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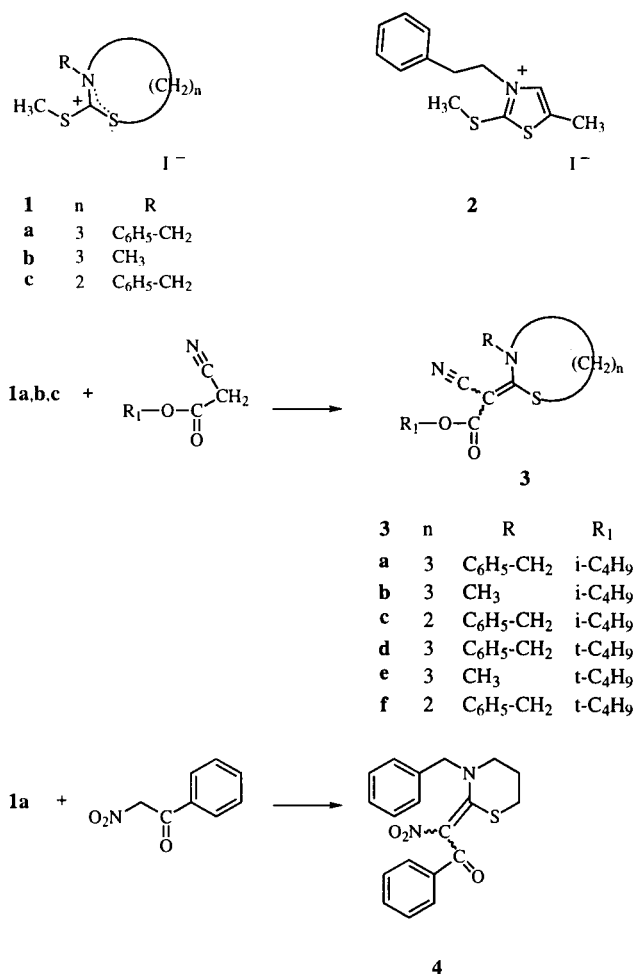
The title compounds **1a-c** and **2** were reacted with several doubly activated methylene components to yield the cyclic ketene *S,N*-acetals **3-10**.

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In the first part of this series we reported on the reaction of the title compounds with some *N*-nucleophiles like *N*-arylsulfonylamides and arylcarbaldehyde hydrazones resulting in the formation of cyclic isothioureas respectively cyclic isothiosemicarbazides [1]. We now wish to report the reaction of the title compounds with some *C*-nucleophiles represented by doubly activated methylene components. We also report the first analytical and spectroscopic characterization of 3-benzyl-2-methylthio-5,6-dihydro-4*H*-1,3-thiazinium iodide (**1a**) and 3-methyl-2-methylthio-4,5-dihydro-2*H*-1,3-thiazinium iodide (**1b**). 3-Benzyl-2-methylthio-4,5-dihydrothiazolium iodide (**1c**) was not stable enough to be fully characterized by analytical and spectroscopic methods. 2-Methylthio-3-phenethylthiazolium iodide (**2**) was prepared *via* methods reported [2,3]. All compounds possess the structure of cyclic iminiumthiocarbonic acid diesters with a strongly electrophilic carbon center which can react with a variety of CH-acidic components yielding cyclic ketene *S,N*-acetals **3-10**. These types of compounds can also be prepared by the reaction of cyclic iminiumthiocarbonic acid ester chloride chlorides with doubly activated methylene components as described earlier [4,5] but the methiodides **1a-c** and **2** are easier to handle and the yields mostly are higher. In contrast to the iminiumthiocarbonic acid ester chloride chlorides which cannot be isolated and have to be reacted after preparation *in situ*, the methiodides **1a-c** and **2** can be isolated and stored for several days at 5° under protection from moisture. The reaction with the CH-acidic components butyl cyanoacetates, 2-nitro-1-phenylethanone (Scheme 1), diethyl malonate, 1,3-dimethylhexahydropyrimidine-2,4,6-trione, tetrahydrofuran-2,4-dione (Scheme 2) and 1,3-propanedinitrile, sulfonylacetonitriles (Scheme 3) is easily accomplished by heating the components in the presence of triethylamine and lead(II) nitrate in dichloromethane for about 3 hours.

Some compounds **3-10** are now being evaluated for activity in the agricultural field.

