

The substance produced a phenylosazone in the usual manner; m. p. 208° (dec., uncor.) which is in good agreement with the reported<sup>16</sup> value of 210–212° (dec., uncor.).

*Anal.* Calcd. for C<sub>20</sub>H<sub>24</sub>O<sub>8</sub>N<sub>4</sub>: C, 57.40; H, 6.26; N, 13.36. Found: C, 57.48; H, 6.08; N, 13.40.

**Acknowledgment.**—One of us (A. T.) acknowledges a stipend from the funds of The Ohio State University Research Foundation administered by the Graduate School.

(16) Ref. 3a, p. 98.

## Summary

1. D-Gluco-L-*tagato*-octose has been synthesized in amorphous form.

2. Sodium D-gluco-D-*gulo*-heptonate hexaacetate trihydrate, 1-diazo-1-desoxy-*keto*-D-gluco-L-*tagato*-octose hexaacetate, *keto*-D-gluco-L-*tagato*-octose heptaacetate and methyl D-gluco-D-*gulo*-heptonate hexaacetate have been synthesized in crystalline form.

COLUMBUS, OHIO

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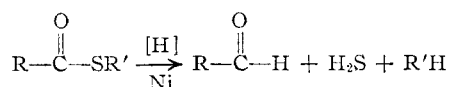
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

## A New Aldehyde Synthesis<sup>1</sup>

BY M. L. WOLFROM AND J. V. KARABINOS

In their important studies on the desulfurization and reducing action of Raney nickel, Bougault, Cattelain and Chabrier<sup>2</sup> attempted to prepare acetaldehyde from thioacetic acid. Using Raney nickel in aqueous ethanol, the only product they isolated was acetic acid, apparently obtained by simple hydrolysis. Mention was made by these workers that acetaldehyde was formed when absolute ethanol was employed as a solvent, a result that is vitiated by the fact that ethanol has been shown<sup>3</sup> to produce acetaldehyde under these conditions.

In an attempt to extend the desulfurization reaction to the synthesis of aldehydes, particularly in connection with *aldehydo*-sugar studies, we have resorted to the reduction of the thiol esters.<sup>1</sup>



The thiol esters were prepared by the reaction of the acid chloride with an excess of ethyl mercaptan in pyridine or by reaction of the acid chloride with lead mercaptide in dry ether. The hydrogenolyses were carried out with Raney nickel in 70–80% ethanol under reflux essentially as described<sup>3</sup> for the hydrogenolysis of thioacetals. The above reaction was established by hydrogenolysis of the thiol esters of benzoic, propionic and tetraacetyl-D-ribonic acids which gave benzaldehyde, propionaldehyde and *aldehydo*-D-ribose tetraacetate, respectively.

The method described herein thus establishes another direct route for the reduction of the carboxyl group to the aldehyde stage and is alterna-

tive to the acid chloride reduction of Rosenmund.<sup>4,4a</sup>

## Experimental

**Hydrogenolysis of Ethyl Thiolbenzoate.**—Ethyl thiolbenzoate, b. p. 155–156° at 52 mm., *n*<sub>D</sub><sup>20</sup> 1.5721 and *d*<sub>4</sub><sup>20</sup> 1.1003,<sup>5</sup> was prepared by the reaction of benzoyl chloride with an excess of ethyl mercaptan in pyridine. Ten grams of the thiol ester was dissolved in 200 cc. of 70% ethanol containing 50 g. of Raney nickel and refluxed for six hours. After removal of the catalyst, the ethanolic solution was distilled and the aldehyde isolated from the distillate by treatment with sodium bisulfite; yield 8.0 g. (62%) of benzaldehyde sodium bisulfite complex. The aldehyde was regenerated from the complex; *n*<sub>D</sub><sup>20</sup> 1.547, melting point of 2,4-dinitrophenylhydrazone 233–235° (accepted values<sup>6</sup> are *n*<sub>D</sub><sup>20</sup> 1.5460 and m. p. 237°).

**Ethyl Thiolpropionate.**—Lead ethylmercaptide<sup>7</sup> (132 g.) was covered with 1500 cc. of ethyl ether and 72 g. of propionyl chloride added dropwise. After standing overnight, the filtered solution was concentrated on a steam-bath to an oil which was distilled through a column of ten theoretical plates; yield of ethyl thiolpropionate 77 g. (82%), b. p. 136°, *n*<sub>D</sub><sup>20</sup> 1.4584, *d*<sub>4</sub><sup>20</sup> 0.9608, m. p. –95°.

