**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 (*p*H 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

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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.

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.

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°.

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.

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