Scheme 1



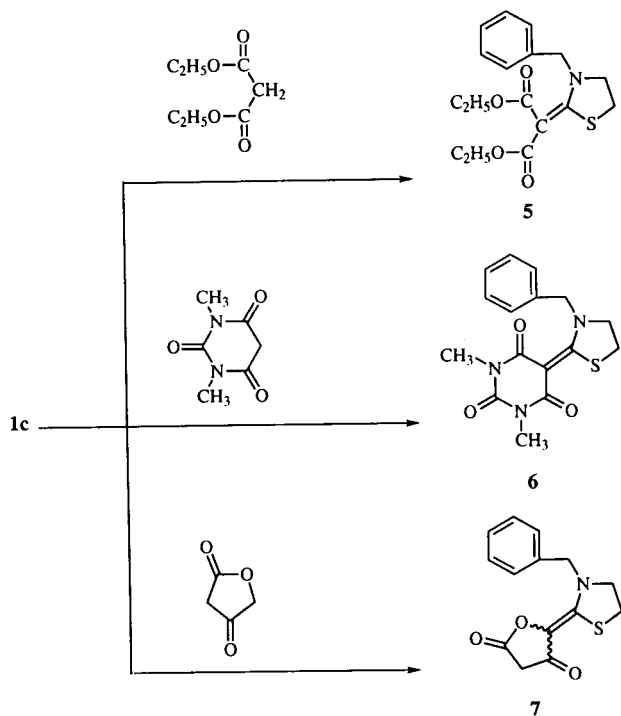
## EXPERIMENTAL

Instrumental equipment and chromatographic conditions were those already described [6].

3-Benzyl-2-methylthio-5,6-dihydro-4*H*-1,3-thiazinium Iodide (**1a**).

This compound was prepared *via* [1] from 2.2 g (0.010 mole)

Scheme 2



of 3-benzyltetrahydro-2H-1,3-thiazine-2-thione and 10 ml of methyl iodide. It was obtained as yellowish crystals, 3.62 g (99%), mp 96°; ir:  $\nu$  C=N 1550  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  2.45-2.48 (m, 2H, 5-H thiazine,  $J = 6$  Hz), 2.89 (s, 3H, SCH<sub>3</sub>), 3.66-3.69 (t, 2H, 6-H thiazine,  $J = 6$  Hz), 4.11-4.14 (t, 2H, 4-H thiazine,  $J = 6$  Hz), 5.28 (s, 2H, CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>), 7.40-7.45 ppm (m, 5H, C<sub>6</sub>H<sub>5</sub>);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  17.2 (SCH<sub>3</sub>), 21.1 (C-5 thiazine), 30.0 (C-6 thiazine), 52.9 (C-4 thiazine), 62.5 (CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>), 128.0-129.6 (C-2,3,4,5,6 phenyl), 131.1 (C-1 phenyl), 187.1 ppm (C-2 thiazine); ms:  $m/z$  225 (11), 224 (15), 223 (100, 3-benzyltetrahydro-2H-1,3-thiazine-2-thione).

Anal. Calcd. for C<sub>12</sub>H<sub>16</sub>INS<sub>2</sub> (365.30): C, 39.46; H, 4.41; N, 3.83; S, 17.55. Found: C, 39.18; H, 4.33; N, 3.81; S, 17.46.

### 3-Methyl-2-methylthio-4,5-dihydro-2H-1,3-thiazinium Iodide (1b).

This compound was obtained from 1.47 g (0.010 mole) 3-methyltetrahydro-2H-1,3-thiazine-2-thione and 10 ml of methyl iodide as described above as yellowish crystals, 2.86 g (99%), mp 125°; ir:  $\nu$  C=N 1570  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  2.51-2.56 (m, 2H, 5-H thiazine,  $J = 6$  Hz), 2.86 (s, 3H, SCH<sub>3</sub>), 3.63-3.65 (t, 2H, 6-H thiazine,  $J = 6$  Hz), 3.72 (s, 3H, NCH<sub>3</sub>), 4.22-4.25 ppm (t, 2H, 4-H thiazine,  $J = 6$  Hz);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  17.0 (SCH<sub>3</sub>), 21.1 (C-5 thiazine), 29.3 (C-6 thiazine), 47.2 (NCH<sub>3</sub>), 55.5 (C-4 thiazine), 185.7 ppm (C-2 thiazine).

Anal. Calcd. for C<sub>6</sub>H<sub>12</sub>INS<sub>2</sub> (289.20): C, 24.92; H, 4.18; N, 4.84; S, 22.17. Found: C, 24.90; H, 4.14; N, 4.47; S, 22.36.

### General Procedure for the Condensation of the 2-Methylthio-4,5-dihydro-2H-1,3-thiazinium-, 2-Methylthio-4,5-dihydrothiazolium- and 2-Methylthio-5-methylthiazolium Iodides 1a-c, 2 with Methylene Active Compounds.

