Anal. Calcd. for $C_{17}H_{19}NO_2S_2$: C, 61.23; H, 5.74. Found: C, 61.48; H, 6.03.

3-Methylthiochroman.—A solution of 14.5 cc. (0.14 mole) of thiophenol, 14 g. (0.14 mole) of methyl methacrylate and 3 drops of dry piperidine was heated until the reflux temperature increased from 130 to 250°; about 10 hr. was required. On cooling, the crude ester was hydrolyzed with 100 cc. of dilute hydrochloric acid in 150 cc. of acetone for 12 hr. at reflux temperature. The mixture was diluted with water, extracted with ether and the combined ether extracts were washed with saturated aqueous sodium bicarbonate solution. Acidification caused the separation of an oil which was collected by ether extraction. Evaporation of the ether from the dried ether extracts gave a residue which was distilled to give 11.5 g. (42%) of **α-methyl-β-(phenylmercapto)-propionic acid,** b.p. 188–190° (pot temperature) (12 mm.). The oil slowly solidified and melted, after crystallization from pentane, at 31.5–32°.

Anal. Calcd. for $C_{10}H_{12}O_2S$: C, 61.20; H, 6.17. Found: C, 61.47; H, 6.13.

The above acid (10 g.) was cyclized in the presence of 100 g. of concentrated sulfuric acid by a previous described method[23] to give 5.3 g. (59%) of 3-methylthiochromanone as a colorless oil, b.p. 146–150° (pot temperature) (10 mm.). The oil slowly solidified and was recrystallized from pentane to give needles of m.p. 41–42°.

Anal. Calcd. for $C_{10}H_{10}OS$: C, 67.38; H, 5.66. Found: C, 67.37; H, 5.50.

The ketone (4.0 g.) was reduced by the exact method used above for the reduction of 2-methylthiochromanone. **2-Methylthiochroman** was isolated in 63% yield (2.38 g.) as a colorless oil, b.p. 132–134° (pot temperature) (10 mm.), $n^{20}D$ 1.6020.

Anal. Calcd. for $C_{10}H_{12}S$: C, 73.12; H, 7.37. Found: C, 73.34; H, 6.97.

The sulfilimine melted at 142–143° and gave a depression on mixed melting with the sulfilimine of 2-ethyldihydrobenzothiophene.

Anal. Calcd. for $C_{17}H_{19}NO_2S_2$: C, 61.33; H, 5.74. Found: C, 61.38; H, 5.85.

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE FULMER LABORATORY, DEPARTMENT OF CHEMISTRY, THE STATE COLLEGE OF WASHINGTON]

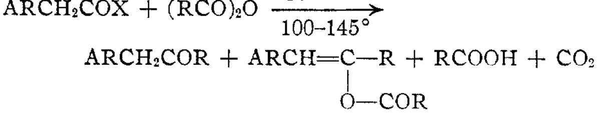
Preparation of Ketones and their Enol Esters by the Base-catalyzed Condensation of Acids and Acid Derivatives with Anhydrides[1,2]

BY GRANT GILL SMITH

RECEIVED APRIL 1, 1952

The condensation of phenylacetic acid with anhydrides in the presence of pyridine to produce benzyl ketones has been shown to be general for a number of aliphatic acid anhydrides, but not for aromatic acid anhydrides. Enol esters of the ketones were isolated as secondary products. Although condensation was slow with phenylacetic acid, the reaction rate was considerably increased by use of phenylacetic anhydride, phenylacetyl chloride or acids with more reactive α-hydrogens, such as p-nitrophenylacetic acid. Under the same conditions ethyl phenylacetate and cinnamic acid did not condense.

