Iminium Carbonic Acid Derivative Salts. XII [1]. Electrophilic Reactions of 2-Methylthio-4,5-dihydrothiazolium Iodides, 5-Methyl-2-methylthiothiazolium Iodides and 2-Methylthio-5,6-dihydro-1,3-thiazinium Iodides. Part III. With Vinylogous and Phenylogous Active Methylene Compounds

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3-Benzyl-2-methylthio-4,5-dihydrothiazolium iodide (**1**), 5-metlyl-2-methylthio-3-phenethylthiazolium iodide (**4**) and 3-methyl and 3-benzyl-2-methylthio-5,6-dihydro-1,3-thiazinium iodides **7a,b** were reacted with the vinylogous doubly activated CH-acidic compounds **2a-d** and the phenylogous doubly activated components **8, 11, 16, 19** and **21** to yield new types of *S,N*-heterocycles **3, 5, 6, 9, 10, 12, 13, 14, 15** with the partial structure of push-pull substituted butadienes and **17, 18, 20, 22, 23** and **24** with the character of push-pull substituted phenyl ketene *S,N*-acetals.

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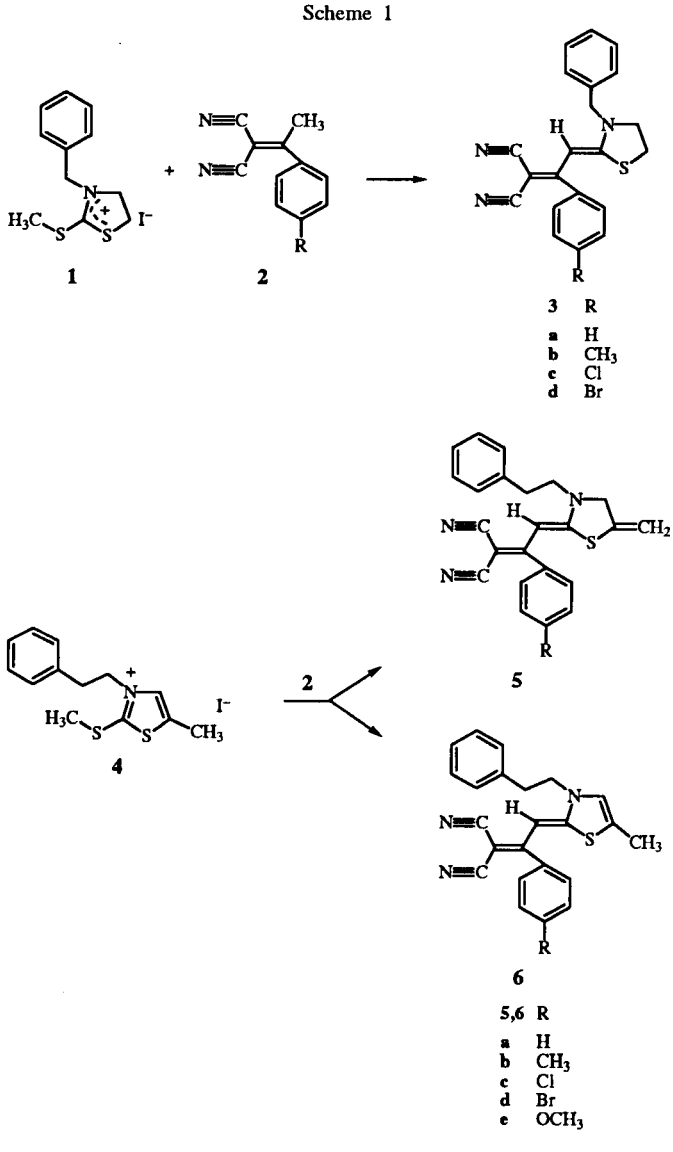
In a preceeding paper [2] we described the reaction of 3-benzyl-2-methylthio-4,5-dihydrothiazolium iodide (**1**), 5-methyl-2-methylthio-3-phenethylthiazolium iodide (**4**) and 3-methyl and 3-benzyl-2-methylthio-5,6-dihydro-1,3-thiazinium iodides **7a,b** with doubly activated CH-acidic compounds forming ketene *S,N*-acetals. We now extend the scope of this reaction to doubly activated vinylogous and phenylogous CH-acidic compounds. 3-Aryl-2-cyanobut-2-enenitriles **3a-d** [3] as compounds of the vinylogous CH-acidic type have thus been reacted with **1** respectively **4** in the presence of triethylamine and lead(II) nitrate to yield the new push-pull substituted butadiene systems **3,5** and **6** with a thiazolidine ring involved in this conjugated system. Compounds **5** and **6** resulting pairs of tautomers from the same run and could be separated by column chromatography. The exomethylene compounds **5** are yellow crystals, the exomethyl compounds **6** are orange or red crystals. Compounds **6** in general possess higher melting points than the corresponding tautomers **5**.

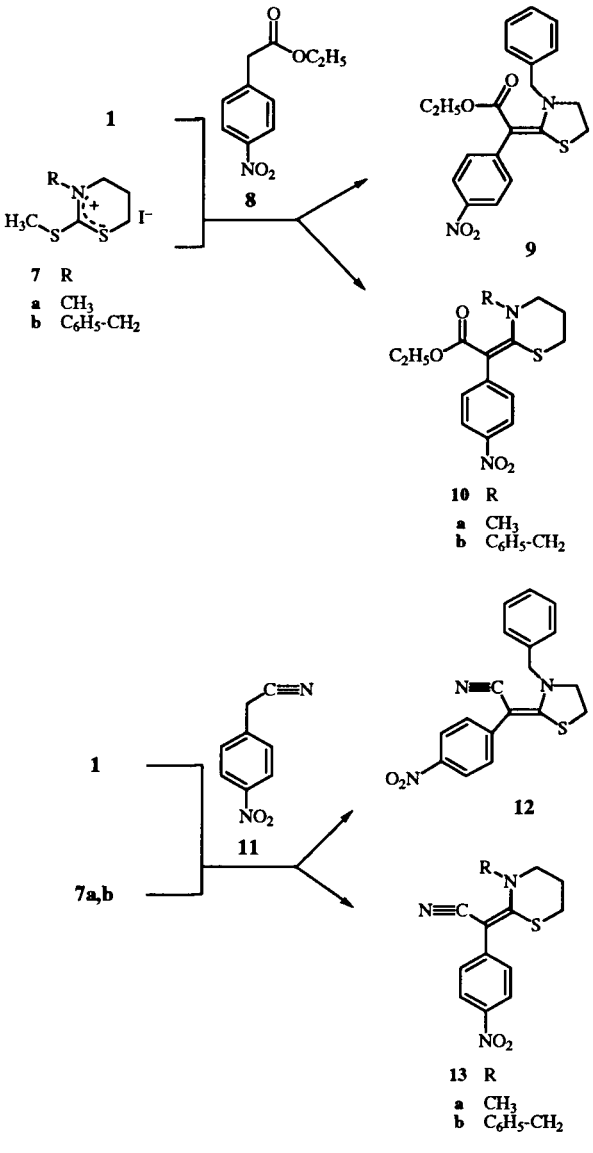
While the principle of condensing vinylogous CH-acidic compounds with **1** and **7b** has already been demonstrated with the sugar derivative methyl 4,6-*O*-benzylidene-2-(dicyanomethylene)-2,3-dideoxy-α-D-*erythro*hexapyranoside [4], the principle of reacting doubly activated phenylogous compounds as CH-acidic components with iminium dithiocarbonic acid diester salts like **1, 4** and **7a,b** has to our knowledge never been reported. The experiments with the phenylogous nitroacetic acid derivatives, ethyl 4-nitrophenylacetate (**8**) and 4-nitrophenylacetonitrile (**11**), were carried out under the same conditions as cited above and led to the new ketene *S,N*-acetals **9, 10, 12** and **13** (Scheme 2) and **14, 15** (Scheme 3).