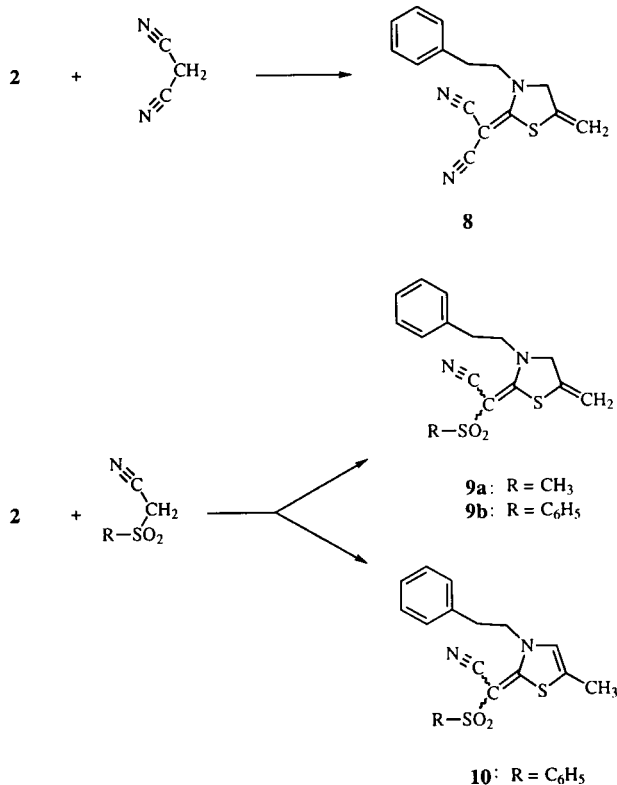
To a solution of equimolar quantities of the active methylene compound and of 1a-c or 2 in 50 ml of dichloromethane were added 2 equivalents of triethylamine and 1.5 equivalents of lead(II) nitrate protected from moisture. The mixture was refluxed for 3 hours. After cooling to room temperature the solids were filtered and the filtrate evaporated *in vacuo*. The residue was purified by recrystallization or column chromatography.

### Isobutyl [2-(3-Benzyltetrahydro-2H-1,3-thiazin-2-ylidene)cianoacetate] (3a).

This compound was obtained from 1.42 g (0.010 mole) of isobutyl cyanoacetate and 3.65 g (0.010 mole) of 1a as colorless crystals (ethanol), 2.0 g (61%), mp 128°; ir: CN 2190, CO 1680  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  0.96-1.01 (d, 6H, 2 CH<sub>3</sub>), 1.82-1.89 (m, 2H, 5-H thiazine), 1.95-2.02 (m, 1H, CH-CH<sub>2</sub>O), 2.87-2.94 (t, 2H, 6-H thiazine,  $J = 7$  Hz), 3.36-3.40 (t, 2H, 4-H thiazine), 3.91-3.92 (d, 2H, CH-CH<sub>2</sub>O), 4.61 (s, 2H, CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>), 7.29-7.31 (m, 2H, phenyl protons);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  26.0 (2 CH<sub>3</sub>), 26.1 (C-5 thiazine), 27.1 (C-6 thiazine), 28.0 (CH-CH<sub>2</sub>O), 47.9 (C-4 thiazine), 61.7 (CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>), 70.4 (CH-CH<sub>2</sub>O), 71.4 (C=C-CN), 119.7 (CN), 128.8-129.1 (C-2,3,4,5,6 phenyl), 135.5 (C-1 phenyl), 164.6 (C-2 thiazine), 176.4 ppm (CO); ms:  $m/z$  331 (15, M<sup>+</sup>), 330 (68), 91 (100).

Anal. Calcd. for C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S (330.45): C, 65.43; H, 6.71; N, 8.48; S, 9.70. Found: C, 65.21; H, 6.87; N, 8.45; S, 9.70.

Scheme 3



Isobutyl [2-(3-Methyltetrahydro-2*H*-1,3-thiazin-2-ylidene)cynoacetate] (**3b**).