*Anal.* Calcd. for C<sub>6</sub>H<sub>10</sub>OS: C, 50.80; H, 8.44; S, 27.12. Found: C, 50.90; H, 8.65; S, 26.89.

**Hydrogenolysis of Ethyl Thiolpropionate.**—Five grams of ethyl thiolpropionate was treated as described above with 50 g. of Raney nickel in 200 cc. of 80% ethanol and the product was isolated in the same manner; yield 5.0 g. (73%) of propionaldehyde sodium bisulfite complex. The 2,4-dinitrophenylhydrazone was prepared; m. p. 153–154° unchanged on admixture with an authentic sample of like melting point.

**Ethyl Thiol-D-ribonate Tetraacetate.**—D-Ribonyl chloride tetraacetate<sup>8</sup> was treated with an excess of ethyl

(4) K. W. Rosenmund, *Ber.*, **51**, 585 (1918).

(4a) Added during the reading of the proof: V. Prelog, J. Norymberski and O. Jeger, *Helv. Chim. Acta*, **29**, 360 (1946), and O. Jeger, J. Norymberski, S. Szpilfogel and V. Prelog, *ibid.*, **29**, 684 (1946), employing similar conditions but using 95% ethanol ("Feinsprit") have reported the reduction of thiol esters to primary alcohols.

(5) L. S. Pratt and E. E. Reid, *THIS JOURNAL*, **37**, 1937 (1915), reported b. p. 146° at 31 mm. and *d*<sub>4</sub><sup>20</sup> 1.0977.

(6) Huntress and Mulliken, "Identification of Pure Organic Compounds, Order I," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 60.

(7) P. Borgstrom, L. M. Ellis, Jr., and E. E. Reid, *THIS JOURNAL*, **51**, 3649 (1929).

(8) R. Pasternack and E. V. Brown, U. S. Patent 2,237,263 (1941); M. L. Wolfrom, A. Thompson and E. F. Evans, *THIS JOURNAL*, **67**, 1793 (1945).

(1) An outline of this work was reported in a preliminary communication: M. L. Wolfrom and J. V. Karabinos, *THIS JOURNAL*, **68**, 724 (1946).

(2) J. Bougault, E. Cattelain and P. Chabrier, *Compt. rend.*, **208**, 657 (1939); *Bull. soc. chim.*, [5] **7**, 781 (1940).

(3) M. L. Wolfrom and J. V. Karabinos, *THIS JOURNAL*, **66**, 909 (1944).

mercaptan in pyridine overnight and after pouring on ice, material separated that slowly crystallized; yield 57%. The filtered material was recrystallized twice from ether and petroleum ether; m. p. 87–87.5°,  $[\alpha]_D^{25} + 17^\circ$  ( $c$  5, chloroform).

Anal. Calcd. for  $C_{15}H_{22}O_3S$ : C, 47.62; H, 5.86; S, 8.46. Found: C, 47.64; H, 5.54; S, 8.59.

**Hydrogenolysis of Ethyl Thiol-D-ribonate Tetraacetate.**—One gram of the thiol ester was refluxed for six hours with 15 g. of Raney nickel in 100 cc. of 80% ethanol and after removal of the catalyst and solvent the residue was dissolved in acetone and methanol and then petroleum ether was added to incipient turbidity, *aldehydo*-D-Ribose tetraacetate crystallized on nucleation; yield 0.19 g. (22%), m. p. 101–102°,  $[\alpha]_D^{25} - 16.2^\circ$  ( $c$  3.3, acetone);  $[\alpha]_D^{25} - 10^\circ$  ( $c$  5, absolute chloroform). Pasternack and

Brown<sup>8</sup> cite the constants: m. p. 98–99°,  $[\alpha]_D^{20} - 16.7^\circ$  ( $c$  5, acetone).

**Acknowledgment.**—We express our thanks to Dr. Alva Thompson for the optical rotations recorded in this publication.

### Summary

Reduction of the carboxyl group to the aldehyde stage is effected through the reductive desulfurization by Raney nickel of the thiol ester. Application of this reaction is made to the synthesis of benzaldehyde, propionaldehyde and *aldehydo*-D-ribose tetraacetate.