When phenylacetic acid reacts with an excess of an aliphatic acid anhydride in the presence of pyridine at elevated temperatures, benzyl alkyl ketones are formed.[3] Since this first report by Dakin and West, the reaction has been studied by several investigators.[4] In this investigation phenylacetic acid, phenylacetyl chloride, phenylacetic anhydride, p-nitrophenylacetic acid and o-chlorophenoxyacetic acid were condensed with acetic anhydride. The first two were also condensed with propionic, butyric and phenylacetic anhydride. The ketones (I) and their enol esters (II) which resulted from this condensation were isolated directly by fractional vacuum distillation.



$$\mathrm{ARCH_2COX + (RCO)_2O \xrightarrow[100-145^\circ]{pyridine} ARCH_2COR + ARCH{=}\underset{\substack{|\\ O-COR}}{C}-R + RCOOH + CO_2}$$

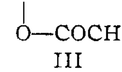
I II

$X = OH, Cl, OCOCH_2C_6H_5$

$R = CH_3, C_2H_5, C_3H_7, C_6H_5CH_2$

$AR = C_6H_5, p\text{-}NO_2C_6H_4, o\text{-}Cl\text{-}C_6H_4\text{-}O\text{-}$

The ketones (I) were characterized by conversion to their semicarbazide and 2,4-dinitrophenylhydrazine derivatives. The structure of the enol esters (II) was established by elementary analysis, their unreactivity to sodium bisulfite, and by the comparison of the infrared curve of the enol acetate of p-nitrophenyl-2-propanone with those of isopropenyl acetate (III) and acetylacetone (IV). If O-acylation took place the product would show infrared absorption bands in the ester and olefin regions similar to those found in isopropenyl acetate. If on the other hand C-alkylation occurred, a 1,3-diketone would have resulted whose infrared bands would correspond to those of acetylacetone in the ketone region.



$$\mathrm{CH_2{=}\underset{\substack{|\\ O-COCH_3}}{C}-CH_3}$$

III

$$\mathrm{CH_3-\underset{\substack{\|\\ O}}{C}-CH_2-\underset{\substack{\|\\ O}}{C}-CH_3}$$

IV

Infrared spectra are given in Fig. 1. The enol acetate of p-nitrophenyl-2-propanone and isopropenyl acetate have strong absorption bands near 1755 and 1672 mμ and no absorption between these figures. For acetylacetone these bands do not appear; however, it shows a characteristic ketone band at 1710 mμ.[5] The characteristic bands for esters are near 1750 mμ[5]; olefins have characteristic bands at 1620 to 1680 mμ.[5] Another typical example of an unsaturated ester similar to isopropenyl acetate is vinyl acetate which has a band at 1660 and 1760 mμ.[5] Hence, it appears quite evi-

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(1) Presented before the Division of Organic Chemistry, 119th Meeting of the American Chemical Society, Boston, Mass., April 4, 1951.

(2) This work was completed prior to the publication by J. A. King and F. H. MacMillan, THIS JOURNAL, **73**, 4911 (1951), and since the work was done independently is being published independently.

(3) H. D. Dakin and R. West, *J. Biol. Chem.*, **78**, 91 (1928).

(4) (a) R. Stoermer and H. Stroh, *Ber.*, **68**, 2112 (1935); (b) C. D. Hurd and C. L. Thomas, THIS JOURNAL, **58**, 1240 (1936); (c) O. U. Magidson and G. A. Garkuska, *J. Gen. Chem.* (*U.S.S.R.*), **11**, 339 (1941); *C. A.*, **35**, 5868 (1941); (d) J. A. King and F. H. McMillan, THIS JOURNAL, **68**, 525 (1946); **73**, 4911 (1951); (e) G. L. Buchmann and J. McArdle, *J. Chem. Soc.*, 2944 (1952).

(5) R. B. Barnes, R. C. Gove, U. Liddel and V. E. Williams, "Infrared Spectroscopy," Reinhold Publ. Corp., New York, N. Y., 1944.

dent that the structures of the acetyl derivatives are enol esters and not 1,3-diketones.