This compound was obtained from 0.71 g (0.005 mole) of isobutyl cyanoacetate and 1.45 g (0.005 mole) of **1b** as colorless crystals (light petroleum/diethyl ether/ethanol), 0.50 g (39%), mp 69°; ir:  $\nu$  CN 2190, CO 1680  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  0.95-0.97 (d, 6H, 2  $\text{CH}_3$ ), 1.94-2.00 (m, 1H,  $\text{CH}-\text{CH}_2\text{O}$ ), 2.24-2.30 (m, 2H, 5-H thiazine,  $J = 6$  Hz), 3.00-3.04 (t, 2H, 6-H thiazine,  $J = 6$  Hz), 3.27 (s, 3H,  $\text{NCH}_3$ ), 3.49-3.53 (t, 2H, 4-H thiazine), 3.88-3.90 ppm (d, 2H,  $\text{CH}-\text{CH}_2\text{O}$ );  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  19.1 (2  $\text{CH}_3$ ), 24.2 (C-5 thiazine), 27.0 (C-6 thiazine), 28.0 ( $\text{CH}-\text{CH}_2\text{O}$ ), 46.6 ( $\text{NCH}_3$ ), 52.1 (C-4 thiazine), 69.7 (C=C-CN), 70.2 ( $\text{CH}-\text{CH}_2\text{O}$ ), 119.8 (CN), 164.6 (C-2 thiazine), 173.7 ppm (CO); ms:  $m/z$  254 (33,  $\text{M}^+$ ), 181 (66), 154 (100).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$  (254.35): C, 56.67; H, 7.13; N, 11.01; S, 12.61. Found: C, 56.72; H, 7.21; N, 11.22; S, 12.64.

Isobutyl [2-(3-Benzylthiazolidin-2-ylidene)cynoacetate] (**3c**).

This compound was obtained from 0.71 g (0.005 mole) of isobutyl cyanoacetate and 1.76 g (0.005 mole) of **1c** [1] as colorless crystals (diethyl ether/ethanol), 0.30 g (19%), mp 79°; ir:  $\nu$  CN 2200, CO 1680  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  0.96-0.97 (d, 6H, 2  $\text{CH}_3$ ), 1.97-2.04 (m, 1H,  $\text{CH}-\text{CH}_2\text{O}$ ), 2.99-3.03 (t, 2H, 5-H thiazolidine,  $J = 8$  Hz), 3.75-3.79 (t, 2H, 4-H thiazolidine,  $J = 8$  Hz), 3.95-3.97 (d, 2H,  $\text{CH}-\text{CH}_2\text{O}$ ), 5.18 (s, 2H,  $\text{CH}_2-\text{C}_6\text{H}_5$ ), 7.26-7.40 ppm (m, 5H, phenyl protons);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  19.0 (2  $\text{CH}_3$ ), 26.4 (C-5 thiazolidine), 27.8 ( $\text{CH}-\text{CH}_2\text{O}$ ), 53.5 (C-4 thiazolidine), 56.4 ( $\text{CH}_2-\text{C}_6\text{H}_5$ ), 70.9 (C=C-CN), 117.5 (CN), 127.6, 128.3, 129.0 (C-2,3,4,5,6 phenyl), 134.8 (C-1 phenyl), 167.2 (C-2 thiazolidine), 172.3 ppm (CO); ms:  $m/z$  317 (11), 316 (52,  $\text{M}^+$ ), 216 (85), 91 (100).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$  (316.42): C, 64.53; H, 6.37; N, 8.85; S, 10.13. Found: C, 64.58; H, 6.33; N, 8.78; S, 10.05.

*tert*-Butyl [2-(3-Benzyltetrahydro-2*H*-1,3-thiazin-2-ylidene)cynoacetate] (**3d**).

This compound was obtained from 1.42 g (0.010 mole) of *tert*-butyl cyanoacetate and 3.62 g (0.010 mole) of **1a** as colorless crystals (ethanol), 0.80 g (24%), mp 123°; ir:  $\nu$  CN 2200, CO 1670  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.51 (s, 9H, 3  $\text{CH}_3$ ), 1.81-1.84 (m, 2H, 5-thiazine), 2.84-2.87 (t, 2H, 6-H thiazine,  $J = 7$  Hz), 3.34-3.38 (t, 2H, 4-H thiazine,  $J = 7$  Hz), 4.58 (s, 2H,  $\text{CH}_2-\text{C}_6\text{H}_5$ ), 7.30-7.32, 7.38-7.40 ppm (m, 5H phenyl protons); ms:  $m/z$  330 (22,  $\text{M}^+$ ), 274 (66), 230 (79), 91 (100).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2\text{S}$  (330.45): C, 65.43; H, 6.71; N, 8.48; S, 9.70. Found: C, 65.16; H, 6.55; N, 8.43; S, 9.71.

*tert*-Butyl [2-(3-Methyltetrahydro-2*H*-1,3-thiazin-2-ylidene)cynoacetate] (**3e**).

