0.6% for all runs except those of vinyl pivalate at 55 and 75° for which the error is ≤±7%. Except where indicated, all values represent the average of two or more runs with an average deviation of ≤2%. [d] Single determination. [e] Average deviation for three runs was ±3%. [f] Average deviation for two runs was ±4.5%.

TABLE II

RELATIVE HYDROLYSIS RATES AT 65°[a]

Compd.	k_2, l./mole sec.	k_{rel}
Vinyl acetate	2.00×10^{-3}	1.00
Vinyl propionate	1.54×10^{-3}	0.77
Vinyl butyrate	9.12×10^{-4}	0.46
Vinyl pivalate	1.21×10^{-4}	0.06
Isopropenyl acetate	1.55×10^{-3}	0.78

[a] In 50 wt. % aqueous dioxane and 1 *N* HCl.

TABLE III

SUMMARY OF ACTIVATION PARAMETERS[a]

Compd.	ΔH^*, kcal./mole[b]	ΔS^*, e.u.[b]
Vinyl acetate	15.5	+0.7
Vinyl propionate	13.2	−6.7
Vinyl butyrate	14.8	−3.0
Vinyl pivalate	22.7[c]	+16.4[c]
Isopropenyl acetate	16.8	+04.0

[a] Values were determined from rate data at three temperatures for vinyl acetate and two temperatures for the remaining compounds. [b] The average deviation for ΔH^* and ΔS^* is ±0.5 kcal./mole and ±0.9 e.u., respectively. [c] These values were determined using the data at 65 and 75° and represent a maximum estimate due to the apparent curvature in the plot of ln k/T *vs.* $1/T$ (see Experimental).

TABLE IV

ACID HYDROLYSIS OF ETHYL ESTERS[a] IN 70% ACETONE–WATER AT 44.7°

Compd.	log pZ	E	$k \times 10^4$
Acetate	7.53	16.2	24.7
Propionate	7.46	16.2	20.7
Butyrate	7.11	16.5[b]	10.8
Pivalate	. . .	≥19[b]	1.1

[a] See ref. 10. [b] H. A. Smith and J. H. Steel, *J. Am. Chem. Soc.*, **63**, 3466 (1941).

formation obtained in this study is entirely consistent with such a mechanistic path and provides additional information on the nature of the rate-determining step.[9]

Consider the rate information tabulated in Table II. Although only a small rate decrease (23%) is observed upon comparison of vinyl acetate and vinyl propionate, a further decrease by a factor of *ca.* 1.7 is observed for vinyl butyrate. Acid-catalyzed hydrolyses carried out in 70% acetone (Table IV[10]) at 44.7° indicate a similarity in the hydrolysis rates of ethyl acetate and propionate with a decrease by a factor of *ca.* 2 for ethyl butyrate, consistent with the steric influence of the alkyl chain as designated by Newman in his rule of six.[11] Such an effect is clearly indicated for the acid-catalyzed hydrolysis of vinyl esters.

The rate ratio of 16.7 between vinyl acetate and pivalate (Table II) compared with the ratio of 22.5 between ethyl acetate and pivalate (Table IV)[12] is in accord with the previously mentioned observations.

That rapid reversible protonation of the carbon–carbon double bond does not occur under the conditions of our kinetic experiments (*ca.* 0.1 *N* acid)[13] was clearly shown by the absence of deuterium incorporation into isopropenyl acetate recovered from a hydrolysis reaction carried out to the extent of 23%[15] in 50 vol. % dioxane–deuterium oxide at pH 1. Furthermore, one observes a small rate decrease on going from vinyl to isopropenyl acetate, a result that is clearly inconsistent with a rate-determined protonation of the olefin to form a carbonium ion.[17] In addition, the slower rate of hydrolysis for isopropenyl acetate is attributed mostly to an enthalpy factor (Table III).

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(9) The path for the breakdown of III to products was suggested by a referee and, although our data provide no direct evidence about this step, one would expect the ester of a hemiacetal to be quite reactive.

(10) G. Davies and D. P. Evans, *J. Chem. Soc.*, 339 (1940).

(11) M. S. Newman, *J. Am. Chem. Soc.*, **72**, 4783 (1950).

(12) Because these rate ratios were measured in aqueous dioxane and aqueous acetone, respectively, no rigorous comparison can be made between the two values.