A mixture of tautomers were obtained from the reaction of **4** with **11** which could be separated by column chromatography to the exomethylene form **14** and the exomethyl form **15**. All compounds exhibit the character of push-pull substituted styrenes.

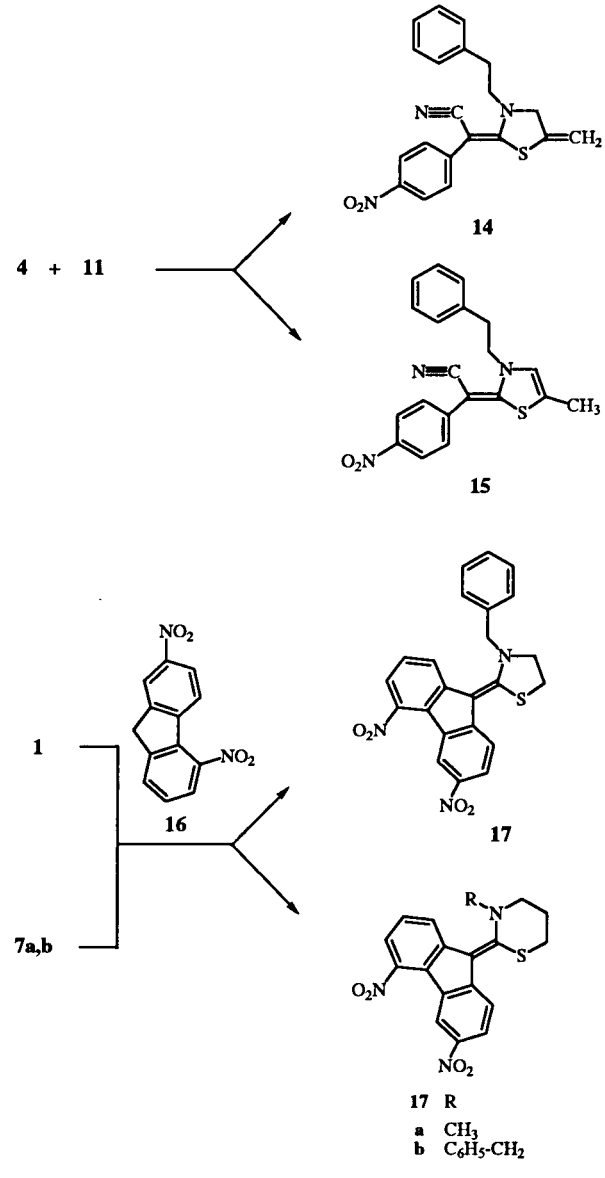
Scheme 1



Scheme 2



Scheme 3



A different type of doubly activated phenylogous CH-acidic compound is represented by 2,5-dinitrofluorene (**16**) which could be reacted with **1** either **7a** or **7b** to yield **17** along with **18a,b** (Scheme 3). These compounds will be tested as potential intercalating agents.

Another variation of the title reaction could be realized with 2,4-dinitrotoluene (**19**) yielding **20** (Scheme 4). 2-Cyanophenylacetonitrile (**21**) as a phenylogous malononitrile reacted with all the electrophilic salts **1, 4** and **7a,b** to the corresponding cyanoketene *S,N*-acetals **22, 23** and **24a,b** (Scheme 4).

The stereochemistry of the new compounds, the *Z/E* isomerism and conformational aspects of the heterocycles will not be subject of this paper but will be discussed in a following contribution in connection with the X-ray structure of a representative compound.

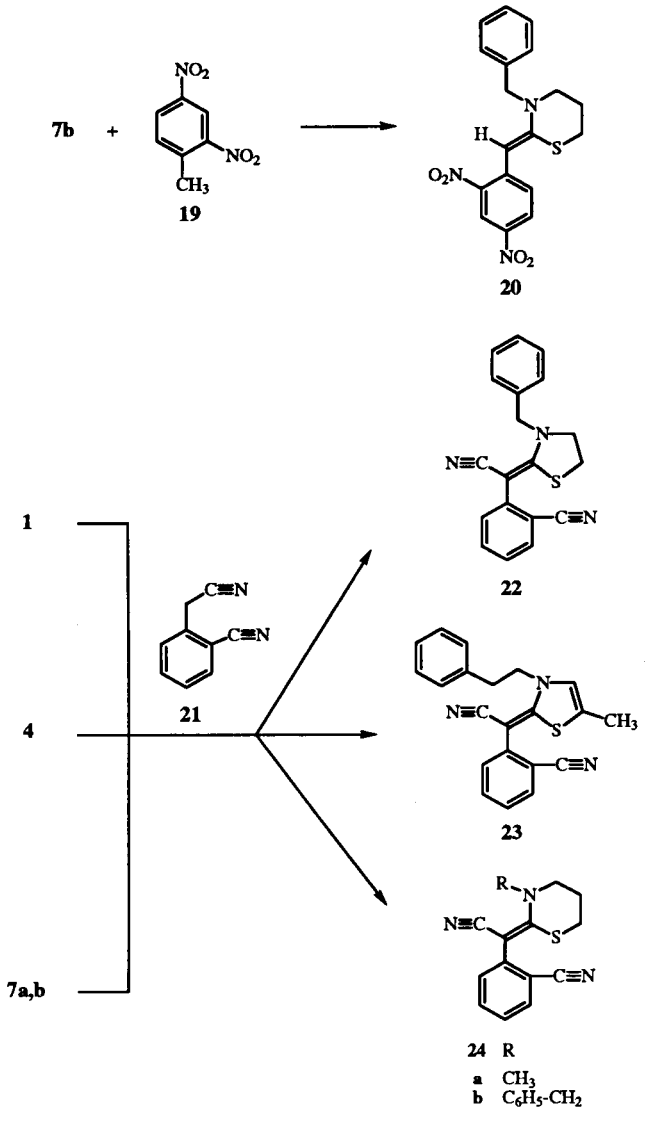
EXPERIMENTAL

Instrumental equipment and chromatographic conditions were those already described [5]. Deuteriochloroform was used as the nmr solvent.

General Procedure for the Condensation of the 2-Methylthio-4,5-dihydrothiazolium-, 5-Methyl 2-methylthiothiazolium- and the 2-Methylthio-4,5-dihydro-2*H*-1,3-thiaziniumiodides **1, 4** and **7a,b** with the Vinylogous and Phenylogous Compounds **2, 8, 11, 16, 19** and **21**.

To a solution of equimolar quantities of the vinylogous or phenylogous methylene active compound and of **1, 4** or **7a,b** in 50

Scheme 4



ml of dichloromethane were added 2 equivalents of triethylamine and 1.5 equivalents of lead(II) nitrate with protection from moisture. The mixture was refluxed for 3 hours in the reactions of **1** with **2a-d** and **8** or stirred at room temperature for 16 hours in most of the other reactions. Exceptions in the reaction conditions are mentioned with the particular compound. After cooling to room temperature the solids were filtered and the filtrate evaporated *in vacuo*. The residue was purified by recrystallization from ethanol or by other methods mentioned for the compound.

4-(3-Benzylthiazolidin-2-ylidene)-2-cyano-3-phenylbut-2-enenitrile (**3a**).