This compound was obtained from 0.71 g (0.005 mole) of *tert*-butyl cyanoacetate and 1.45 g (0.005 mole) of **1b** as colorless crystals (diethyl ether/ethanol), 0.60 g (47%), mp 162°; ir:  $\nu$  CN 2180, CO 1680  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.49 (s, 9H, 3  $\text{CH}_3$ ), 2.24-2.27 (m, 2H, 5-H thiazine), 2.98-3.02 (t, 2H, 6-H thiazine,  $J = 6$  Hz), 3.25 (s, 3H,  $\text{NCH}_3$ ), 3.47-3.50 (t, 2H, 4-H thiazine,  $J = 6$  Hz);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  24.1 (C-5 thiazine), 26.8 (C-6 thiazine), 28.2 ( $\text{C}(\text{CH}_3)_3$ ), 46.4 ( $\text{NCH}_3$ ), 51.8 (C-4 thiazine), 71.3 (C=C-CN), 80.1 ( $\text{C}(\text{CH}_3)_3$ ), 120.0 (CN), 164.1 (C-2 thiazine), 172.9 ppm (CO); ms:  $m/z$  254 (21,  $\text{M}^+$ ), 198 (55), 154 (100).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$  (254.35): C, 56.67; H, 7.13; N, 11.01; S, 12.61. Found: C, 56.56; H, 6.98; N, 11.15; S, 12.58.

*tert*-Butyl [2-(3-Benzylthiazolidin-2-ylidene)cynoacetate] (**3f**).

This compound was obtained from 0.71 g (0.005 mole) of *tert*-butyl cyanoacetate and 1.76 g (0.005 mole) of **1c** as colorless crystals (pentane/toluene), 0.79 g (50%), mp 86°; ir:  $\nu$  CN 2200, CO 1700  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.52 (s, 9H, 3  $\text{CH}_3$ ), 2.95-2.99 (t, 2H, 5-H thiazolidine,  $J = 8$  Hz), 3.71-3.75 (t, 2H, 4-H thiazolidine,  $J = 8$  Hz), 5.15 (s, 2H,  $\text{CH}_2-\text{C}_6\text{H}_5$ ), 7.26-7.37 ppm (m, 5H, phenyl protons);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  26.4 (C-5 thiazolidine), 28.3 (O-C( $\text{CH}_3$ )<sub>3</sub>), 53.5 (C-4 thiazolidine), 56.2 ( $\text{CH}_2-\text{C}_6\text{H}_5$ ), 69.6 (C=C-CN), 81.3 (O-C( $\text{CH}_3$ )<sub>3</sub>), 118.0 (CN), 125.3-129.0 (C-2,3,4,5,6 phenyl), 135.1 (C-1 phenyl), 166.6 (C-2 thiazolidine), 171.7 ppm (CO); ms:  $m/z$  316 (15,  $\text{M}^+$ ), 216 (100).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$  (316.43): C, 64.53; H, 6.37; N, 8.85; S, 10.13. Found: C, 64.76; H, 6.24; N, 8.90; S, 9.99.

2-(3-Benzyltetrahydro-2*H*-1,3-thiazin-2-ylidene)-2-nitro-1-phenylethanone (**4**).

This compound was obtained from 1.65 g (0.005 mole) of 2-nitro-1-phenylethanone and 1.83 g (0.005 mole) of **1a** as a yellow powder (ethanol), 0.10 g (6%), mp 165°; ir:  $\nu$  CO 1595  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  2.09-2.14 (m, 2H, 5-H thiazine,  $J = 6$  Hz), 3.08-3.11 (t, 2H, 6-H thiazine,  $J = 6$  Hz), 3.53-3.55 (t, 2H, 4-H thiazine,  $J = 6$  Hz), 4.81 (s, 2H,  $\text{CH}_2-\text{C}_6\text{H}_5$ ), 7.35-7.45, 7.63-7.65 ppm (m, m, 10H, phenyl protons);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  22.4 (C-5 thiazine), 29.0 (C-6 thiazine), 48.8 (C-4 thiazine), 61.2 ( $\text{CH}_2-\text{C}_6\text{H}_5$ ), 118.1 (=C-NO<sub>2</sub>), 127.8, 127.9, 129.4, 129.5, 130.8 (2x C-2,3,4,5,6 phenyl), 131.9 (C-1 phenyl), 140.0 (CO-C-1 phenyl), 179.2 (C-2 thiazine), 186.6 ppm (CO); ms:  $m/z$  308 (100), 91 (71).

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$  (354.43): C, 64.39; H, 5.12; N, 7.90; S, 9.05. Found: C, 64.32; H, 5.16; N, 7.96; S, 9.12.

