hydrazone of β-ethoxyethyl methyl ketone, m.p. 93.5–96°, caused no depression in melting point.

β-Ethoxyethyl methyl ketone also was obtained from ethyl 3,5-diethoxy-2-pentenoate by saponification to the acid followed by hydrolysis with dilute sulfuric acid.

Hydrogenation of Ethyl 3,5-Diethoxy-2-pentenoate.—The diethoxy ester was hydrogenated to a saturated ester, presumably ethyl 3,5-diethoxypentenoate, which was saponified to 3,5-diethoxypentanoic acid. This acid was unaffected by refluxing with hydrochloric acid. Therefore the ethoxy groups are not on the same carbon atom. The diethoxy ester (21.8 g.) in ethanol (50 ml.) was hydrogenated over Raney nickel (12 g.) at 80°/1500–2000 lb./sq. in. hydrogen for 4 hours. After filtration from catalyst and removal of alcohol, the residual oil was distilled to give a product (21.2 g., 96% yield), b.p. 73–74° (0.6 mm.), $n^{25}\text{D}$ 1.4208.

Anal. Calcd. for $C_{11}H_{22}O_4$: C, 60.52; H, 10.16; sapn. equiv., 218. Found: C, 60.60; H, 10.20; sapn. equiv., 218.

The hydrogenation product (4.8 g., 0.022 mole) was refluxed with aqueous 25% sodium hydroxide (15 ml.) for 3 hours. Then the solution was acidified with hydrochloric acid and extracted with ether. The combined extracts were evaporated on the steam-bath and the residual oil was refluxed with hydrochloric acid (4 ml.) in water (6 ml.) for one hour. The mixture was extracted with ether and the combined extracts were dried over calcium sulfate. Evaporation left an oil which distilled at 99° (0.2 mm.), $n^{25}\text{D}$ 1.4349. This distillate (2.7 g.) reacted vigorously with aqueous 5% sodium bicarbonate but not with 2,4-dinitrophenylhydrazine reagent.

Anal. Calcd. for 3,5-diethoxypentanoic acid, $C_9H_{18}O_4$: C, 56.82; H, 9.54; neut. equiv., 190; ethoxyl, 47.37. Found: C, 56.61; H, 9.39; neut. equiv., 188; ethoxyl, 47.10.

Polymerization of Ethyl 3-Ethoxy-2,4-pentadienoate.[3]—The diene ester (10 g.) was mixed with water (30 g.), potassium persulfate (0.2 g.), sodium bisulfate (0.05 g.), sodium lauryl sulfate (0.5 g.) and disodium phosphate (0.5 g.), and the mixture was heated at 50° for 10 hours in a pressure bottle mounted in a tumbler. The emulsion was coagulated by addition of alcohol and the polymer was collected by filtration. The colorless solid was washed with water and alcohol and then dried at 60° (0.5 mm.) to give 9 g. (90% yield) of polymer. The material melted at 90–125° and on cooling formed a hard brittle film. It had an inherent viscosity of 1.70 (0.1% solution in benzene at 25°) and a relative viscosity of 1.185.

Polymeric ethyl 3-ethoxy-2,4-pentadienoate (0.5 g.) was refluxed with methanol (4 ml.) and hydrochloric acid (0.24 ml.) for 5 minutes. The mixture was neutralized with ammonium hydroxide. The polymer was collected and then dissolved in boiling methanol (5 ml.). A solution of cupric acetate (0.3 g.) in the minimum amount of boiling water was added with vigorous shaking. The pale green solid which separated was insoluble in boiling water and did not soften as did the original polymer. This polymeric copper chelate did not melt below 205°. The analysis for copper indicated that about 23% of the β-keto ester groups had reacted.

Anal. Calcd. for $C_{14}H_{18}O_6Cu$: Cu, 18.38. Found: Cu, 4.3.

Polymeric ethyl 3-ethoxy-2,4-pentadienoate which had not been hydrolyzed with acid did not give a copper chelate with cupric acetate.

Ethyl 5-Dimethylamino-3-ethoxy-2-pentenoate.—The diene ester (26.2 g., 0.154 mole), anhydrous dimethylamine (7.3 g., 0.166 mole) and potassium carbonate (7.8 g.) were charged into a pressure bottle which was capped and placed in a rocker bath for 17 hours. After standing at room temperature for 6 more hours the bottle was opened and the contents were filtered from potassium carbonate which was washed with 2 10-ml. portions of ether. The combined filtrate and ether washings were distilled under reduced pressure leaving a residual oil which on distillation gave 24.5 g. (74% yield) of an amine adduct, b.p. 85.5–86° (1 mm.), $n^{25}\text{D}$ 1.4609.

Anal. Calcd. for $C_{11}H_{21}O_3N$: C, 61.36; H, 9.83; N, 6.51; neut. equiv., 215. Found: C, 61.57; H, 9.96; N, 6.62; neut. equiv., 217.