The condensation of phenylacetic acid with aliphatic acid anhydrides and pyridine took place slowly at 130°; in some cases several days were required before carbon dioxide evolution was complete. Progress of the reaction was followed by weighing the carbon dioxide which was evolved during the formation of the ketones. Yields of ketones were 55–67%; the per cent. carbon dioxide ranged from 65–82%. When the chloride or anhydride of phenylacetic acid was employed, however, the rate of the reaction was increased considerably. With phenylacetyl chloride, acetic anhydride and pyridine, some carbon dioxide was evolved immediately. (The temperature rose to 52° as a result of pyridinium salt formation.) At reflux temperature (130°), the evolution of carbon dioxide was completed in two hours. With phenylacetic anhydride, acetic anhydride and pyridine, an endothermic reaction occurred and only a negligible amount of carbon dioxide was evolved spontaneously; at 100° the reaction was very rapid, and at 133° it was complete in 1.5 hours.

The rate of the reaction was increased when *p*-nitrophenylacetic acid was allowed to react with acetic anhydride and pyridine; carbon dioxide was evolved from the reaction mixture at room temperature. Within 20 minutes, 8% of the theoretical amount of carbon dioxide was evolved spontaneously from the reaction mixture at room temperature. If the reaction mixture was heated to 90–100°, the reaction was virtually complete after 1.5 hours. When *p*-nitrophenylacetyl chloride was employed, the initial rate was even more rapid due to the rise in temperature resulting from salt formation. In the more rapid reactions, however, yields of ketones and carbon dioxide were 10–20% lower than in the slower ones.

When reaction mixtures were not treated with alkali, but were isolated directly by distillation, the O-acyl derivatives of the enol forms of the ketones were obtained. When *p*-nitrophenylacetic acid was allowed to react with acetic anhydride and pyridine, the only product isolated was the enol acetate of *p*-nitrophenyl-2-propanone. These derivatives were readily hydrolyzed by alkali to the corresponding ketones and reformed when the ketones were refluxed with the anhydride and pyridine. The double bond is quite probably conjugated with the aromatic rings. These O-acyl derivatives were not reported by other investigators whose isolation procedures involved a hydrolytic step. Wiley and Borum[6] reported acetamidoacetone and an acetyl derivative of acetamidoacetone when glycine was refluxed with acetic anhydride in pyridine and an acetyl derivative of N-methylacetamidoacetone as well as N-methylacetamidoacetone when acetylsarcosine was refluxed with acetic anhydride and pyridine.[7] No structure proof of the acetyl derivatives of these compounds was given.

o-Chlorophenoxyacetic acid reacted more slowly than phenylacetic acid, and a yield of only 17% of the expected ketone, *o*-chlorophenoxy-2-propanone, was obtained. Ethyl phenylacetate,[4e] diphenylacetic acid and cinnamic acid did not condense with acetic anhydride under the conditions of these experiments. The interaction of diphenylacetic acid and acetic anhydride resulted in the liberation of 17% of the expected amount of carbon dioxide, but no ketone was isolated. Neither benzoic anhydride nor *p*-nitrobenzoic anhydride reacted to any appreciable extent with phenylacetic acid or phenylacetyl chloride.

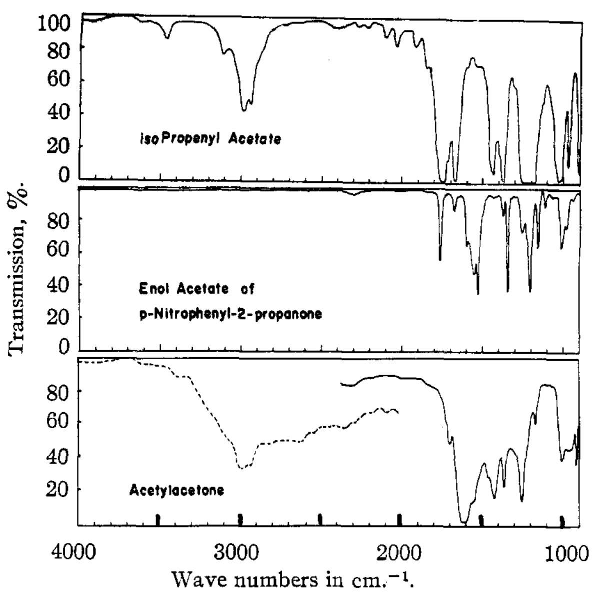

Fig. 1.—Infrared absorption spectra: isopropenyl acetate, 0.10 mm. thickness, pure sample; enol acetate of *p*-nitrophenyl-2-propanone, 0.10 mm. thickness, 87% solution in carbon tetrachloride; acetylactone: —, 0.025 mm. thickness, pure sample; ----, 0.10 mm. thickness, 5% solution in carbon tetrachloride.

