

## Facile Catalytic Conversion of Carboxylic Acids into Thiocarboxylic S-Acids by the Ph<sub>3</sub>SbO/P<sub>4</sub>S<sub>10</sub> System

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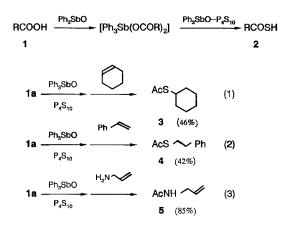
Received June 11, 1990

Key Words: Triphenylstibine oxide / Phosphorus(V) sulfide / Thiocarboxylic S-acids, preparation of / Carboxylic acids, sulfuration of

Thiocarboxylic S-acids 2 are readily prepared by direct sulfuration of the corresponding carboxylic acids 1 catalyzed by  $Ph_3SbO/P_4S_{10}$  under mild conditions.

Although tetraphosphorus decasulfide  $(P_4S_{10})$  is one of a most readily accessible sulfurating agent for carbonyl derivatives<sup>1</sup>, some serious limitations prevent its wide use in organic synthesis: namely low reactivity under mild conditions and low selectivity under practical conditions<sup>2</sup>). On the other hand, Lawesson's reagent<sup>3</sup>) and its analogs represent the successful modifications of P<sub>4</sub>S<sub>10</sub> and are useful even under mild conditions for the sulfuration of carbonyl compounds. The use of Lawesson's reagent, however, generally gives a mixture of thiocarboxylic O- and S-acids in the sulfuration of carboxylic acid derivatives<sup>4</sup>). Consequently, the preparation of thiocarboxylic S-acids, which are efficient acylating agents<sup>5</sup>), has predominantly been limited to the classical hydrogen sulfide promoted thiolation<sup>6</sup>, and hydrolysis of thiocarboxamides<sup>7</sup> so far. In this communication, we report on a new and alternative activation process of P<sub>4</sub>S<sub>10</sub> using Ph<sub>3</sub>SbO as a catalyst effective in the conversion of carboxylic acids into thiocarboxylic S-acids.

First, we have found that triphenylantimony diacetate [Ph<sub>3</sub>Sb-(OAc)<sub>2</sub>], which is readily prepared in situ from Ph<sub>3</sub>SbO and a stoichiometric amount of acetic acid (**1a**), reacts smoothly with P<sub>4</sub>S<sub>10</sub> in benzene to give **2a** in good yield. In addition, Ph<sub>3</sub>SbO can be recovered in high yield. In previous papers<sup>8</sup> we have demonstrated the useful activation procedure of carboxylate moieties involving in situ formation of an Sb – OC(O)R linkage in the direct amidation and that Ph<sub>3</sub>SbO can be recycled. Similarly, it should be expected that Ph<sub>3</sub>SbO can also activate carboxylic moieties toward nucleophilic attack by S<sub>3</sub>P<sup>⊕</sup> – S<sup>⊕</sup> that is believed to be an active species of P<sub>4</sub>S<sub>10</sub><sup>2d</sup>. Thus, we have attempted to carry out the catalytic sul-



furation of several carbocyclic acids using  $Ph_3SbO$ , and the results obtained are summarized in Table 1.

Table 1. Catalytic sulfuration of 1 by  $Ph_3SbO/P_4S_{10}$ 

Compound	R	<i>T</i> [°C]	<i>t</i> [h]	yield [%] <sup>a</sup>
 1 a/2 a	Me	40	1	92
1 b/2 b	Ph	50	1	82
1 c/2 c	Pr	40	1	82
1 d/2 d	iPr	40	1	95
1 e/2 e	tBu	70	3	87
1 f/2 f	CHEtBu	80	1	94
1 g/2 g	HOOC[CH <sub>2</sub> ] <sub>4</sub> / HSOC[CH <sub>2</sub> ] <sub>4</sub>	80	6	64
1 h/2 h	$CH_2 = CH$	50	3	85 <sup>b,c)</sup>

<sup>a)</sup> Isolated yields with respect to the amounts of 1 used. - <sup>b)</sup> Vacuum distillation of the reaction mixture resulted in the formation of resinous solid. - <sup>c)</sup> Crude yield.

The catalytic conversion of carbocyclic acids into thiocarboxylic S-acids in the presence of  $Ph_3SbO/P_4S_{10}$  smoothly proceeds even under mild conditions, and thiocarboxylic S-acids 2a - g were isolated by distillation in excellent yields. In the controlled reactions without  $Ph_3SbO$  under similar conditions, 2 has been obtained in yields <10%. Steric hindrance in 1 is slightly influenced by the reaction temperature and periods, but  $Ph_3SbO/P_4S_{10}$  effectively promotes the thiolation of 1 below 80°C. Although the formation of 2h in the reaction mixture has been detected by IR and NMR spectroscopy, attempts to isolate 2h failed because of the high polymerizability of the latter.