(13) In concentrated deuteriosulfuric acid at room temperature, vinyl proton exchange is too rapid to measure by observing a change in relative peak area (n.m.r.) as a function of time.[14]

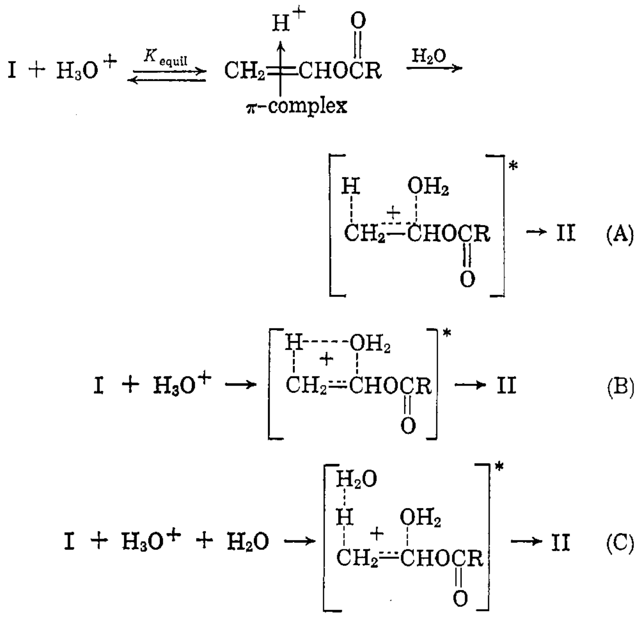
(14) J. A. Landgrebe, *J. Org. Chem.*, **30**, 2105 (1965).

(15) Although the extent of reaction is not large, deuterium incorporation should be easily observed because proton expulsion from the deuterated ester is favored by a statistical factor of 5 to 1 as well as a kinetic isotope effect of *ca.* 2 to 1.[16]

(16) V. J. Shiner, *J. Am. Chem. Soc.*, **75**, 2927 (1953).

(17) Studies of the hydration of olefins by Taft,[18] in which a considerable amount of diverse evidence is explained by assuming a rapid reversible equilibrium to a π-complex which rearranges in the slow step to a carbonium ion like transition state, have shown a reactivity order of ethylene ≪ propylene ≪ isobutylene.[18d]

(18) (a) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 5372 (1952); (b) R. W. Taft, Jr., E. L. Purlee, P. Riesz, and C. A. De Fazio, *ibid.*, **77**, 1584 (1955); (c) E. L. Purlee and R. W. Taft, Jr., *ibid.*, **78**, 5807 (1956); (d) P. Riesz, R. W. Taft, Jr., and R. H. Boyd, *ibid.*, **79**, 3724 (1957); (e) R. H. Boyd, R. W. Taft, Jr., A. P. Wolf, and D. R. Christman, *ibid.*, **82**, 4729 (1960), and references cited therein.



The above data would appear to be consistent with any of several reasonable mechanistic paths. For example, one might envision a rate-determined attack by water on a reversibly formed π-complex (path A) or slow addition of hydronium ion to the olefin (B or C.)

In comparing the hydration of vinyl esters with that of simple olefins, one would not necessarily expect an identical rate-determining step, since it has been pointed out that, as the stability of the carbonium ion formed by protonation of the olefin becomes greater, the transition state for hydration of the olefin will come to resemble an oxonium ion.[18c,19,20] This idea is born out by the observation that, while the slow step for hydration of simple olefins has been intepreted as the formation of a carbonium ion,[17] the different acidity dependence found for the hydration of crotonaldehyde has been explained by assuming a rate-determined attack on the protonated substrate.[18a] The well-known stability of oxocarbonium ions[21] would suggest that rate-determined attack by water in the hydration of vinyl esters is a very reasonable possibility. It is of interest that a similar slow step which involves the rate-determined attack of water on a protonated carbonyl group has been postulated in the mechanism for acid-catalyzed hydrolysis of simple aliphatic esters.[22]

The activation parameters are of particular significance since a plot of activation enthalpy *vs.* activation entropy (Figure 1) is linear[23] with a slope of 409°K. ($r = 0.98$); however, a plot of ln k/T *vs.* $1/T$ for all four compounds[24] shows four lines with multiple intersection points, clearly indicating that the slope of the original enthalpy–entropy plot does not represent a true isokinetic temperature.[25,26] This fact should not in any way alter the significance of such a linear relationship.