Experimental

Apparatus.—A 500-ml. three-necked flask was fitted with a mechanically-driven sealed stirrer, a thermometer so adjusted that the bulb extended into the reactants, a nitrogen inlet tube and a reflux condenser attached to a series of three 50-ml. filter flasks to serve as traps. The middle flask contained sulfuric acid. The outlet from the traps led to a three-way stopcock to which were attached two weighed Ascarite tubes; these were used *alternately* for collecting the liberated carbon dioxide. A cone-type heater, regulated by a Powerstat, was used to maintain desired temperatures.

Ketones and Their Enol Esters.—The following example is illustrative: A mixture of 40.9 g. (0.3 mole) of phenylacetic acid, 120 g. (1.5 moles) of pyridine and 290 g. (2.85 moles) of acetic anhydride was heated with stirring for a

TABLE I

MELTING POINTS OF SEMICARBAZONES

Semicarbazone of	Melting points, °C. Reported	Observed Freshly prepared	Observed After one recrystn.	Observed After two recrystn.
1-Phenyl-2-propanone	197,[a] 188,[b] 184[c]	185	178	177
1-Phenyl-2-butanone	155,[b] 146,[d] 135[c]	148	135	118
1-Phenyl-2-pentanone	121,[e] 82[c]	120	108	187

[a] M. Porcher, *Bull. soc. chim. France*, [4] **31**, 336 (1922). [b] G. T. Morgan, H. D. Drew and C. R. Porter, *Ber.*, **58**, 340 (1925). [c] J. B. Senderens, *Compt. rend.*, **150**, 1338 (1910). [d] Reference 10. [e] J. Levy and F. Dvoleitzka-Gombinska, *Bull. soc. chim. France*, [4] **49**, 1770 (1931).

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[6] R. H. Wiley and O. H. Borum, THIS JOURNAL, **70**, 2005 (1948).

[7] R. H. Wiley and O. H. Borum, *ibid.*, **72**, 1626 (1950).

TABLE II

Reactants	Heating, hr.	Products	Yield, %[a]	B.p.		M.p., °C. Semicarbazone	n^{25}_{D}	CO_2, %	Emp. formula	Analyses Carbon, %		Hydrogen, %	
				°C.	Mm.					Calcd.	Found	Calcd.	Found
$C_6H_5CH_2COOH$, $(CH_3CO)_2O$	67	$C_6H_5CH_2COCH_3$	28	60–62[b]	0.8	184–185[b]	1.5180[b]	75					
		Enol acetate	33	67–69	0.8		1.5320		$C_{11}H_{12}O_2$	75.01	74.89	6.87	6.85
$C_6H_5CH_2COOH$, $(C_2H_5CO)_2O$	42	$C_6H_5CH_2COC_2H_5$	50	66–69[c]	1.0	118	1.5096[c]	74					
		Enol propionate	16	82–84	1.0		1.5212		$C_{13}H_{16}O_2$	76.44	76.29	7.90	7.67
$C_6H_5CH_2COOH$, $(n\text{-}C_3H_7CO)_2O$	31	$C_6H_5CH_2COC_3H_7\text{-}n$	38	77–79[d]	1.0	87	1.5028[d]	65					
		Enol butyrate	18	105–110	1.0		1.5130		$C_{15}H_{20}O_2$	77.54	77.20	8.68	8.42
$(C_6H_5CH_2CO)_2O$, $(CH_3CO)_2O$	1.5	$C_6H_5CH_2COCH_3$	64[e]	56	1.2	184–185[b]	1.5140	73					
		$C_6H_5CH_2COCH_2C_6H_5$	Small	110–119	0.6	123–124[f]							
$C_6H_5CH_2COCl$, $(CH_3CO)_2O$	2	$C_6H_5CH_2COCH_3$	40[e]	68–70	1.5	184–185[b]	1.5173						
		$C_6H_5CH_2COCH_2C_6H_5$	Small			123[f]							
$(C_6H_5CH_2CO)_2O$, $C_6H_5CH_2COCl$	2	$C_6H_5CH_2COCH_2C_6H_5$	35[g]	110–117	0.6	123[f]		72					
$p\text{-}O_2NC_6H_4CH_2COOH$, $(CH_3CO)_2O$	4	Enol acetate of $p\text{-}O_2NC_6H_4CH_2COCH_3$	48	145–150[h]	1.0			64	$C_{11}H_{11}NO_4$[i,j]	61.15	61.22	5.02	4.98
$o\text{-}ClC_6H_4OCH_2COOH$, $(CH_3CO)_2O$	50	$o\text{-}ClC_6H_4OCH_2COCH_3$	17[k]	90–92	1.6		1.5388	47	$C_{10}H_{12}ClO_2N_3$[l]	49.69	49.99	5.00	5.10