Further, we have treated 1a with olefins and allylamine in the presence of Ph<sub>3</sub>SbO/P<sub>4</sub>S<sub>10</sub> [eqs. (1)-(3)]. In all runs, the expected products such as the thiocarboxylic S-esters 3, 4 and N-allylacetamide (5) have been obtained in good yields. Especially, it is noteworthy that the aminolysis of 1a by allylamine is completed within half an hour. Conclusively, we feel that these results should open a new procedure for the preparation of S-esters and amides<sup>9</sup>.

## Experimental

IR and <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded with a Hitachi 260-30 spectrophotometer and a Hitachi R 90 H FT spectrometer,

Chem. Ber. 123 (1990) 2081 – 2082 (C) VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1990 0009 – 2940/90/1010 – 2081 \$ 3.50 + .25/0

respectively. - Mass spectra were measured with a JEOL JMS-DX 303 (Faculty of Engineering, Osaka University). - All spectra were consistent with the assigned structures.

Sulfuration of Triphenylantimony Diacetate  $[Ph_3Sb(OAc)_2]$  by  $P_4S_{10}$ : Acetic acid (1a, 120 mg, 2.0 mmol) was added dropwise to a suspension of triphenylstibine oxide (Ph<sub>3</sub>SbO, 369 mg, 1.0 mmol)<sup>10</sup> in benzene (20 ml) at room temp. The precipitate gradually disappeared, and a clear solution of Ph<sub>3</sub>Sb(OAc)<sub>2</sub> was obtained after 1 h. Then powdery  $P_4 S_{10}^{(11)}$  (89 mg, 0.2 mmol) was added to the solution which was heated at 40°C for 1 h. Some yellowish precipitate was filtered off, and careful fractional distillation of the filtrate gave colorless 2a in 74% yield (113 mg).

Ethanethioic S-Acid (2a): B. p. 90°C (ref.<sup>12)</sup>: 93°C).

General Procedure for the Catalytic Sulfuration of Carboxylic Acids by the  $Ph_3SbO/P_4S_{10}$  System: To a suspension of 5.0 mmol (2.22 g) of P<sub>4</sub>S<sub>10</sub> and 2.5 mmol (923 mg) of Ph<sub>3</sub>SbO in 50 ml of benzene was added 50 mmol of the corresponding carboxylic acid. After the reaction, 2a - g were separated by kugelrohr distillation.

Benzenethioic S-Acid (2b): B. p.  $75^{\circ}C/3$  Torr (ref.<sup>12</sup>):  $85-87^{\circ}C/3$ 10 Torr).

Butanethioic S-Acid (2c): B. p. 130°C (ref.<sup>12)</sup>: 128-132°C).

2-Methylpropanethioic S-Acid (2d): B. p. 120°C. - IR (KRS-5):  $\tilde{v} = 2550 \text{ cm}^{-1} (\text{S}-\text{H}), 1700 (\text{C}=\text{O}), - {}^{1}\text{H} \text{ NMR} (\text{CDCl}_{3}); \delta =$ 1.20 (d, J = 7.0 Hz, 6H, CH<sub>3</sub>), 2.51 (sept, 1H, CH), 9.3 (br., 1H, COSH).  $-{}^{13}$ C NMR (CDCl<sub>3</sub>):  $\delta = 19.1$  (q, CH<sub>3</sub>), 44.4 (d, CH), 201.9 (s, COSH). - MS (70 eV): m/z (%) = 104 (100) [M<sup>+</sup>].

> C<sub>4</sub>H<sub>8</sub>OS (104.2) Calcd. C 46.11 H 7.74 S 30.77 Found C 46.20 H 7.81 S 31.00

2,2-Dimethylpropanethioic S-Acid (2e): B. p. 118-120°C. - IR (KRS-5):  $\tilde{v} = 2550 \text{ cm}^{-1}$  (S-H), 1683 (C=O). - <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 2.53$  (s, 9 H, CH<sub>3</sub>), 7.8 (br., 1 H, COSH).  $- {}^{13}C$  NMR  $(CDCl_3)$ :  $\delta = 26.4$  (q, CH<sub>3</sub>), 48.5 [s,  $C(CH_3)_3$ ], 198.0 (s, COSH). MS (70 eV): m/z (%) = 118 (28) [M<sup>+</sup>], 56 (100) [M<sup>+</sup> - COSH].

