



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** [ $\text{Ph}_3\text{Sb}(\text{OAc})_2$ ] by  $\text{P}_4\text{S}_{10}$ : Acetic acid (**1a**, 120 mg, 2.0 mmol) was added dropwise to a suspension of triphenylstibine oxide ( $\text{Ph}_3\text{SbO}$ , 369 mg, 1.0 mmol)<sup>10</sup> in benzene (20 ml) at room temp. The precipitate gradually disappeared, and a clear solution of  $\text{Ph}_3\text{Sb}(\text{OAc})_2$  was obtained after 1 h. Then powdery  $\text{P}_4\text{S}_{10}$ <sup>11</sup> (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  $\text{Ph}_3\text{SbO}/\text{P}_4\text{S}_{10}$  System**: To a suspension of 5.0 mmol (2.22 g) of  $\text{P}_4\text{S}_{10}$  and 2.5 mmol (923 mg) of  $\text{Ph}_3\text{SbO}$  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°C/3 Torr (ref.<sup>12</sup>: 85–87°C/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):  $\tilde{\nu} = 2550 \text{ cm}^{-1}$  (S—H), 1700 (C=O). — <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta = 1.20$  (d,  $J = 7.0$  Hz, 6H,  $\text{CH}_3$ ), 2.51 (sept, 1H, CH), 9.3 (br., 1H, COSH). — <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta = 19.1$  (q,  $\text{CH}_3$ ), 44.4 (d, CH), 201.9 (s, COSH). — MS (70 eV):  $m/z$  (%) = 104 (100) [ $\text{M}^+$ ].

$\text{C}_4\text{H}_8\text{OS}$  (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):  $\tilde{\nu} = 2550 \text{ cm}^{-1}$  (S—H), 1683 (C=O). — <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta = 2.53$  (s, 9H,  $\text{CH}_3$ ), 7.8 (br., 1H, COSH). — <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta = 26.4$  (q,  $\text{CH}_3$ ), 48.5 [s,  $\text{C}(\text{CH}_3)_3$ ], 198.0 (s, COSH). — MS (70 eV):  $m/z$  (%) = 118 (28) [ $\text{M}^+$ ], 56 (100) [ $\text{M}^+ - \text{COSH}$ ].

$\text{C}_5\text{H}_{10}\text{OS}$  (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):  $\tilde{\nu} = 2550 \text{ cm}^{-1}$  (S—H), 1702 (C=O). — <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta = 0.89$  and  $0.91$  (t,  $J = 7.0$  Hz, 6H,  $\text{CH}_3$ ), 1.0–2.2 (m, 8H,  $\text{CH}_2$ ), 2.40 (quint,  $J = 7.1$  Hz, 1H, CH), 4.90 (br. s, COSH). — <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta = 11.5$  and  $13.8$  (q,  $\text{CH}_3$ ), 22.5 (t,  $\text{CH}_2$ ), 25.7 (t,  $\text{CH}_2$ ), 29.2 (t,  $\text{CH}_2$ ), 32.0 (t,  $\text{CH}_2$ ), 57.4 (d, CH), 201.7 (s, COSH). — MS (70 eV):  $m/z$  (%) = 160 (100) [ $\text{M}^+$ ].

$\text{C}_8\text{H}_{16}\text{OS}$  (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):  $\tilde{\nu} = 2545 \text{ cm}^{-1}$  (S—H), 1685 (C=O). — <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta = 1.54$  (br. t,  $J = 6.8$  Hz, 4H,  $\text{CH}_2\text{CH}_2$ ), 3.11 (dt, 4H,  $\text{CH}_2\text{COSH}$ ), 6.12 (s, 2H, COSH). — <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta = 24.1$  (d,  $\text{CH}_2$ ), 45.0 (t,  $\text{CH}_2\text{COSH}$ ), 196.8 (s, COSH). — MS (70 eV):  $m/z$  (%) = 178 (100) [ $\text{M}^+$ ].

$\text{C}_6\text{H}_{10}\text{O}_2\text{S}_2$  (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):  $\tilde{\nu} = 2540 \text{ cm}^{-1}$  (S—H), 1720 (C=O). — <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta = 5.6$ – $6.7$  (m, 3H, vinylic H), 9.8 (s, 1H, COSH). — <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta = 128.4$  (s, =CH), 135.7 (d,  $\text{CH}_2=$ ), 196.1 (s, COSH).

**Reactions of Acetic Acid (1a) with Olefins and Allylamine in the Presence of  $\text{Ph}_3\text{SbO}/\text{P}_4\text{S}_{10}$** : To a benzene (20 ml) solution of **1a** (120 mg, 2 mmol),  $\text{P}_4\text{S}_{10}$  (89 mg, 0.2 mmol), and  $\text{Ph}_3\text{SbO}$  (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°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 /  $\text{Ph}_3\text{SbO}$ : 4756-75-6 /  $\text{P}_4\text{S}_{10}$ : 15857-57-5 / cyclohexene: 110-83-8 / styrene: 100-42-5 / allylamine: 107-11-9

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