

# SYNTHESIS OF $\beta$ -ISOPROPYLTHIOETHYL ESTERS OF SOME THIO ACIDS OF TRIVALENT ARSENIC

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In continuation of our investigations on the synthesis and study of the properties of organoarsenic compounds with possible pesticidal properties [1-6], we have performed the transesterification [4, 7] of esters of acids of trivalent arsenic with  $\beta$ -isopropylthioethyl mercaptan and have obtained the  $\beta$ -isopropylthioethyl esters of some thio acids of trivalent arsenic. The reaction took place in accordance with the following general scheme

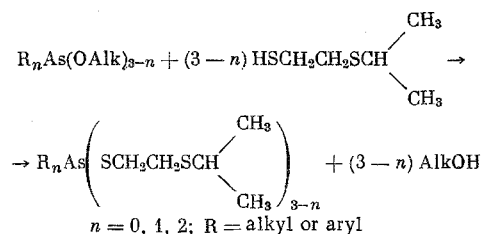
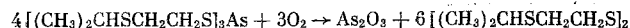


Table 1 gives the yields, some physical constants, and the analytical data for the thio esters synthesized. All of them except for the crystalline  $\beta$ -isopropylthioethyl ester of thiophenarsazinous acid (V) consisted of colorless or faintly yellow mobile liquids possessing an unpleasant sharp odor resembling that of the initial mercaptan. They were readily soluble in organic solvents and insoluble in water. On storage, and even more rapidly under the action of atmospheric oxygen, they decomposed yielding the corresponding disulfides and arsenic oxide, for example



## EXPERIMENTAL

The initial  $\beta$ -isopropylthioethyl mercaptan is not described in the literature. We obtained it by the method of Goldsnorthy et al. [8] from  $\beta$ -isopropylthioethyl chloride and sodium hydrogen sulfide with a yield of 80.6%, bp 68.5-71° (12 mm).

**Preparation of the di-( $\beta$ -Isopropylthioethyl) Ester of Dithiophenylarsinous Acid (II).** To 6 g of dimethyl phenylarsenite was added 7.6 g of  $\beta$ -isopropylthioethyl mercaptan, the mixture becoming hot. After standing for 30 min, the reaction mixture was heated to the boil and the methanol liberated was distilled off (1.8 ml). When the residue was distilled in vacuum, 6.7 g of (II) with bp 204° (0.003 mm) was obtained.

The tri-( $\beta$ -isopropylthioethyl) ester of trithioarsenious acid (I), the di-( $\beta$ -isopropylthioethyl) ester of dithioethylarsinous acid (III), the  $\beta$ -isopropylthioethyl ester of thiodiphenylarsinous acid (IV), and the  $\beta$ -isopropylthioethyl ester of thiophenarsazinous acid (V) were synthesized similarly.

**Action of Atmospheric Oxygen on tri-( $\beta$ -Isopropylthioethyl) Trithioarsenite (I).** Dry air was passed through 5 g of the thio ester under investigation for 15 h and the white precipitate that separated out was filtered off, washed several times with acetone, dried, and analyzed. This gave 0.9 g (90%) of arsenic trioxide. Found %: As 75.87.  $\text{As}_2\text{O}_3$ . Calculated %: As 75.73.

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Table 1

| No. | Compound   | Yield, % | bp, °C<br>(p, mm Hg)      | $n_D^{20}$ | $d_4^{20}$ | MR<br>found | $\frac{AR}{\text{for As}}$<br>found | Yield, % |       | Empirical<br>formula                             | Calculated, % |       |
|-----|--|----------|---------------------------|------------|------------|-------------|-------------------------------------|----------|-------|--|---------------|-------|
|     |  |          |                           |            |            |             |                                     | As       | S     |  | As            | S     |
| I   | $\text{As} \left( \text{SCH}_2\text{CH}_2\text{SCH} \begin{array}{c} \text{CH}_3 \\ \text{CH}_3/3 \end{array} \right)$                     | 97.5     | Oil                       | 1.5971     | 1.2042     | 136.03      | 12.07                               | 15.08    | 40.97 | $\text{C}_{15}\text{H}_{38}\text{S}_9\text{As}$  | 15.58         | 40.02 |
| II  | $\text{As} \left( \text{SCH}_2\text{CH}_2\text{SCH} \begin{array}{c} \text{CH}_3 \\ \text{CH}_3/2 \end{array} \right)$                     | 52.2     | 204 (0.003)               | 1.6128     | 1.2252     | 119.92      | 12.08                               | 17.53    | 30.62 | $\text{C}_{16}\text{H}_{37}\text{S}_4\text{As}$  | 17.74         | 30.37 |
| III | $\text{C}_2\text{H}_5\text{As} \left( \text{SCH}_2\text{CH}_2\text{SCH} \begin{array}{c} \text{CH}_3 \\ \text{CH}_3/2 \end{array} \right)$ | 41.5     | 151 (0.09)                | 1.5810     | 1.1849     | 105.32      | 12.35                               | 19.78    | 34.81 | $\text{C}_{12}\text{H}_{27}\text{S}_4\text{As}$  | 20.00         | 34.24 |
| IV  | $(\text{C}_6\text{H}_5)_3\text{AsSCH}_2\text{CH}_2\text{SCH} \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array}$                      | 53.3     | 182 (0.002)               | 1.6390     | 1.2638     | 103.74      | 12.01                               | 20.81    | 18.03 | $\text{C}_{17}\text{H}_{21}\text{S}_2\text{As}$  | 20.55         | 17.60 |
| V   | $\text{HN}(\text{C}_6\text{H}_5)_2\text{AsSCH}_2\text{CH}_2\text{SCH} \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array}$             | 74.0     | mp 89–91<br>(cyclohexane) | —          | —          | —           | —                                   | 19.59    | 17.76 | $\text{C}_{17}\text{H}_{19}\text{NS}_2\text{As}$ | 19.90         | 17.03 |

Distillation of the filtrate yielded 2.1 g (50%) of a substance with bp 128.5-129° (0.006 mm);  $n_D^{20}$  1.5542;  $d_4^{20}$  1.0663. Found %: S 47.34, MR 81.33.  $C_{10}H_{22}S_4$ . Calculated %: S 47.41, MR 80.66. From the analytical results, the substance isolated was pure  $\beta$ -isopropylthioethyl disulfide.

#### CONCLUSIONS

Five previously unknown  $\beta$ -isopropylthioethyl esters of thioarsenious, ethylthioarsinous, phenylthioarsinous, diphenylthioarsinous, and thiophenarsazinous acids have been synthesized; their properties have been described.

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