> C<sub>5</sub>H<sub>10</sub>OS (118.2) Calcd. C 42.84 H 8.53 S 27.09 Found C 42.91 H 8.49 S 27.02

2-Ethylhexanethioic S-Acid (2f): B. p. 22°C/1.5 Torr. - IR (KRS-5):  $\tilde{v} = 2550 \text{ cm}^{-1} (\text{S}-\text{H}), 1702 (\text{C}=\text{O}). - {}^{1}\text{H} \text{ NMR (CDCl}_{3}): \delta =$ 0.89 and 0.91 (t, J = 7.0 Hz, 6H, CH<sub>3</sub>), 1.0 - 2.2 (m, 8H, CH<sub>2</sub>), 2.40 (quint, J = 7.1 Hz, 1H, CH), 4.90 (br. s, COSH).  $- {}^{13}C$  NMR  $(CDCl_3)$ :  $\delta = 11.5$  and 13.8 (q, CH<sub>3</sub>), 22.5 (t, CH<sub>2</sub>), 25.7 (t, CH<sub>2</sub>), 29.2 (t, CH<sub>2</sub>), 32.0 (t, CH<sub>2</sub>), 57.4 (d, CH), 201.7 (s, COSH). - MS  $(70 \text{ eV}): m/z (\%) = 160 (100) [M^+].$ 

> C<sub>8</sub>H<sub>16</sub>OS (160.3) Calcd. C 59.94 H 10.06 S 20.00 Found C 60.08 H 10.11 S 20.15

Hexanedithioic S-Acid (2g): B. p. 120°C/0.8 Torr. – IR (KRS-5):  $\tilde{v} = 2545 \text{ cm}^{-1} (\text{S}-\text{H}), 1685 (\text{C}=\text{O}). - {}^{1}\text{H} \text{ NMR} (\text{CDCl}_{3}): \delta =$ 1.54 (br. t, J = 6.8 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>), 3.11 (dt, 4H, CH<sub>2</sub>COSH), 6.12 (s, 2H, COSH). - <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 24.1 (d, CH<sub>2</sub>), 45.0 (t, CH<sub>2</sub>COSH), 196.8 (s, COSH). – MS (70 eV): m/z (%) = 178  $(100) [M^+].$ 

> $C_6H_{10}O_2S_2$  (178.3) Calcd. C 40.42 H 5.65 S 35.96 Found C 40.51 H 5.77 S 36.11

2-Propenethioic S-Acid (2h): Crude 2h was obtained after filtration and concentration of the reaction mixture, but purification by vacuum distillation failed because of higher polymerizability even at 30 °C. – IR (KRS-5):  $\tilde{v} = 2540 \text{ cm}^{-1}$  (S–H), 1720 (C=O). – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 5.6 - 6.7$  (m, 3H, vinylic H), 9.8 (s, 1H, COSH).  $-{}^{13}C$  NMR (CDCl<sub>3</sub>):  $\delta = 128.4$  (s, =CH), 135.7 (d, CH<sub>2</sub>=), 196.1 (s, COSH).

Reactions of Acetic Acid (1a) with Olefins and Allylamine in the Presence of  $Ph_3SbO/P_4S_{10}$ : To a benzene (20 ml) solution of 1a (120 mg, 2 mmol), P<sub>4</sub>S<sub>10</sub> (89 mg, 0.2 mmol), and Ph<sub>3</sub>SbO (37 mg, 0.1 mmol), 2.0 mmol (164 mg) of cyclohexene, styrene (208 mg), or allylamine (114 mg) was added dropwise, and the mixture was stirred for ca. 12 h at 50°C. Fractional distillation gave the corresponding thioesters 3 and 4 or allylamide 5, respectively.

S-Cyclohexyl Thioacetate (3): B. p. 64°C/3 Torr (ref.<sup>13)</sup>: 77°C/5.8 Torr), yield 146 mg (46%).

S-(2-Phenylethyl) Thioacetate (4): B. p. 90°C/0.5 Torr (ref.<sup>14)</sup>.  $80 - 84 \degree C/0.3$  Torr), yield 151 mg (42%).

*N*-(2-Propenyl)acetamide (5): B. p. 90°C/5 Torr (ref.<sup>15)</sup>: 87°C/5 Torr), yield 169 mg (85%).

## CAS Registry Numbers

1a:  $64-19-7 / 1b: 65-85-0 / 1c: 107-92-6 / 1d: 79-31-2 / 1e: 75-98-9 / 1f: 149-57-5 / 1g: 124-04-9 / 1h: 79-10-7 / 2a: 507-09-5 / 2b: 98-91-9 / 2c: 3931-64-4 / 2d: 44296-44-8 / 2e: 55561-02-9 / 2f: 128600-83-9 / 2g: 10604-70-3 / 2h: 88947-37-9 / 3: 10039-63-1 / 4: 35065-97-5 / 5: 692-33-1 / Ph_3SbO: 4756-75-6 / P_4S_{19}: 15857-57-5 / 2675-6 /$ cyclohexcne: 110-83-8 / styrene: 100-42-5 / allylamine: 107-11-9

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