This compound was obtained from 0.9 g (0.005 mole) of 2-cyano-3-phenylbut-2-enenitrile (**2a**) [3] and 1.76 g (0.005 mole) of **1** [6] as yellow crystals, purified by flash chromatography with dichloromethane, 0.8 g (47%), mp 240°; ir: ν CN 2200 cm^{-1}; ^1H nmr: δ 2.88-2.92 (t, 2H, 5-H thiazolidine, J = 7.5 Hz), 3.59-3.76 (t, 2H, 4-H thiazolidine, J = 7.5 Hz), 4.67 (s, 2H, CH_2-C_6H_5), 6.19 (s, 1H, =CH-C-C_6H_5), 7.24-7.28, 7.34-7.51 ppm (m, m, 10H, phenyl protons); ^{13}C nmr: δ 28.2 (C-5 thiazolidine), 52.7 (C-4 thiazolidine), 55.3 (CH_2-C_6H_5), 66.1 (=C(CN)$_2$), 93.4 (=CH-C-C_6H_5), 116.3, 116.7 (2 CN), 127.7-130.4 (2x C-2,3,4,5,6 phenyl), 134.1, 135.0 (2x C-1 phenyl), 166.0 (C=C(CN)$_2$, 170.6 ppm (C-2 thiazolidine); ms: m/z 344 (22), 343 (89, M^+), 91 (100).

Anal. Calcd. for $C_{21}H_{17}N_3S$ (343.45): C, 73.44; H, 4.99; N, 12.23; S, 9.34. Found: C, 73.15; H, 5.07; N, 12.31; S, 9.28.

4-(3-Benzylthiazolidin-2-ylidene)-2-cyano-3-tolylbut-2-enenitrile (**3b**).

This compound was obtained from 0.9 g (0.005 mole) 2-cyano-3-tolylbut-2-enenitrile (**2b**) [3] and 1.76 g (0.005 mole) **1** as yellow crystals, purified by flash chromatography with dichloromethane. 0.79 g (44%), mp 178°; ir: ν CN 2200 cm^{-1}; ^1H-nmr: δ 2.41 (s, 3H, CH_3), 2.88-2.92 (t, 2H, C-5 thiazolidine, J = 7.5 Hz), 3.72-3.76 (t, 2H, C-4 thiazolidine, J = 7.5 Hz), 4.66 (s, 2H, CH_2-C_6H_5), 6.17 (s, 1H, =CH-C-C_6H_4), 7.14-7.43 ppm (m, 9H, phenyl protons); ^{13}C nmr: δ 21.6 (CH_3), 28.2 (C-5 thiazolidine), 52.7 (C-4 thiazolidine), 55.3 (CH_2-C_6H_5), 65.6 (=C(CN)$_2$), 93.4 (=CH-C-C_6H_4), 116.5, 117.0 (2x CN), 127.7-129.9 (C-2,3,4,5,6 phenyl, C-2,3,5,6 tolyl), 131.9, 134.1, 140.8 (C-1 phenyl, C-1 and C-4 tolyl), 166.1 (C=C(CN)$_2$), 170.9 ppm (C-2 thiazolidine); ms: m/z 357 (29, M^+), 91 (100).

Anal. Calcd. for $C_{22}H_{19}N_3S$ (357.47): C, 73.92; H, 5.36; N, 11.75; S, 8.97. Found: C, 73.75; H, 5.32; N, 11.60; S, 8.94.

4-(3-Benzylthiazolidin-2-ylidene)-3-(4-chlorophenyl)-2-cyanobut-2-enenitrile (**3c**).

This compound was obtained from 1.0 g (0.005 mole) of 3-(4-chlorophenyl)-2-cyanobut-2-enenitrile (**2c**) [3] and 1.76 g (0.005 mole) of **1** as green-yellow crystals (ethanol/toluene), 0.89 g (47%), mp 200°; ir: ν CN 2200 cm^{-1}; ^1H nmr: δ 2.88-2.96 (t, 2H, 5-H thiazolidine, J = 7.5 Hz), 3.75-3.79 (t, 2H, 4-H thiazolidine, J = 7.5 Hz), 4.66 (s, 2H, CH_2-C_6H_5), 6.15 (s, 1H, = CH-C-C_6H_4), 7.17-7.27 and 7.39-7.47 ppm (m, m, 9H, phenyl protons); ^{13}C nmr: δ 28.1 (C-5 thiazolidine), 52.7 (C-4 thiazolidine), 55.5 (CH_2-C_6H_5), 65.5 (=C(CN)$_2$), 93.2 (=CH-C-C_6H_4), 116.1, 116.7 (2x CN), 127.7-130.4 (C-2,3,4,5,6 C_6H_5, C-2,3,5,6 C_6H_4), 133.3, 133.9 (C-1, C-4 C_6H_4), 136.8 (C-1 C_6H_5), 166.3 (C=C(CN)$_2$), 169.1 ppm (C-2 thiazolidine); ms: m/z 378 (39), 377 (100, M^+).

Anal. Calcd. for $C_{21}H_{16}ClN_3S$ (377.89): C, 66.75; H, 4.27; N, 11.12; Cl, 9.38; S, 8.48. Found: C, 66.64; H, 4.22; N, 11.14; Cl, 9.30; S, 8.76.

4-(3-Benzylthiazolidin-2-ylidene)-2-cyano-3-(4-bromophenyl)-but-2-enenitrile (**3d**).

This compound was obtained from 1.3 g (0.005 mole) of 3-(4-bromophenyl)-2-cyanobut-2-enenitrile (**2d**) [3] and 1.76 g (0.005 mole) of **1** as yellow crystals purified by flash chromatography with dichloromethane. 0.3 g (24%), mp 222°; ir: ν CN 2200 cm^{-1}; ^1H nmr: δ 2.93-2.97 (t, 2H, 5-H thiazolidine, J = 7.5 Hz), 3.75-3.79 (t, 2H, 4-H thiazolidine, J = 7.5 Hz), 4.67 (s, 2H, $CH_2C_6H_5$), 6.16 (=CH-C-C_6H_4), 7.12-7.15 (m, 2H, C_6H_4), 7.25-7.27, 7.35-7.52, (m, m, 5H, C_6H_5), 7.58-7.61 ppm (m, 2H, C_6H_4); ^{13}C nmr: δ 28.2 (C-5 thiazolidine), 52.7 (C-4 thiazolidine), 55.4 (CH_2-C_6H_5), 65.9 (=C(CN)$_2$), 93.2 (=CH-C-C_6H_4), 116.0, 116.5 (2x CN), 125.1 (C-4 C_6H_4), 127.7-128.6 and 129.3-132.3 (C-2,3,4,5,6 C_6H_5, C-2,3,5,6 C_6H_4), 133.8, 133.9 (C-1 C_6H_5, C-1 C_6H_4), 166.0 (C=C(CN$_2$), 169.1 ppm (C-2 thiazolidine); ms: m/z 423 (61), 422 (26, M^+).

Anal. Calcd. for $C_{21}H_{16}BrN_3S$ (422.35): C, 59.72; H, 3.82; N, 9.95; Br, 18.92; S, 7.59. Found: C, 59.71; H, 3.86; N, 9.69; Br, 18.62; S, 7.71.

2-Cyano-4-(5-methylene-3-phenethylthiazolidine-2-ylidene)-3-phenylbut-2-enenitrile (**5a**).