[a] The ratio of ketone to acyl derivative varied with reaction time. [b] M.p. 27° reported by O. Wallach, *Ann. chim. phys.*, **332**, 317 (1904), b.p. 100–101° (14 mm.), n^{20}_{D} 1.5168, m.p. 27°; semicarbazone, m.p. 184–185°. [c] A. I. Vogel, *J. Chem. Soc.*, 615 (1948); b.p. 113.5 (17 mm.), n^{20}_{D} 1.5115. [d] 243.5–244 (757 mm.); n^{20}_{D} 1.5062; *ibid.* [e] In this experiment the reaction mixture, after being stripped of excess reagents, was subjected to alkaline hydrolysis in order to destroy any of the acylated derivative which had been formed. [f] E. Wedekind, *Ber.*, **34**, 2076 (1901), reported two melting points for this derivative: 146° from absolute alcohol and 125–126° from dilute alcohol; the material melting at 125–126° was reported to be the hydrate of the other although analytical data were inconclusive. This ketone was also converted to its 2,4-dinitrophenylhydrazone, m.p. 108°. C. F. H. Allen and J. H. Richmond [*J. Org. Chem.*, **2**, 224 (1937)] reported a m.p. of 100° for this compound. In this work, also, products melting at 100° were obtained from dibenzyl ketone prepared as described and from dibenzyl ketone (Eastman), but three recrystallizations (from dilute or absolute ethanol) of the samples raised their melting points to 108°. Mixtures of the different samples melted at this same temperature. *Anal.* Calcd. for $C_{21}H_{18}N_4O_4$: C, 64.61; H, 4.65; N, 14.35. Found: C, 64.58; H, 4.72; N, 14.31. [g] In this experiment the cooled reaction mixture was made basic with NaOH, steam distilled, and the distillate extracted with ether to obtain the product. [h] The material solidified and after three recrystallizations from aqueous ethanol, it melted at 99.5–100°. [i] Calcd.: N, 6.34; found: N, 6.75. [j] After the acetate was hydrolyzed to *p*-nitrophenyl-2-propanone, m.p. 63° [F. Arndt, B. Eistert and W. Ender, *Ber.*, **62B**, 44 (1929), reported 62°], with aqueous ethanolic potassium hydroxide, it was converted to the 2,4-dinitrophenylhydrazone, m.p. 176–178° (from 95% ethanol). [k] This experiment was carried out by Mr. James Groves. [l] Analysis is of the semicarbazone of *o*-chlorophenoxy-2-propanone.