The relatively small range of rate constant values (a factor of *ca.* 2) for the four compounds indicated in Figure 1 is readily explained by the compensation of increased activation enthalpy by a more positive activation entropy. If one assumes that the rate-determining step is the attack of water on a π-complex (path A),[27] an increased activation enthalpy would imply a more advanced transition state and therefore a more tightly bound water molecule. If the newly forming carbon–oxygen bond becomes shorter as one precedes from vinyl propionate to isopropenyl acetate (Figure 1), one would expect more extensive charge delocalization onto the oxygen atom and this should result in a more loosly solvated transition state which would correspond to a more positive activation entropy. Although entropy changes in the solvent layer are of great importance, the net negative entropy of activation observed for the hydrolysis of vinyl propionate and vinyl butyrate clearly indicates the significance of other factors which are not easily evaluated. A comparison of acid-catalyzed enol ester and enol ether hydrolysis data indicates that the mechanistic paths are not the same, in opposition to the assumption made by Kiprianova and Rekasheva.[28] Evidence is available for the relative ease of addition of electrophilic entities to the double bonds of enol ethers,[29,30] but more recent deuteration studies on various conjugated dienol ethers have clearly indicated that the proton addition step is rate determining with subsequent rapid attack by water.[31,32]

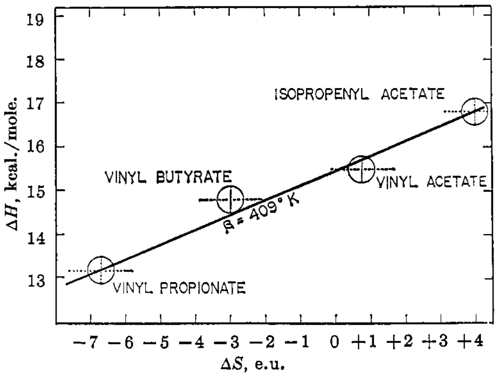
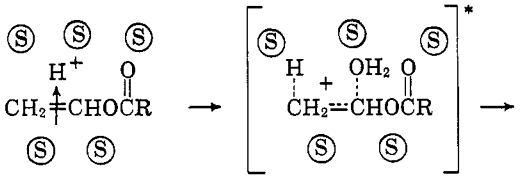


Figure 1.



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(19) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 639 (1956).

(20) M. M. Kreevoy and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **79**, 4020 (1957).

(21) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 26.

(22) M. L. Bender, *Chem. Rev.*, **60**, 68 (1960).

(23) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

(24) The point for vinyl pivalate has been omitted from Figure 1 because the activation parameters for this compound have a much greater margin of error than those determined for the other compounds in the series.

(25) R. C. Petersen, *J. Org. Chem.*, **29**, 3133 (1964).

(26) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 324.

(27) The same reasoning can be applied equally well to path B or C and is meant only to provide a rationale for the observed linear enthalpy–entropy relationship.

(28) L. A. Kiprianova and A. F. Rekasheva, *Dokl. Akad. Nauk SSSR*, **144**, 386 (1962).

(29) T. Mukaiyama and H. Nohiro, *Bull. Chem. Soc. Japan*, **33**, 1716 (1960).

(30) W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, **79**, 2828 (1952).

(31) S. K. Malhotra and H. J. Ringold, *ibid.*, **85**, 1538 (1963).

(32) N. A. J. Rogers and A. Sattar, *Tetrahedron Letters*, **No. 21**, 1311 (1964).

Experimental[33]

Materials.—Isopropenyl acetate and stabilized vinyl acetate from the Matheson Co. were used without further purification. Eastman practical grade vinyl propionate and vinyl butyrate were redistilled prior to use, b.p. 93 and 114°, respectively. Vinyl pivalate was prepared according to the method described by Adelman,[34] b.p. 103.5° uncor. (lit.[34] b.p. 110–112°). Because of the boiling point difference, the structure was confirmed with an n.m.r. spectrum which shows a singlet at τ 8.76 (area 9.4) and an ABC pattern similar to that of vinyl acetate with two groups of peaks centered at τ 2.75 and 5.32, respectively (total area 3.0). For comparison, the singlet methyl peak of vinyl acetate is at τ 7.92 and the singlet butyl group of ethyl pivalate is at τ 8.94.

The solvent used in the kinetic study was prepared as a 1:1 (w./w.) solution of water, and dioxane which had been freshly distilled from sodium. The aqueous solution had n^{26} 1.3805 and $\rho^{20.5}$ 1.022 ± 0.002. Hydrogen chloride was introduced as a dry gas until the normality of acid was *ca.* 0.1.

Kinetic Procedure.—Approximately 0.15 g. of vinyl ester together with a small crystal of *p-t*-butylcatechol[35] were dissolved in 100 ml. of the acidic aqueous dioxane and the solution was sealed in 3-ml. ampoules. After a given period of time in the kinetic bath, each ampoule was quenched, and two 1-ml. aliquots (in excess water) were titrated independently to a phenolphthalein end point with a standardized solution of sodium methoxide in methanol. An infinity titer was obtained after 10 half-lives. Table V contains data from a typical kinetic run.

TABLE V

ACID HYDROLYSIS OF VINYL PROPIONATE[a]

Elapsed time, min.	0.1315 N base, ml.[b]	−Ln [ester]
0	1.015	2.60
10	1.083	2.73
20	1.160	2.90
30	1.222	3.06
40	1.270	3.20
50	1.314	3.36
60	1.352	3.51
70	1.380	3.64
	1.579	. . .