Diethyl [2-(3-Benzylthiazolidin-2-ylidene)malonate] (**5**).

This compound was obtained from 0.8 g (0.005 mole) of diethyl malonate and 1.76 g (0.005 mole) of **1c** as a colorless oil after flash chromatography with dichloromethane, 0.34 g (26%); ir:  $\nu$  2 CO, 1710, 1670  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.19-1.29 (t, 6H, 2x O- $\text{CH}_2-\text{CH}_3$ ), 2.92-2.95 (t, 2H, 5-H thiazolidine,  $J = 7$  Hz), 3.59-3.62 (t, 2H, 4-H thiazolidine,  $J = 7$  Hz), 4.09-4.14 (q, 4H, 2x O- $\text{CH}_2-\text{CH}_3$ ), 4.45 (s, 2H,  $\text{CH}_2-\text{C}_6\text{H}_5$ ), 7.22-7.24, 7.30-7.37 ppm (m, 5H, phenyl protons);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  14.2 (2  $\text{CH}_3$ ), 26.8 (C-5 thiazolidine), 54.6 (C-4 thiazolidine), 55.1 ( $\text{CH}_2-\text{C}_6\text{H}_5$ ), 60.5 (2x O- $\text{CH}_2-\text{CH}_3$ ), 91.3 (C=C-COOC<sub>2</sub>H<sub>5</sub>), 127.6, 128.0, 128.9 (C-2,3,4,5,6 phenyl), 135.7 (C-1 phenyl), 167.3, 167.5 ppm (2 CO, C-2 thiazolidine); ms:  $m/z$  335 (50,  $\text{M}^+$ ), 91 (100).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{21}\text{NO}_4\text{S}$  (335.43): C, 60.87; H, 6.31; N, 4.18; S, 9.56. Found: C, 60.78; H, 6.24; N, 4.28; S, 9.54.

5-(3-Benzylthiazolidin-2-ylidene)-1,3-dimethylhexahydropyrimidine-2,4,6-trione (**6**).

This compound was obtained from 0.78 g (0.005 mole) of 1,3-dimethylhexahydropyrimidine-2,4,6-trione and 1.76 g (0.005 mole) of **1c** as yellow crystals (ethanol), 0.80 g (60%), mp 164°; ir:  $\nu$  CO 1700, 1640  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  3.11-3.15 (t, 2H, 5-H thiazolidine,  $J = 8$  Hz), 3.33 (s, 6H, 2  $\text{CH}_3$ ), 3.85-3.88 (t, 2H, 4-H thiazolidine,  $J = 8$  Hz),

4.77 (s, 2H,  $\text{CH}_2\text{-C}_6\text{H}_5$ ), 7.23-7.25, 7.34-7.37 ppm (m, m, 5H phenyl);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  27.2 (C-5 thiazolidine), 28.0 (2  $\text{CH}_3$ ), 55.3 (C-4 thiazolidine), 58.3 ( $\text{CH}_2\text{-C}_6\text{H}_5$ ), 88.9 ( $=\text{C-CO}$ ), 128.3, 128.8, 129.2 (C-2,3,4,5,6 phenyl), 134.6 (C-1 phenyl), 152.0 (C-2 thiazolidine), 161.6 (N-CO-N), 179.8 ppm (2 CO); ms: m/z 331 (100,  $\text{M}^+$ ).

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_3\text{S}$  (331.40): C, 57.99; H, 5.17; N, 12.68; S, 9.68. Found: C, 57.95; H, 5.05; N, 12.83; S, 9.51.

### 3-(3-Benzylthiazolidin-2-ylidene)tetrahydrofuran-2,4-dione (7).

This compound was obtained from 0.35 g (0.0034 mole) tetrahydrofuran-2,4-dione and 1.23 g (0.0034 mole) of **1c** as yellowish crystals (ethanol), 0.60 g (65%), mp 129°; ir:  $\nu$  2 CO 1720, 1640  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  3.20-3.24 (t, 2H, 5-H thiazolidine), 3.87-3.91 (t, 2H, 4-H thiazolidine), 4.45 (s, 2H,  $\text{CH}_2\text{-C}_6\text{H}_5$ ), 5.42 (s, 2H, 5-H tetrahydrofuran), 7.25-7.29, 7.34-7.40 ppm (m, m, 5H, phenyl protons);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  27.5 (C-5 thiazolidine), 56.3 (C-4 thiazolidine), 57.0 ( $\text{CH}_2\text{-C}_6\text{H}_5$ ), 71.3 (C-5 tetrahydrofuran), 89.0 (C-3 tetrahydrofuran), 128.0-129.1 (C-2,3,4,5,6 phenyl), 134.8 (C-1 phenyl), 172.6, 174.0 (C-2 thiazolidine, CO-OCH<sub>2</sub>), 191.5 ppm (CO-CH<sub>2</sub>); ms: m/z 275 (82,  $\text{M}^+$ ), 91 (100).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{13}\text{NO}_3\text{S}$  (275.33): C, 61.07; H, 4.76; N, 5.09; S, 11.65. Found: C, 61.05; H, 4.77; N, 5.04; S, 11.70.