period of 67 hours at 120°. The liberated carbon dioxide (75%) was collected in a tube containing Ascarite. The pyridine and excess acetic anhydride were removed by vacuum distillation. Fractional vacuum distillation of the residue through 15 cm. of glass helices yielded two products, 1-phenyl-2-propanone and its enol acetate. The ketones were characterized by comparison of their physical properties with values found in the literature (see Table II). The material which analyzed satisfactorily (see Table II) for the enol ester of the ketone was further characterized by alkaline hydrolysis to the ketone which was identified as its semicarbazone. The enol ester derivative could again be reformed by refluxing (48 hours) the ketone with an excess of anhydride and pyridine. Additional structure proof of the acetyl derivatives was obtained by comparison of the infrared spectrum of the enol ester of *p*-nitrophenyl-2-propanone with those of isopropenyl acetate and acetylacetone (see Fig. 1).

Infrared Spectra.—Infrared absorption curves for the isopropenyl acetate, acetylacetone and the enol acetate of *p*-nitrophenyl-2-propanone was obtained using a Perkin–Elmer infrared spectrophotometer Model 21 with a NaCl prism.[8]

Melting Points of Semicarbazones.—An interesting phenomenon was observed when the semicarbazones of 1-phenyl-2-propanone, 1-phenyl-2-butanone and 1-phenyl-2-pentanone were recrystallized from water–ethanol solutions. Recrystallization of freshly prepared samples of these derivatives from this solvent lowered the melting points. The fact that these derivatives exist in geometrically isomeric forms (alpha[9] and beta[10]) may explain the several previously reported melting points. Bruzan[11] repeatedly crystallized the semicarbazone of 1-phenyl-2-propanone and examined the ultraviolet absorption spectra of the various samples. It was concluded there are two tautomeric forms in addition to the well known geometric isomers. One form has a saturated C-atom next to the benzene nucleus and the other an unsaturated C-atom adjoining the benzene nucleus. A number of different melting points are listed in Table I; included are the extreme values reported in the literature and some observed in this Laboratory.

It is doubtful that these variations in melting points result from hydration, which may occur when certain compounds are recrystallized from aqueous solvents. This was investigated in the case of the semicarbazone of 1-phenyl-2-pentanone. Although the melting point of this compound was lowered from 120 to 87° by repeated recrystallization from a water–ethanol solution, the carbon and hydrogen analyses of the lower melting substance were in agreement with the calculated value for the unhydrated form.

Anal. Calcd. for $C_{12}H_{17}ON_3$: C, 65.72; H, 7.82. Found: C, 66.01; H, 7.54.

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[8] The coöperation of Mr. David L. Little, deceased, of the Division of Industrial Research, Washington State College for his assistance in obtaining the infrared absorption curves is gratefully acknowledged.

[9] M. Tiffeneau, *Ann. chim. phys.*, [8] **10**, 369 (1907); *C. A.*, **2**, 265 (1908).

[10] E. Fourneau, *Compt. rend.*, **146**, 699 (1908).

[11] (Mme.) Bruzan, *Ann. chim.*, [11], **1**, 257 (1934).

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PULLMAN, WASHINGTON

[FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS]

The Anomerization of Sugar Acetates. Glucose Pentaacetates in Acetic Acid–Acetic Anhydride Mixtures Catalyzed by Sulfuric and Perchloric Acids

BY EDGAR PAGE PAINTER

RECEIVED JULY 21, 1952

Perchloric acid behaves as a strong and sulfuric acid as a weak acid when compared by their catalysis of the anomerization of glucose pentaacetates in the solvent acetic acid–acetic anhydride. When perchloric acid is the catalyst the rate in approximately 98% acetic anhydride is about 600 times the rate in acetic acid. The suggested mechanism considers the anomerization a displacement process and the rate dependent upon the formation of sugar acetate carbonium ion. The formation of the carbonium ion from the conjugate acid of the sugar acetate [$SOAcH^+$] can account for the rate in acetic acid but not the rapid increase in concentrated solutions of acetic anhydride. If the species Ac^+ is present in acetic anhydride solutions, and a carbonium ion is formed by dissociation of $SOAc_2^+$, suggested equilibria can account for the rapid increase in rate. Calculated rates assuming the rate of anomerization will follow an expression of the type: rate = $k_a[SOAcH^+] + k_b[SOAc_2^+]$, agree quite well with experimental rates. The chief obstacle seems to be the uncertainty in the equilibria which involve acid species in the solvent system.