This compound was obtained from 0.84 g (0.005 mole) of **2a** and 1.82 g (0.005 mole) of 5-methyl-2-methylthio-3-phenethylthiazolium iodide (**4**) [6] after stirring for 16 hours at room temperature and separation by column chromatography (solvents dichloromethane/cyclohexane/methanol 900/93/7) from the first fraction, 0.10 g (7%), mp 205°; ir: ν CN 2200 cm^{-1}; ^1H nmr: δ 3.03-3.04 (t, 2H, C*H*$_2$-C_6H_5, J = 7 Hz), 3.71-3.73 (t, 2H, CH_2-N, J = 7 Hz), 4.22-4.23 (m, 2H, 4-H thiazolidine), 4.88-4.90 (m, 1H, =CH_2), 5.03-5.05 (m, 1H, = CH_2), 6.04 (s, 1H, =C*H*-C-C_6H_5), 7.21-7.64 ppm (m, 10H, phenyl protons); ^{13}C nmr: δ 32.7 (*C*H$_2$-C_6H_5), 50.5 (CH_2-N), 60.3 (C-4 thiazolidine), 66.0 (=*C*(CN)$_2$), 92.6 (=*C*H-C-C_6H_5), 104.7 (C=*C*H$_2$), 116.3, 116.6 (2 CN), 127.3-129.3 (C-2,3,4,5,6 C_6H_5), 134.2 (C-1 C_6H_5), 136.0 (C-1 C_6H_5), 137.0 (C-5 thiazolidine), 163.9 (*C*=C(CN)$_2$), 170.0 ppm (C-2 thiazolidine); ms: m/z 369 (25, M^+), 104 (100).

Anal. Calcd. for $C_{23}H_{19}N_3S$ (369.48)•0.5H_2O (378.50): C, 72.99; H, 5.33; N, 11.10; S, 8.47. Found: C, 73.05; H, 5.14; N, 11.18; S, 8.48.

2-Cyano-4-(5-methyl-3-phenethylthiazolin-2-ylidene)-3-phenylbut-2-enenitrile (**6a**).

This compound was obtained from the foregoing run from the second fraction as orange crystals, 0.15 g (11%), mp 240°; ir: ν CN 2190 cm^{-1}; ^1H nmr: δ 1.96 (s, 3H, CH_3), 3.06-3.09 (t, 2H, C*H*$_2$-C_6H_5), J = 7 Hz), 4.07-4.10 (t, 2H, CH_2-N, J = 7 Hz), 6.08 (s, 1H, =C*H*-C-C_6H_5), 6.23 (s, 1H, 4-H thiazoline), 7.17-7.36 (m, 7H, phenyl protons), 7.50-7.53 (m, 3H, phenyl protons); ^{13}C nmr: δ 11.8 (CH_3), 34.4 (*C*H$_2$-C_6H_5), 51.5 (CH_2-N), 91.1 (=*C*H-C-C_6H_5), 118.0, 118.4 (2 CN), 122.0 (C-5 thiazoline), 126.7 (C-4 thiazoline), 126.7-130.3 (C-2,3,4,5,6 phenyl), 135.2, 136.2 (2x C-1 C_6H_5), 162.8 (*C*=C(CN)$_2$), 165.7 ppm (C-2 thiazoline); ms: m/z 370 (5, M^+), 104 (100).

Anal. Calcd. for $C_{23}H_{19}N_3S$ (369.48)•0.5 H_2O (378.50): C, 72.99; H, 5.33; N, 11.10; S, 8.47. Found: C, 73.28; H, 5.06; N, 11.24; S, 8.50.

2-Cyano-4-(5-methylene-3-phenethylthiazolidin-2-ylidene)-3-(4-tolyl)but-2-enenitrile (**5b**).

This compound was obtained from 0.91 g (0.005 mole) of **2b** and 1.54 g (0.005 mole) of **4** after column chromatography from the first fraction as yellow crystals, 0.20 g (10%), mp 185°; ir: ν CN 2200 cm^{-1}; ^1H nmr: δ 2.43 (s, 3H, CH_3), 2.99-3.03 (t, 2H, C*H*$_2$-C_6H_5, J = 7 Hz), 3.68-3.72 (t, 2H, CH_2N, J = 7 Hz), 4.22-4.23 (m, 2H, 4-H thiazolidine), 4.91 (m, 1H, = CH_2), 5.03-5.04 (m, 1H, =CH_2), 6.03 (s, 1H, = C*H*-C-C_6H_4-CH_3), 7.10-7.37 ppm (m, 9H, phenyl protons); ^{13}C nmr: δ 21.6 (C_6H_4-*C*H$_3$), 32.7 (*C*H$_2$-C_6H_5), 50.5 (CH_2-N), 60.3 (C-4 thiazolidine), 66.0 (=*C*(CN)$_2$), 92.6 (=*C*H-C-C_6H_4-CH_3), 105.6 (=CH_2), 116.4, 116.7 (2 CN), 127.2-129.8 (C-2,3,4,5,6 C_6H_5, C-2,3,5,6 C_6H_4), 131.1, 136.2, 141.1 (C-1 C_6H_5, C-1, C-4 C_6H_4), 137.0 (C-5 thiazolidine), 163.8 (C=(CN)$_2$), 170.4 ppm (C-2 thiazolidine); ms: m/z 384 (11, M^+), 104 (100).

Anal. Calcd. for $C_{24}H_{21}N_3S$ (383.52): C, 75.16; H, 5.52; N, 10.96; S, 8.36. Found: C, 74.92; H, 5.44; N, 11.24; S, 8.32.

2-Cyano-4-(5-methyl-3-phenethylthiazolin-2-ylidene-3-(4-tolyl)but-2-enenitrile (**6b**).

This compound was obtained from the foregoing run from the second fraction as red crystals, 0.25 g (13%), mp 272°; ir: ν CN 2200 cm^{-1}; ^1H nmr: δ 1.97 (s, 3H, C*H*$_3$), 2.44 (s, 3H, C_6H_4-C*H*$_3$), 3.05-3.08 (t, 2H, C*H*-C_6H_5, J = 7 Hz), 4.05-4.09 (t, 2H, CH_2-N, J = 7 Hz), 6.07 (s, 1H, =C*H*-C-C$_6$H$_4$-CH_3), 6.24 (s, 1H, 4-H thiazoline), 7.08-7.36 ppm (m, 9H, phenyl protons); ^{13}C nmr: δ 11.9 (CH_3), 21.6 (C_6H_4-*C*H$_3$), 34.4 (*C*H$_2$-C_6H_5), 51.4 (CH_2-N), 59.1 (*C*(CN)$_2$), 91.2 (=*C*H-C-C_6H_4-CH_3), 118.1, 118.6 (2 CN), 122.0 (C-5 thiazoline), 126.7 (C-4 thiazoline), 127.4-130.9 (C-2,3,4,5,6 C_6H_5, C-2,3,5,6 C_6H_4), 132.1, 136.2, 140.5 (C-1 C_6H_5, C-1, C-4 C_6H_4-CH_3), 162.8 (*C*=C(CN)$_2$), 166.0 ppm (C-2 thiazoline); ms: m/z 384 (7, M^+), 104 (100).

Anal. Calcd. for $C_{24}H_{21}N_3S$ (383.52): C, 75.16; H, 5.52; N, 10.96; S, 8.36. Found: C, 74.99; H, 5.42; N, 10.98; S, 8.32.

3-(4-Chlorophenyl)-2-cyano-4-(methylene-3-phenethylthiazolidin-2-ylidene)but-2-enenitrile (**5c**).