### 2-(5-Methylene-3-phenethylthiazolidin-2-ylidene)propanedinitrile (8).

This compound was obtained from 0.15 g (0.0022 mole) of propanedinitrile and 0.80 g (0.0022 mole) of **2** [1] as greenish crystals (ethanol), 0.30 g (51%), mp 158°; ir:  $\nu$  CN 2200  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  3.05-3.08 (t, 2H,  $\text{CH}_2\text{-C}_6\text{H}_5$ , J = 7 Hz), 3.96-4.00 (t, 2H,  $\text{NCH}_2$ , J = 7 Hz), 4.43-4.44 (m, 2H, 4-H thiazolidine), 5.20-5.22 (m, 1H,  $=\text{CH}_2$ ), 5.23-5.25 (m, 1H,  $=\text{CH}_2$ ), 7.26-7.36 ppm (m, 5H, phenyl protons);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  34.4 ( $\text{CH}_2\text{-C}_6\text{H}_5$ ), 45.9 ( $=\text{C}(\text{CN})_2$ ), 51.0 ( $\text{NCH}_2$ ), 65.1 (C-4 thiazolidine), 107.8 ( $=\text{CH}_2$ ), 114.7 (CN), 116.2 (CN), 127.4-129.0 (C-2,3,4,5,6 phenyl), 132.6, 136.6 (C-5 thiazolidine, C-1 phenyl), 170.6 ppm (C-2 thiazolidine); ms: m/z 267 (34,  $\text{M}^+$ ), 104 (100).

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{13}\text{N}_3\text{S}$  (267.35): C, 67.39; H, 4.90; N, 15.72; S, 11.99. Found: C, 67.30; H, 4.87; N, 15.61; S, 12.02.

### 2-(5-Methylene-3-phenethylthiazolidin-2-ylidene)-2-methylsulfonylacetonitrile (9a).

This compound was obtained from 0.60 g (0.005 mole) of methylsulfonylacetonitrile and 1.82 g (0.005 mole) of **2** as light-brown crystals (dichloromethane/ethanol), 0.9 g (56%), mp 198°; ir:  $\nu$  CN 2180,  $\text{SO}_2$  1310, 1140  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  3.10 (s, 3H,  $\text{CH}_3$ ), 3.08-3.12 (t, 2H,  $\text{CH}_2\text{-C}_6\text{H}_5$ , J = 7 Hz), 4.06-4.10 (t, 2H,  $\text{CH}_2\text{N}$ , J = 7 Hz), 4.35-4.36 (m, 2H, 4-H thiazolidine), 5.19-5.21 (m, 2H,  $=\text{CH}_2$ ), 7.26-7.36 ppm (m, 5H, phenyl protons);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  34.3 ( $\text{CH}_2\text{-C}_6\text{H}_5$ ), 43.5 ( $\text{CH}_3$ ), 51.9 ( $\text{CH}_2\text{N}$ ), 62.7 (C-4 thiazolidine), 106.7 ( $=\text{CH}_2$ ), 115.6 (CN), 127.3-129.1 (C-2,3,4,5,6 phenyl), 134.2 (C-1 phenyl), 136.9 (C-5 thiazolidine), 167.3 ppm (C-2

thiazolidine); ms: m/z 241 (26), 104 (100).

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2\text{S}_2$  (320.44): C, 56.23; H, 5.03; N, 8.74; S, 20.01. Found: C, 56.02; H, 4.96; N, 8.68; S, 19.81.