The infrared spectrum of this amino ester is very similar to that of ethyl 3,5-diethoxy-2-pentenoate, except for dimethylamino bands at 3.6 and 6.8 μ.

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[3] V. A. Engelhardt, U. S. Patent 2,647,106 (1953).

The Dissociation Constants of 7-Methyl- and 1,7-Dimethyluric Acid

BY SHABTAY DIKSTEIN AND FELIX BERGMANN

RECEIVED APRIL 14, 1955

In a recent paper[1] it was shown that in substituted uric acids ionization of the NH-groups occurs in the order 9 — 3 — 1. However, uric acid itself possesses only two dissociation constants, identified as pK_9 and pK_3. As further support of this statement we now have measured the pK values of 7-methyluric acid, applying our spectrophotometric method,[1] and the results (see Fig. 1) confirm our observation that pre-occupation of the two oxygens in position 2 and 6 by charge distribution from N^3 and N^9 prevents ionization at N^1. Indeed, the constants obtained for 7-methyluric acid are very close to those for uric acid and its 1,7-dimethyl derivative, as shown in Table I. The latter compound has been studied systematically for the first time, and the curve representing λ_{max} as function of pH has been included in Fig. 1.

TABLE I

DISSOCIATION CONSTANTS OF URIC ACID, 7-METHYL- AND 1,7-DIMETHYLURIC ACID

	pK_9	pK_3
Uric acid	5.75	10.3
7-Methyluric acid	5.6	10.3
1,7-Dimethyluric acid	5.5	10.6

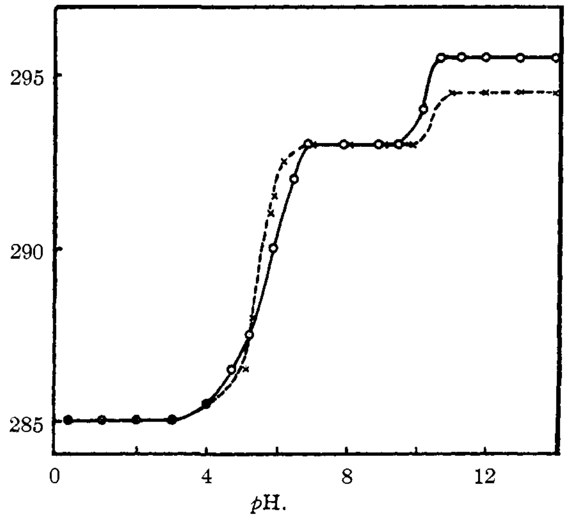

Fig. 1.—Long-wave absorption maxima as function of pH: ○—○—, 7-methyluric acid; ×---×---, 1,7-dimethyluric acid.

Experimental

7-Methyluric acid was synthesized according to Fischer and Clemm[2] and Biltz and Damm.[3]

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[1] F. Bergmann and S. Dikstein, THIS JOURNAL, **77**, 691 (1955).

[2] E. Fischer, *Ber.*, **30**, 561 (1897); E. Fischer and H. Clemm, *ibid.*, **30**, 3091 (1897).

[3] H. Biltz and P. Damm, *ibid.*, **46**, 3670 (1913); H. Biltz, K. Marwitzky and M. Heyn, *Ann.*, **423**, 127 (1921).

1,7-Dimethyluric Acid.—Through the courtesy of Prof. D. Keilin, Molteno Institute, Cambridge, England, we obtained a sample of 1,7-dimethyl-8-acetoxyxanthine. The material apparently had undergone deacetylation in storage, since it proved to be 1,7-dimethyluric acid. This could be shown in the following way: (a) The absorption spectrum remained constant in alkaline solution (pH 10.5 or 14) during 24 hours. The spectrum measured immediately showed the characteristic pK values, reported in Table I. (b) When the substance was dissolved in alkaline hydroxylamine, no acethydroxamic acid was formed. (c) The R_f value of the substance was identical with those of 1,3- and 3,7-dimethyluric acids. The chromatographic experiments will be described elsewhere.

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The Acetylation of Mercaptans with Ketene

BY R. E. DUNBAR AND A. N. BOLSTAD[1]

RECEIVED APRIL 8, 1955

An extension, with slight modifications, of the method of Hurd and Williams[2] recently has been applied to the preparation of six additional thioacetates. These authors reported the preparation of ethyl thioacetate in 92.6% yield by allowing liquid ketene and ethanethiol to stand for three days at −80°. Apparently no catalyst was used and no attempt was made to acetylate other mercaptans. Since typical esters can be produced readily in good yields by the action of ketene on alcohols, it seemed highly probable that the corresponding sulfur-containing thiolic esters could be produced by analogous treatment of mercaptans with ketene.