This compound was obtained from 1.0 g (0.005 mole) of **2c** and 1.82 g (0.005 mole) of **4** after column chromatography from the first fraction as yellow crystals, 0.30 g (15%), mp 197°; ir: ν CN 2200 cm^{-1}; ^1H nmr: δ 3.00-3.03 (t, 2H, C*H*$_2$-C_6H_5, J = 7 Hz), 3.70-3.74 (t, 2H, CH_2-N, J = 7 Hz), 4.25-4.29 (m, 2H, 4-H thiazolidine), 4.96-4.98 (m, 1H, =CH_2), 5.07-5.09 (m, 1H, =CH_2), 6.01 (s, 1H, =C*H*-C-C_6H_4-Cl), 7.16-7.47 ppm (m, 9H, phenyl protons); ^{13}C nmr: δ 32.7 (*C*H$_2$-C_6H_5), 50.5 (CH_2-N), 60.3 (C-4 thiazolidine), 66.2 (*C*(CN)$_2$), 92.4 (=*C*H-C-C_6H_4-Cl), 106.2 (=CH_2), 116.0, 116.3 (2 CN), 127.3-130.4 (C-2,3,4,5,6 C_6H_5, C-2,3,5,6 C_6H_4), 132.6, 135.6 (C-1, C-4 C_6H_4), 136.9 (C-1 C_6H_5), 137.1 (C-5 thiazolidine), 163.7 (*C*=C(CN)$_2$), 168.5 ppm (C-2 thiazolidine); ms: m/z 403 (16, M^+), 104 (100).

Anal. Calcd. for $C_{23}H_{18}ClN_3S$ (403.94): C, 68.39; H, 4.49; N, 10.40; Cl, 8.78; S, 7.94. Found: C, 68.32; H, 4.53; N, 10.35; Cl 8.88; S, 8.15.

3-(4-Chlorophenyl)-2-cyano-4-(5-methyl-3-phenethylthiazolin-2-ylidene)but-2-enenitrile (**6c**).

This compound was obtained from the foregoing run from the second fraction as red crystals, 0.15 g (8%), mp 278°; ir: ν CN 2200 m^{-1}; ^1H nmr: δ 2.00-2.01 (s, 3H, CH_3), 3.05-3.09 (t, 2H, C*H*$_2$-C_6H_5, J = 7 Hz), 4.07-4.11 (t, 2H, CH_2-N, J = 7 Hz), 6.06 (s, 1H, =C*H*-C-C_6H_4-Cl), 6.26 (s, 1H, 4-H thiazoline), 7.15-7.52 ppm (m, 9H, phenyl protons); ^{13}C nmr: δ 11.9 (CH_3), 34.5 (*C*H$_2$-C_6H_5), 51.5 (CH_2-N), 59.4 (*C*(CN)$_2$), 91.0 (=*C*H-C-C_6H_4-Cl), 117.7, 118.2 (2 CN), 122.1 (C-5-thiazoline), 126.9 (C-4 thiazoline), 127.5-130.5 (C-2,3,4,5,6 C_6H_5, C-2,3,5,6 C_6H_4), 133.6, 136.7 (C-1, C-4 C_6H_4), 162.5 (*C*=C(CN)$_2$), 164.2 ppm (C-2 thiazoline); ms: m/z 404 (M^+, 6), 104 (100).

Anal. Calcd. for $C_{23}H_{18}ClN_3S$ (403.94): C, 68.39; H, 4.49; N, 10.40; S, 7.94. Found: C, 68.17; H, 4.49; N, 10.25; S, 8.05.

3-(4-Bromophenyl)-2-cyano-4-(5-methylene-3-phenethylthiazolidin-2-ylidene)but-2-enenitrile (**5d**).

This compound was obtained from 0.99 g (0.005 mole) of **2d** and 1.82 g (0.005 mole) of **4** after column chromatography from the first fraction as yellow crystals, 0.15 g (7%), mp 201°; ir: ν CN 2200 cm^{-1}; ^{13}C nmr: δ 32.7 (*C*H$_2$C$_6$H$_5$), 50.5 (CH_2-N), 60.3 (C-4 thiazolidine), 66.0 (C=*C*(CH)$_2$), 92.4 (=*C*H-C-C_6H_4-Br), 106.3 (=CH_2), 116.0, 116.3 (2x CN), 125.4 (C-4 C_6H_4-Br), 127.3-132.4 (C-2,3,4,5,6 C_6H_5, C-2,3,5,6 C_6H_4-Br), 133.1 and

135.5 (C-1 C_6H_5/C-1 C_6H_4-Br), 136.9 (C-5 thiazolidine), 163.8 (C=C(CN)$_2$), 168.5 ppm (C-2 thiazolidine); ms: m/z 449 (15, M^+), 104 (100).

Anal. Calcd. for $C_{23}H_{18}BrN_3S$ (448.39): C, 61.61; H, 4.05; N, 9.37; S, 7.15. Found: C, 61.48; H, 4.03; N, 9.40; S, 7.16.

3-(4-Bromophenyl)-2-cyano-4-(5-methyl-3-phenethylthiazolin-2-ylidene)but-2-enenitrile (**6d**).

This compound was obtained from the foregoing run as orange crystals, 0.15 g (7%), mp 266°; ir: ν CN 2200 cm^{-1}; ^{1}H nmr: δ 2.00-2.17 (s, 3H, CH_3), 3.05-3.09 (t, CH_2-C_6H_5, J = 7 Hz), 4.07-4.11 (t, 2H, N-CH_2, J = 7 Hz), 6.05 (s, 1H, CH=C-C_6H_4-Br), 6.26 (s, 1H, 4-H thiazoline), 7.09-7.67 ppm (m, 9H, phenyl protons); ^{13}C nmr: δ 11.9 (CH_3), 34.5 (CH_2-C_6H_5), 51.5 (N-CH_2), 90.9 (CH=C-C_6H_4-Br), 117.7, 118.2 (2x CN), 122.2 (C-5 thiazoline), 127.5-133.5 (C-2,3,4,5,6 C_6H_5, C-2,3,5,6 C_6H_4-Br), 134.1, 136.0 (C-1 C_6H_5, C-1 and C-4 C_6H_4), 162.5 (C=C(CN)$_2$), 164.2 ppm (C-2 thiazoline); ms: m/z 449 (14, M^+), 104 (100).

Anal. Calcd. for $C_{23}H_{18}BrN_3S{\cdot}H_2O$ (466.39): C, 59.23; H, 4.32; N, 9.01; S, 6.87. Found: C, 59.45; H, 3.86; N, 9.03; S, 6.89.

2-Cyano-3-(4-methoxyphenyl)-4-(5-methylene-3-phenethylthiazolidin-2-ylidene)-but-2-enenitrile (**5e**).