Introduction

Acid catalysts are commonly used in the preparation of sugar acetates. When a pure form of a sugar (α or β) is the starting material, it is possible with acid catalysts to obtain good yields of the acetate corresponding to the anomer used, providing the rate of esterification at the anomeric center greatly exceeds the rate of anomerization. If the reaction goes to completion, the composition is dependent upon the equilibrium

$$\alpha\text{-acetate} \rightleftharpoons \beta\text{-acetate}$$

In many cases the equilibrium lies so far in favor of one of the anomers that it is the only one isolated.

Sulfuric acid has probably been used more than any other acid as a catalyst for acetylation and anomerization but Lewis acids are good catalysts in these reactions.

The first report on rates of isomerization was by Jungius[1] who used zinc chloride in acetic anhydride. Freudenberg and Soff[2] followed the changes in rotation when α- and β-forms of glucose acetates were dissolved in acetic acid–acetic anhydride mixtures containing sulfuric acid, but they did not calculate rates. Recently Bonner[3] reported on the kinetics of the anomerization of glucose pentaacetates by sulfuric acid in mixtures of acetic acid and acetic anhydride. In the present paper the rate of anomerization in acetic acid and in mixtures of acetic acid and acetic anhydride up to about 98% acetic anhydride is reported when the reaction is catalyzed by sulfuric and perchloric acids. Our interpretation of the kinetics, based on results with perchloric acid, differs from that suggested by Bonner, and a different mechanism of the anomerization is proposed.

Equilibrium of the Reaction.—When sulfuric or perchloric acid is added to either α- or β-1,2,3,4,6-pentaacetylglucose dissolved in mixtures of acetic acid and acetic anhydride the rotation changes to the same constant value. Typical curves are shown in Fig. 1.

The composition at equilibrium calculated from the rotations of the α- and β-forms was approximately 87% α and 13% β. This assumes the above α- and β-forms were the only products in the equilibrium mixture. Bonner[3] presented convincing evidence that this is so in acetates isolated from the anomerization. He found 83.5% α and 16.5% β in the product isolated. Jungius found approximately 90% α and 10% β at equilibrium and Freudenberg and Soff 88% α and 12% β. In nearly all solvent mixtures the rotation reached the same final equilibrium with either catalyst in our runs.

Rate Constants and Sugar Acetate Concentration.—The reversible reaction

$$\alpha\text{-acetate} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \beta\text{-acetate} \qquad (1)$$

is analogous to the mutarotation of sugars. Solution of the equation

$$-\,d[\alpha]/dt = d[\beta]/dt = k_1[\alpha] - k_2[\beta] \qquad (2)$$

and expressing concentrations in terms of rotation gives the expression

$$k_1 + k_2 = \frac{1}{t}\, 2.303 \log \frac{a_0 - a_\infty}{a_t - a_\infty} \qquad (3)$$

first applied by Hudson.[4]

Typical rate constants obtained in three runs using both acids in solvents of different compositions and calculated by equation 3 are shown in Table I.

Rate constants held up well throughout individual runs in nearly all cases. In the examples shown the calculations were continued until the rotation change was more than 90% completed. The last column shows that satisfactory constants can be obtained when the reaction is rapid. With perchloric acid there was no indication of a drift in rates during runs, except in some of the runs when the catalyst concentration was less than 0.001 *M* in nearly 100% acetic anhydride. Apparently some perchloric acid is lost due to the presence of a

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(1) C. L. Jungius, *Z. physik. Chem.*, **52**, 97 (1905).

(2) K. Freudenberg and K. Soff, *Ber.*, **69**, 1245 (1936).

(3) W. J. Bonner, THIS JOURNAL, **73**, 2059 (1951).

(4) C. S. Hudson, *Z. physik. Chem.*, **44**, 487 (1903).