[a] At 65.00 ± 0.05° in 50 wt. % aqueous dioxane containing 0.1334 N HCl. [b] Each value is the average of two titrations.

Rate constants were determined by the method of least squares[36] and, except for runs pertaining to vinyl pivalate, have a least-squares error less than 0.6% for any individual run. The average deviation among several repeated runs was ≤2% with the exception of vinyl butyrate at 55° (±3% deviation) and vinyl pivalate at 75° (±4.5% deviation).

Singular difficulty was encountered with the determination of the vinyl pivalate rate constants. The solubility of the compound in the solvent system was sufficiently low that the solution had to be saturated at a temperature slightly above room temperature. During the initial 10–20% reaction period the titrations would often be erratic apparently associated with the presence of very finely divided droplets of unreacted vinyl pivalate in the cooled ampoules. For reasons as yet unknown, end-point determinations toward the end of the run also became erratic. Because of the apparent curvature in the activation plot, maximum estimates for ΔH^* and ΔS^* were obtained from data at 65 and 75°. Similar difficulties have been reported for the determination of the activation parameters for the acid-catalyzed hydrolysis of ethyl pivalate.[10]

Hydrolysis of Isopropenyl Acetate in a Deuterated Medium.—A solution of 50 vol. % dioxane in deuterium oxide, which contained a trace of hydroquinone and sufficient concentrated hydrochloric acid to make an over-all 0.104 N hydrogen ion concentration, was saturated with isopropenyl acetate at room temperature, heated for 1 hr. at 55°, cooled, and diluted with 15 ml. of cold saturated sodium chloride solution. The unreacted starting material was quickly extracted with carbon tetrachloride, washed several times with more salt solution, and dried over magnesium sulfate. A n.m.r. spectrum indicated no deuterium incorporation into the isopropenyl group under conditions which had produced 23% over-all hydrolysis of the starting compound.

That rapid exchange had not taken place during the work-up procedure was ascertained by observing the appearance of the vinyl protons (by n.m.r.) during the course of the hydrolysis. The relative area of the vinyl to acetyl protons in the isopropenyl acetate showed no discernible change during 1 or 2 hr. at 55°.

Acknowledgment.—The author wishes to thank the University of Kansas for the award of an Elizabeth M. Watkins Faculty Fellowship during the summer of 1964. He is also indebted to Professor Richard Schowen for helpful discussions during the course of this work.

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(33) All n.m.r. spectra were obtained on a Varian A-60 n.m.r. spectrometer. Unless otherwise specified, chemical shift values are reported in units of τ (internal tetramethylsilane standard).

(34) R. L. Adelman, *J. Org. Chem.*, **14**, 1057 (1949).

(35) Vinyl acetate was used only with the commercial stabilizer present.

(36) L. P. Hammett, "Introduction to the Study of Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1952, p. 410.

The Direction of Enolization of Benzoylacetones[1]

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The enolic character and direction of enolization of some substituted benzoylacetones have been studied by infrared, ultraviolet, and n.m.r. spectroscopy. The spectra are interpreted to show that the benzoylacetones are over 90% enolic in a nonpolar solvent and are enolized toward the phenyl group, and some contain a few per cent of a nonchelated enol, thought to be the *trans* isomer **3**.

The keto–enol equilibrium of 1,3 diketones has been the object of many studies, probably because the system provides an interesting case for the application of the prevailing concepts of organic chemistry.[2] Not only is the position of equilibrium of general interest, but also the direction of enolization. Thus, for a 1,3 diketone of the type Ar—CO—CH_2—CO—CH_3, where Ar represents an aryl group, it is desirable to know the population of the enols in the equilibrium mixture A. It is a reasonable assumption that the amount of enol present involving the CH_3 group, Ar—CO—CH_2—C(OH)=CH_2, is insignificant.[2] This is evident from the n.m.r. spectra of the benzoylacetones **6–10**. For almost all diketones studied,[3] even including those of α-keto esters,[4] the per cent and direction of enolization

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(1) Taken in part from the Ph.D. Dissertation of J. U. Lowe, June 1963.

(2) L. N. Ferguson, "Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963, Chapter 4.

(3) R. P. Barnes, *et al.*, *J. Am. Chem. Soc.*, **69**, 3132 (1947), and earlier papers; R. D. Campbell and H. M. Gilow, *ibid.*, **82**, 2389 (1960); P. B. Russell, *Chem. Ind.* (London), 326 (1956).

(4) A. M. Stock, N. E. Donahue, and E. D. Amstutz, *J. Org. Chem.*, **23**, 1840 (1958).