This compound was obtained from 0.99 g (0.005 mole) of 2-cyano-3-(4-methoxyphenyl)but-2-enenitrile (**2e**) [3] and 1.82 g (0.005 mole) of **4** after column chromatography from the first fraction as yellow crystals, 0.15 g (8%), mp 160°; ir: ν CN 2200 cm^{-1}; ^{1}H nmr: δ 3.00-3.04 (t, 2H, CH_2-C_6H_5, J = 7 Hz), 3.69-3.73 (t, 2H, CH_2-N, J = 7 Hz), 3.88 (s, 3H, C_6H_4-OCH_3), 4.22-4.23 (m, 2H, 4-H thiazolidine), 4.92-4.94 (m, 1H, =CH_2), 5.03-5.05 (m, 1H, =CH_2), 6.03 (s, 1H, CH=C-C_6H_4-OCH_3), 6.96-7.38 ppm (m, 9H, phenyl protons); ^{13}C nmr: δ 32.7 (CH_2-C_6H_5), 50.5 (CH_2-N), 55.4 (C_6H_4-OCH_3), 60.2 (C-4 thiazolidine), 66.0 (C(CN)$_2$), 92.7 (=CH-C-C_6H_4-OCH_3), 105.6 (=CH_2), 114.5 (C-3,5 C_6H_4-OCH_3), 116.5, 116.9 (2x CN), 126.0 (C-5 thiazolidine), 127.2-130.7 (C-2,3,4,5,6 C_6H_5, C-2,6 C_6H_4-OCH_3), 136.3, 137.0 (C-1, C_6H_5, C-1 C_6H_4-OCH_3), 161.8 (C-4, C_6H_4-OCH_3), 163.7 (C=C(CN)$_2$), 170.2 ppm (C-2 thiazolidine); ms: m/z 399 (48, M^+), 295 (100), 104 (71).

Anal. Calcd. for $C_{24}H_{21}N_3OS$ (399.52): C, 72.15; H, 5.30; N, 10.52; S, 8.03. Found: C, 71.94; H, 5.24; N, 10.44; S, 8.00.

2-Cyano-3-(4-methoxyphenyl)-4-(5-methyl-3-phenethylthiazolin-2-ylidene)but-2-enenitrile (**6e**).

This compound was obtained from the foregoing run from the second fraction as orange crystals, 0.40 g (20%), mp 225°; ir: ν CN 2200 cm^{-1}; ^{1}H nmr: δ 1.98 (s, 3H, CH_3), 3.05-3.09 (t, 2H, CH_2-C_6H_5, J = 7 Hz), 3.88 (s, 3H, C_6H_4-OCH_3), 4.05-4.09 (t, 2H; CH_2-N, J = 7 Hz), 6.07 (s, 1H, = CH-C-C_6H_4-OCH_3), 6.23 (s, 1H, 4-H thiazoline), 7.02-7.38 ppm (m, 9H, phenyl protons); ^{13}C nmr: δ 11.9 (CH_3), 34.4 (CH_2-C_6H_5), 51.5 (CH_2-N), 55.4 (C_6H_4-OCH_3), 59.2 (C=C(CN)$_2$), 91.3 (=CH-C-C_6H_4-OCH_3), 115.6 (C-3,5 C_6H_4-OCH_3), 118.2, 118.7 (2x CN), 121.9 (C-5 thiazoline), 126.6 (C-4 thiazoline), 127.0 (C-1, C_6H_4-OCH_3), 127.4-129.8 (C-2,3,4,5,6 C_6H_5, C-2,6 C_6H_4-OCH_3), 136.2 (C-1 C_6H_5), 161.4 (C-4 C_6H_4-OCH_3), 162.8 (C=C(CN_2), 165.8 ppm (C-2 thiazoline); ms: m/z 400 (12, M^+), 295 (100), 104 (65).

Anal. Calcd. for $C_{24}H_{21}N_3OS$ (399.52): C, 72.15; H, 5.30; N, 10.52; S, 8.03. Found: C, 72.06; H, 5.30; N, 10.58; S, 8.09.

Ethyl [2-(3-Benzylthiazolidin-2-ylidene)-4-nitrophenylacetate] (**9**).

This compound was obtained from 0.56 g (0.003 mole) of ethyl 4-nitrophenylacetate (**8**) and 1.10 g (0.003 mole) of **1** as yellow crystals, 0.30 g (26%), mp 106°; ir: ν CO 1660 cm^{-1}; ^{1}H nmr: δ 1.13-1.16 (t, 3H, O-CH_2-CH_3), 2.95-2.99 (t, 2H, 5-H thiazolidine, J = 7 Hz), 3.60-3.63 (t, 2H, 4-H thiazolidine, J = 7 Hz), 3.94 (s, 2H, CH_2-C_6H_5), 4.10-4.15 (q, 2H, O-$CH_2$$CH_3$), 6.93-6.95 (m, 2H, C_6H_5), 7.22-7.27 (m, 3H, C_6H_5), 7.30-7.34 (m, 2H, C_6H_4), 7.99-8.03 ppm (m, 2H, C_6H_4); ^{13}C nmr: δ 14.4 (O-CH_2-CH_3), 27.6 (C-5 thiazolidine), 55.5 (CH_2-C_6H_5 and C-4 thiazolidine), 60.1 (O-$CH_2$$CH_3$), 96.4 (=$C$-$COOC_2H_5$), 122.9-132.3 (C-2,3,4,5,6 C_6H_5, C-2,3,5,6 C_6H_4), 136.2 (C-1 C_6H_5), 145.3, 145.9 (C-1, C-4 C_6H_4), 165.6 (C-2 thiazolidine), 167.8 ppm (C=O); ms: m/z 385 (24), 384 (100, M^+).

Anal. Calcd. for $C_{20}H_{20}N_2O_4S$ (384.40): C, 62.48; H, 5.24; N, 7.29; S, 8.34. Found: C, 62.19; H, 5.21; N, 7.16; S, 8.34.

Ethyl [2-(3-Methyltetrahydro-2*H*-1,3-thiazin-2-ylidene)-4-nitrophenylacetate] (**10a**).

This compound was obtained from 1.95 g (0.010 mole) of ethyl 4-nitrophenylacetate (**8**) and 2.89 g (0.010 mole) of 3-methyl-2-methylthio-5,6-dihydro-1,3-thiaziniumiodide **7a** [6] as yellow crystals, 0.58 g (36%), mp 89°; ir: ν CO 1670 cm^{-1}; ^{1}H nmr: δ 1.13-1.16 (t, 3H, O-CH_2-CH_3), 2.20-2.26 (m, 2H, 5-H thiazine), 2.85-2.91 (t, 2H, 6-H thiazine, J = 7 Hz), 2.94 (s, 3H, N-CH_3), 3.43-3.44 (t, 2H, 4-H thiazine, J = 7 Hz), 4.10-4.16 (q, 2H, O-CH_2-CH_3), 7.32-7.35 (m, 2H, C_6H_4), 8.09-8.12 ppm (m, 2H, C_6H_4); ^{13}C nmr: δ 14.5 (O-CH_2-CH_3), 24.8 (C-5 thiazine), 27.3 (C-6 thiazine), 45.4 (N-CH_3), 50.8 (C-4 thiazine), 59.6 (O-CH_2-CH_3), 98.4 (=C-$COOC_2H_5$), 123.0 (C-3 and C-5 C_6H_4), 132.3 (C-2 and C-6 C_6H_4), 145.0 (C-1 C_6H_4), 148.0 (C-4 C_6H_4), 165.5 (C-2 thiazine), 166.6 ppm (C=O); ms: m/z 323 (28), 322 (100, M^+).

Anal. Calcd. for $C_{15}H_{18}N_2O_4S$ (308.38): C, 55.89; H, 5.63; N, 8.69; S, 9.94. Found: C, 55.87; H, 5.82; N, 8.49; S, 9.75.

Ethyl [2-(3-Benzyltetrahydro-2*H*-1,3-thiazin-2-ylidene)-4-nitrophenylacetate] (**10b**).