### 2-(5-Methylene-3-phenethylthiazolidin-2-ylidene)-2-phenylsulfonylacetonitrile (9b).

This compound was obtained from 0.83 g (0.005 mole) of phenylsulfonylacetonitrile and 1.82 g (0.005 mole) of **2** after column chromatography with dichloromethane from the first fraction of the eluate as light-brown crystals, 1.0 g (51%), mp 180°; ir:  $\nu$  CN 2190,  $\text{SO}_2$  1310, 1150  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  2.99-3.03 (t, 2H,  $\text{CH}_2\text{-C}_6\text{H}_5$ , J = 7 Hz), 3.97-4.01 (t, 2H,  $\text{CH}_2\text{-CH}_2\text{N}$ , J = 7 Hz), 4.27-4.28 (m, 2H, 4-H thiazolidine), 5.12-5.14, 5.16-5.18 (m, m, 2H,  $=\text{CH}_2$ ), 7.16-7.30 (m, 5H, phenyl protons), 7.60-7.83 (m, 3H,  $\text{C}_6\text{H}_5\text{-SO}_2$ ), 8.00-8.03 ppm (m, 2H,  $\text{C}_6\text{H}_5\text{-SO}_2$ );  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  34.2 ( $\text{CH}_2\text{-C}_6\text{H}_5$ ), 52.0 ( $\text{NCH}_2$ ), 62.9 (C-4 thiazolidine), 106.3 ( $=\text{CH}_2$ ), 115.93 (CN), 127.0-127.2, 128.8-129.1 (C-2,3,4,5,6  $\text{C}_6\text{H}_5\text{-SO}_2$ , C-2,3,4,5,6 phenyl), 133.1 ( $=\text{C-CN}$ ), 134.3 (C-1 phenyl), 136.8 (C-5 thiazolidine), 142.5 (C-1  $\text{C}_6\text{H}_5\text{-SO}_2$ ), 166.9 ppm (C-2 thiazolidine); ms: m/z 241 (22), 104 (100).

*Anal.* Calcd. for  $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_2\text{S}_2$  (382.51): C, 62.80; H, 4.74; N, 7.32; S, 16.77. Found: C, 62.54; H, 4.70; N, 7.28; S, 16.59.

### 2-(5-Methyl-3-phenethylthiazolidin-2-ylidene)-2-phenylsulfonylacetonitrile (10).

This compound was obtained from the foregoing run as the second fraction from the chromatography as light brown crystals, 1.0 g (38%), mp 184°; ir:  $\nu$  CN 2190,  $\text{SO}_2$  1320, 1150  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  2.12 (s, 3H,  $\text{CH}_3$ ), 2.91-2.95 (t, 2H,  $\text{CH}_2\text{-C}_6\text{H}_5$ ), 4.07-4.12 (t, 2H,  $\text{NCH}_2$ , J = 7 Hz), 6.19-6.20 (s, 1H, 4H thiazolidine), 6.98-7.01, 7.19-7.41 (m, 6H,  $\text{C}_6\text{H}_5\text{-SO}_2$ ,  $\text{C}_6\text{H}_5$ ), 7.42-7.43 (m, 2H,  $\text{C}_6\text{H}_5\text{-SO}_2$ ), 7.86-7.89 ppm (m, 2H,  $\text{C}_6\text{H}_5\text{-SO}_2$ );  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  12.4 ( $\text{CH}_3$ ), 34.5 ( $\text{CH}_2\text{-C}_6\text{H}_5$ ), 49.6 ( $\text{NCH}_2$ ), 107.1 (C-5 thiazolidine), 119.2 (CN), 123.0 (C-4 thiazolidine), 126.9-128.9 (C-2,3,4,5,6 phenyl, C-2,3,4,5,6  $\text{C}_6\text{H}_5\text{-SO}_2$ ), 137.0 (C-1 phenyl), 138.0 ( $=\text{C-CN}$ ), 141.0 (C-1  $\text{C}_6\text{H}_5\text{-SO}_2$ ), 165.7 ppm (C-2 thiazolidine).

*Anal.* Calcd. for  $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_2\text{S}_2$  (382.51): C, 62.80; H, 4.74; N, 7.32; S, 16.77. Found: C, 62.72; H, 4.67; N, 7.27; S, 16.53.

## REFERENCES AND NOTES

- [1] W. Hanefeld, H. Harms and M. Schlitzer, *Arch. Pharm. (Weinheim)*, **328**, 431 (1996).
- [2] W. Hanefeld, M. Schlitzer and J. v. Gösseln, *Arch. Pharm. (Weinheim)*, **318**, 185 (1985).
- [3] W. Hanefeld, *Arch. Pharm. (Weinheim)*, **317**, 297 (1984).
- [4] W. Hanefeld and B. Borho, *Arch. Pharm. (Weinheim)*, **322**, 593 (1989).
- [5] W. Hanefeld and B. Borho, *Arch. Pharm. (Weinheim)*, **323**, 619 (1990).
- [6] W. Hanefeld, M. Naeeni and M. Schlitzer, *J. Heterocyclic Chem.*, **33**, 1785 (1996).