COLUMBUS, OHIO

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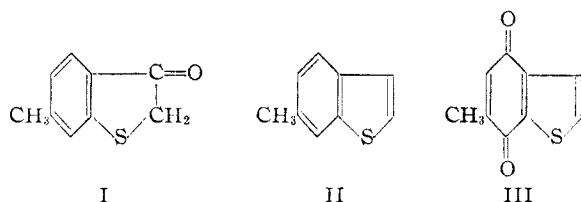
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

## Syntheses in the Thionaphthene Series

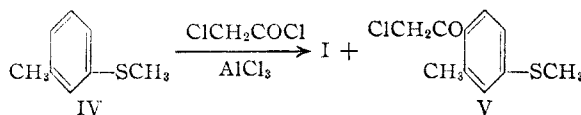
BY D. S. TARBELL AND D. K. FUKUSHIMA

It was shown recently<sup>1</sup> that 5-methyl-4,7-thionaphthenequinone, an isostere of 2-methyl-1,4-naphthoquinone, could be prepared readily by oxidation of 5-methylthionaphthene with chromic acid. The present paper describes experiments designed to prepare 6-methyl-4,7-thionaphthenequinone (III), the isomer of the compound previously reported, by the same general method. It has been possible to obtain a very low yield of this substance.

The necessary intermediates for the synthesis are 6-methyl-3-keto-2,3-dihydrothionaphthene (I) and 6-methylthionaphthene (II), obtained from I by reduction. The preparation of I caused

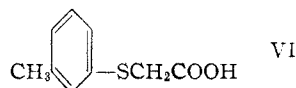


much more difficulty than was anticipated from our previous experience with its isomer; the action of chloroacetyl chloride and aluminum chloride on methyl *m*-tolyl sulfide<sup>2</sup> (IV) gave poor and inconsistent yields of impure I, along with a side-product V, which was proved to be 2-methyl-4-methylmercapto- $\omega$ -chloroacetophenone as will be shown later. The use of anhydrous stannic chloride as the catalyst instead of aluminum chloride gave none of the desired product.



In view of these unsatisfactory results, atten-

tion was turned to the cyclization of *m*-thiocre-soxyacetic acid VI.



Cyclization of the acid chloride with aluminum chloride gave as poor results as in the previous case, and stannic chloride gave no ring closure. Treatment of the acid VI with acetic anhydride, acetic acid and anhydrous zinc chloride,<sup>3</sup> which it was hoped would produce the enol acetate of I, gave only starting material, and cyclization with 80% sulfuric acid<sup>4</sup> was equally unsuccessful. The best method of preparing I was the cyclization of VI with anhydrous hydrogen fluoride, which gave a fair yield of I, containing some impurities. Attempts at purifying the product were unsatisfactory, since I is very easily oxidized by air, so that the crude product was reduced directly to the thionaphthene II with zinc and acetic acid.<sup>5</sup>

Oxidation of the thionaphthene II with chromic acid in acetic acid gave less than 0.1% yield of the desired quinone III; this was identified by analysis, by a positive Craven<sup>5a</sup> test and by its absorption spectrum, which as shown in Fig. 1, is almost identical with that of the 5-methyl isomer.<sup>1</sup> In the oxidation, a colorless neutral substance was obtained in 10–15% yield, which is believed to be the sulfone VII derived from 6-methyl-2,3-dihydrothionaphthene; this struc-

(3) Fieser and Hershberg, *THIS JOURNAL*, **59**, 1028 (1937).

(4) Haworth, *J. Chem. Soc.*, 1125 (1932).

(5) Alternative methods for the preparation of ketodihydrothionaphthenes, such as the ring closure of *o*-carboxythiophenoxyacetic acids, followed by decarboxylation (*e. g.*, Auwers and Thies, *Ber.*, **53**, 2291 (1920), and numerous patents) or alkaline fusion of *o*-methylmercaptobenzoic acids (Auwers and Thies, *loc. cit.*; Lucius and Bruning, German Patent 204,763), were not investigated for the preparation of I, because of the inaccessibility of the necessary starting materials.

(5a) Craven, *ibid.*, 1605 (1931).

(1) Tarbell, Fukushima and Dam, *THIS JOURNAL*, **67**, 1643 (1945).

(2) Auwers and Arndt, *Ber.*, **42**, 537 (1909).