This compound was obtained from 1.95 g (0.010 mole) of **8** and 3.65 g (0.010 mole) of 3-benzyl-2-methylthio-5,6-dihydro-1,3-thiaziniumiodide (**7b**) [6] as orange crystals, 1.0 g (25%), mp 141°; ir: ν CO 1650 cm^{-1}; ^{1}H nmr: δ 1.19-1.23 (t, 3H, O-CH_2-CH_3), 1.80-1.86 (m, 2H, 5-H thiazine), 2.75-2.79 (t, 2H, 6-H thiazine, J = 7 Hz), 3.33-3.37 (t, 2H, 4-H thiazine, J = 7 Hz), 4.14-4.19 (q, 2H, O-CH_2-CH_3), 4.23 (s, 2H, CH_2-C_6H_5), 7.30-7.32 (m, 2H, C_6H_4), 7.35-7.40 (m, 5H, C_6H_5), 8.12-8.15 ppm (m, 2H, C_6H_4); ^{13}C nmr: δ 14.5 (O-CH_2-CH_3), 26.4 (C-5 thiazine), 27.2 (C-6 thiazine), 47.1 (C-4 thiazine), 59.7 (CH_2-C_6H_5), 61.0 (O-CH_2-CH_3), 100.3 (=C-$COOC_2H_5$), 123.1 (C-3,5 C_6H_4), 128.3, 128.8, 128.9, 132.2, (C-2,6 C_6H_4, C-2,3,4,5,6 C_6H_5), 137.2 (C-1 C_6H_5), 145.2 (C-1 C_6H_4), 147.8 (C-4 C_6H_4), 165.6 (C-2 thiazine), 168.5 ppm (C =O); ms: m/z 399 (25), 398 (100, M^+).

Anal. Calcd. for $C_{21}H_{22}N_2O_4S$ (398.48): C, 63.30; H, 5.56; N, 7.03; S, 8.05. Found: C, 63.22; H, 5.59; N, 7.13; S, 7.94.

2-(3-Benzylthiazolidin-2-ylidene)-4-nitrophenylacetonitrile (**12**).

This compound was obtained from 0.81 g (0.005 mole) of 4-nitrophenylacetonitrile (**11**) and 1.76 g (0.005 mole) of **1** after flash chromatography with diethyl ether as yellow crystals (pentane/toluene), 1.0 g (60%), mp 90°; ir: ν CN 2180 cm^{-1}; ^{1}H nmr: δ 3.08-3.11 (t, 2H, 5-H thiazolidine, J = 7 Hz), 3.75-3.79 (t, 2H, 4-H thiazolidine, J = 7 Hz), 5.10 (s, 2H, CH_2-C_6H_5), 7.27-7.41 (m, 5H,

(m, 5H, C_6H_5), 7.63-7.67, 8.14-8.16 ppm (m, 4-H, C_6H_4); ^{13}C nmr: δ 27.8 (C-5 thiazolidine), 54.1 (C-4 thiazolidine), 56.0-56.4 (CH_2-C_6H_5), 72.5 (C=*C*-CN), 119.8 (CN), 123.7, 127.4-129.1, (C-2,3,4,5,6 C_6H_5, C-2,3,5,6 C_6H_4), 135.5 (C-1 C_6H_5), 144.5, 145.4 (C-1, C-4 C_6H_4), 164.9 ppm (C-2 thiazolidine); ms: m/z 338 (15), 337 (70, M^+).

Anal. Calcd. for $C_{18}H_{15}N_3O_2S$ (337.40): C, 64.08; H, 4.48; N, 12.45; S, 9.50. Found: C, 63.82; H, 4.42; N, 12.58;. S, 9.78.

2-(3-Methyl-tetrahydro-2*H*-1,3-thiazin-2-ylidene)-4-nitrophenyl-acetonitrile (**13a**).

This compound was obtained from 0.81 g (0.005 mole) of **11** and 1.45 g (0.005 mole) of **7a** as yellow crystals, 2.0 g (73%), mp 186°; ir: ν CN 2180 cm^{-1}; ^1H nmr: δ 2.25-2.32 (m, 2H, 5-H thiazine), 2.98 (s, 3H, CH_3), 3.04-3.08 (t, 2H, 6-H thiazine), 3.48-3.51 (t, 2H, 4-H thiazine), 7.27-7.37 (m, 2H, C_6H_4), 8.11-8.15 ppm (m, 2H, C_6H_4); ^{13}C nmr: δ 24.2 (C-5 thiazine), 27.1 (C-6 thiazine), 44.8 (CH_3), 51.0 (C-4 thiazine), 78.4 (=C-CN), 121.3 (CN), 123.7 and 127.4 (C-2,6 and C-3,5 C_6H_4), 143.4 and 144.2 (C-1, C-4 C_6H_4), 166.4 ppm (C-2 thiazine); ms: m/z 276 (19), 275 (100, M^+).

Anal. Calcd. for $C_{13}H_{13}N_3O_2S$ (275.33): C, 56.71; H, 4.76; N, 15.26; S, 11.65; Found: C, 56.48; H, 4.78; N, 15.25; S, 11.78.

2-(3-Benzyltetrahydro-2*H*-1,3-thiazin-2-ylidene)-4-nitrophenyl-acetonitrile (**13b**).

This compound was obtained from 0.81 g (0.005 mole) of **11** and 1.83 g (0.005 mole) of **7b** as yellow crystals, 1.1 g (69%), mp 123°; ir: ν CN 2180 cm^{-1}; ^1H nmr: δ 1.79-1.85 (m, 2H, 5-H thiazine), 2.85-2.91 (t, 2H, 6-H thiazine, J = 7 Hz), 3.41-3.48 (t, 2H, 4-H thiazine, J = 7 Hz), 4.22 (s, 2H, CH_2-C_6H_5), 7.24-7.48 and 8.13-8.20 ppm (m, 4H, C_6H_4), (m, 5H, C_6H_5); ^{13}C nmr: δ 26.0 (C-5 thiazine), 27.0 (C-6 thiazine), 47.3 (C-4 thiazine), 60.4 (CH_2-C_6H_5), 78.3 (=*C*-CN), 121.4 (CN), 123.9-128.8 (C-2,3,4,5,6 C_6H_5, C-2,3,5,6 C_6H_4), 135.8 (C-1 C_6H_5), 143.4 and 144.5 (C-1, C-4 C_6H_4), 168.0 ppm (C-2 thiazine); ms: m/z 352 (27), 351 (100, M^+).

Anal. Calcd. for $C_{19}H_{17}N_3O_2S$ (351.43): C, 64.94; H, 4.88; N, 11.96; S, 9.12. Found: C, 64.82; H, 4.82; N, 11.91; S, 9.26.

2-(5-Methylene-3-phenethylthiazolidin-2-ylidene)-4-nitrophenyl-acetonitrile (**14**).

This compound was obtained from 0.35 g (0.0035 mole) of **11** and 1.27 g (0.0035 mole) of **4** by stirring at room temperature for 16 hours and chromatography with dichloromethane from the first fraction as yellow crystals, 0.20 g (16%), mp 74°; ir: ν CN 2180 cm^{-1}; ^1H nmr: δ 3.14-3.18 (t, 2H, CH_2-C_6H_5 J = 7 Hz), 4.07-4.11 (t, 2H, CH_2-N, J = 7 Hz), 4.39-4.40 (m, 2H, 4-H thiazolidine), 5.08-5.10 (m, 1H, =CH_2), 5.16-5.18 (m, 1H, =CH_2), 7.26-7.35 (m, 5H, C_6H_5), 7.56-7.59, 8.16-8.19 ppm (4H, C_6H_4); ^{13}C nmr: δ 34.4 (CH_2-C_6H_5), 52.0 (CH_2N), 62.7 (=C-CN), 105.6 (=CH_2), 119.9 (CN), 123.9-129.2 (C-2,3,4,5,6 C_6H_5, C-2,3,5,6 C_6H_4), 135.1 (C-4 thiazolidine), 137.6 (C-1 C_6H_5), 143.8, 145.9 (C-1, C-4 C_6H_4), 163.6 ppm (C-2 thiazolidine); ms: m/z 363 (M^+, 12), 104 (100).