TABLE I

YIELDS AND PROPERTIES OF THIOACETATES

Alkyl group present	Yield, %	B.p.° Obsd.	B.p.° Reptd.[a]	d^{30}_4	$n^{30}D$	M_D Obsd.	M_D Calcd.
Methyl	22.5	97.5–98.8	95.6	1.013[e]	1.4972[e]	24.30	24.035
Ethyl[b]	23.4	113.0–114.5	116–117	0.971	1.4473	28.30	28.653
2-Methyl-2-propyl[c]	17.5	130–133	.....	.918	1.4435	38.4	37.899
1-Propyl	46.0	137.0–139.5	135–137	.955	1.4533	33.6	33.27
2-Propyl	22.5	124.0–125	124–127	.952	1.4445	33.2	33.27
2-Butyl[d]	59.0	148–151.5	.....	.933	1.4528	38.25	37.889

[a] Y. Sakurada, *Mem. Coll. Sci., Kyoto*, **10**, 67 (1926) (*Brit. Chem. Abstracts*, 133 (1927)). [b] Y. Sakurada (footnote *a*) reports d^{28}_4 0.9755, $n^{30}D$ 1.4503. [c] Calcd. for $C_6H_{12}OS$: S, 24.24. Found: S, 24.40. [d] Calcd. for $C_6H_{12}OS$: S, 24.24. Found: S, 23.8. [e] At 25°.

Methanethiol, ethanethiol, 1-propanethiol, 2-propanethiol, 2-butanethiol and 2-methyl-2-propanethiol each in turn were acetylated with ketene using various conditions, and sulfuric acid as a catalyst. The thiols having sufficiently high boiling points were treated with ketene in a carbon tetrachloride solution at room temperature. Others were acetylated with liquid ketene at a temperature of −68 to −72° again using sulfuric acid as a catalyst. The 2-methyl-2-propanethiol did not acetylate appreciably at room temperature in a carbon tetrachloride solution, but the reaction proceeded satisfactorily at the lower temperature with liquid ketene. Some difficulty again was experienced in acetylating tertiary mercaptans with ketene.[2] *t*-Butyl, amyl and dodecyl mercaptans in carbon tetrachloride, containing two drops of sulfuric acid, did not acetylate appreciably at room temperature.

The yields of thiolic esters are frequently low. This may be due in part to numerous side reactions that consume sizeable quantities of ketene or mercaptans. Acetone was present in appreciable quantities in the reaction gases and probably reacted with a portion of mercaptans forming the thiol acetal.[3] The mercaptans are likewise easily

$$(CH_3)_2C{=}O + 2HSR \longrightarrow (CH_3)_2C(SR)_2 + H_2O$$

oxidized to the disulfides or under more drastic conditions to the sulfonic acids. Additional unsaturated gases, other than ketene, produced in the generator, also may react with the mercaptans.

Experimental

The ketene was generated by the pyrolysis of acetone using the lamp previously described by Dunbar and Bolstad.[4]

The nine mercaptans were each individually placed in the gas absorption apparatus designed by Dunbar and Bolstad,[5] and then individually treated with a theoretical excess of ketene. The preparation of, and physical constants of 2-butyl thioacetate and 2-methyl-2-propyl thioacetate are reported for the first time.

A 20-g. portion of 95% methanethiol, b.p. 5–7°; 22.4 g. of ethanethiol, b.p. 34–36°; and 18 g. of 2-methyl-2-propanethiol, b.p. 62–64°, were each separately treated with two drops of sulfuric acid and an excess of ketene at the rate of 0.13 mole per hour for 2 to 5 hours as required for complete reaction. The temperature of the reaction was held at −68 to −72° by the use of a Dry Ice–chloroform mixture. The reaction product then was fractionated twice in each case, with yields and properties of thioacetates produced, as recorded in Table I.

A 22.83-g. portion of 1-propanethiol, b.p. 67–69°; 22.95 g. of 2-propanethiol, b.p. 52–54°; and 22.43 g. of 2-butanethiol each were dissolved separately in 40–50 ml. of carbon tetrachloride, containing one drop of sulfuric acid, and treated at room temperature with an excess of ketene at the rate of 0.13 mole per hour for 4.6 to 7.2 hours as required for complete reaction. The reaction product was likewise twice fractionated in each case with yields and properties of thioacetates as recorded in Table I.

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[1] This paper represents part of a thesis submitted by A. N. Bolstad in partial fulfillment of the requirements for the M.S. degree in the North Dakota State College.

[2] C. D. Hurd and J. W. Williams, THIS JOURNAL, **58**, 962 (1936).

[3] T. M. Lowry and E. H. Magson, *J. Chem. Soc.*, **93**, 107, 119 (1908).

[4] R. E. Dunbar and L. L. Bolstad, *J. Org. Chem.*, **9**, 219 (1944).

[5] R. E. Dunbar and A. N. Bolstad, *Anal. Chem.*, **18**, 337 (1946).