Anal. Calcd. for $C_{20}H_{17}N_3O_2S$ (363.43): C, 66.09; H, 4.71; N, 11.56; S, 8.82. Found: C, 66.03; H, 4.74; N; 11.32; S, 8.89.

2-(5-Methyl-3-phenethylthiazoline-2-ylidene)-4-nitrophenyl-acetonitrile (**15**).

This compound was obtained from the second fraction of the foregoing run as red crystals, 0.20 g (16%), mp 78°; ir: ν CN 2180 cm^{-1}; ^1H nmr: δ 2.10-2.11 (s, 3H, CH_3), 3.16-3.19 (t, 2H, CH_2-C_6H_5, J = 7 Hz), 4.42-4.46 (t, 2H, CH_2-N, J = 7 Hz), 6.17-6.18 (s, 1H, 4-H thiazoline), 7.23-7.34 (m, 5H, C_6H_5), 7.63-7.67, 8.14-8.18 ppm (m, 4H, C_6H_4); ^{13}C nmr: δ 11.9 (CH_3), 35.3 (CH_2-C_6H_5), 52.4 (CH_2-N), 68.0 (=*C*-CN), 117.0 (CN), 121.2 (C-5 thiazoline), 127.1 (C-4 thiazoline), 124.3-125.6, 128.2-129.0 (C-2,3,4,5,6 C_6H_5, C-2,3,5,6 C_6H_4), 136.9 (C-1 C_6H_5), 143.9, 144.7 (C-1, C-4 C_6H_4), 162.6 ppm (C-2 thiazoline); ms: m/z 363 (11, M^+), 104 (100).

Anal. Calcd. for $C_{20}H_{17}N_3O_2S$ (363.43): C, 66.09; H, 4.71; N, 11.56; S, 8.82. Found: C, 65.84; H, 4.70; N, 11.72; S, 8.77.

9-(3-Benzylthiazolidin-2-ylidene)-2,5-dinitrofluorene (**17**).

This compound was obtained from 0.64 g (0.0025 mole) of 2,5-dinitrofluorene (**16**) and 0.88 g (0.0025 mole) of **1** as dark red crystals, 0.20 g (19%), mp 225°; ^1H nmr: δ 2.95 (t, 2H, 5-H thiazolidine), 3.92-3.95 (t, 2H, 4-H thiazolidine), 4.71 (s, 2H, CH_2-C_6H_5), 7.21-7.26 and 7.33-7.37 (m, m, 7H, dinitrofluorene and C_6H_5), 7.76-7.78 (m, 1H, dinitrofluorene), 7.53-7.57 (m, 1H, dinitrofluorene), 8.09-8.12 (m, 1H, dinitrofluorene), 8.22-8.24 ppm (m, 1H, dinitrofluorene); ^{13}C nmr: δ 29.9 (C-5 thiazolidine), 53.2 (C-4 thiazolidine), 60.3 (CH_2-C_6H_5), 117.8-129.2 (C-2,3,4,5,6 C_6H_5, C-1,3,4,4a,4b,6,7,8,8a,9 dinitrofluorene), 135.9 (C-1 C_6H_5), 145.8 and 146.7 (C-2 and C-5 dinitrofluorene), 164.0 ppm (C-2 thiazolidine); ms: m/z 431 (13, M^+), 91 (100).

Anal. Calcd. for $C_{23}H_{17}N_3O_4S$ (431.47): C, 64.03; H, 3.97; N, 9.74; S, 7.43. Found: C, 63.89; H, 3.99; N, 9.81; S, 7.24.

9-(3-Methyltetrahydro-2*H*-1,3-thiazin-2-ylidene)-2,5-dinitro-fluorene (**18a**).

This compound was obtained from 2.56 g (0.010 mole) of **16** and 2.89 g (0.010 mole) of **7a** by stirring in 150 ml dichloromethane and 20 ml ethanol for 12 hours at room temperature after column chromatography with ethyl acetate/cyclohexane 2/1 as dark red crystals, 1.0 g (27%), mp 248°; ^1H nmr: δ 2.43-2.50 (m, 2H; 5-H thiazine), 3.30 (s, 3H, CH_3), 3.36-3.39 (t, 2H, 6-H thiazine, J = 7 Hz), 3.77-3.80 (t, 2H, 4-H thiazine, J = 7 Hz), 8.05-8.12 (m, 4H, dinitrofluorene), 8.82 ppm (s, 2H, dinitrofluorene); ^{13}C nmr: δ 23.8 (C-5 thiazine), 28.1 (C-6 thiazine), 45.6 (N-CH_3), 50.7 (C-4 thiazine), 104.5 (C-9a, C-4b dinitrofluorene), 116.8, 117.0, 120.7 (C-1,3,4,6,7,8 dinitrofluorene), 136.7 (C-4a und C-8a dinitrofluorene), 138.5 (C-9 dinitrofluorene), 146.9 (C-2 and C-5 dinitrofluorene), 164.7 ppm (C-2 thiazine); ms: m/z 370 (22), 369 (100, M^+).

Anal. Calcd. for $C_{18}H_{15}N_3O_4S$ (369.58): C, 58.53; H, 4.09; N, 11.38; S, 8.68. Found: C, 58.54; H, 4.36; N, 11.29; S, 8.53.

9-(3-Benzyltetrahydro-2*H*-1,3-thiazin-2-ylidene)-2,5-dinitrofluorene (**18b**).

This compound was obtained from 2.65 g (0.010 mole) of **16** and 3.65 g (0.010 mole) of **7b** by stirring in 60 ml of ethanol and 70 ml of dichloromethane at room temperature for 5 hours after flash chromatography with ethyl acetate/cyclohexane 2/1 as dark red crystals, 0.80 g (18%), mp 248°; ^1H nmr: δ 1.85-1.94 (m, 2H, 5-H thiazine), 2.99-3.03 (t, 2H, 6-H thiazine, J = 7 Hz), 3.79-3.81 (t, 2H, 4-H thiazine, J = 7 Hz), 4.63 (s, 2H, CH_2-C_6H_5), 7.22-7.28 and 7.30 (m, m, 5H C_6H_5), 7.45-7.51 (m, 1H, dinitrofluorene), 7.70-7.72 (m, 1H, dinitrofluorene), 8.03-8.06 (m, 1H, dinitrofluorene), 8.21-8.23 (m, 1H, dinitrofluorene), 8.30-8.32 (m, 1H, dinitrofluorene), 8.92-8.93 ppm (m, 1H, dinitrofluorene), ms: m/z 446 (28), 445 (100, M^+).

Anal. Calcd. for $C_{24}H_{19}N_3O_4S$ (445.50): C, 64.71; H, 4.30; N, 9.43; S, 7.20. Found: C, 64.58; H, 4.31; N, 9.47; S, 7.05.

3-Benzyl-2-(2,4-dinitrobenzylidene)tetrahydro-2*H*-1,3-thiazine (**20**).

This compound was obtained from 1.82 g (0.010 mole) of 2,4-dinitrotoluene (**19**) and 3.97 g (0.010 mole) of **7b** after 4.5 hours heating and 2 runs of flash chromatography, first with dichloromethane and increasing amounts of methanol, second with dichloromethane/ethyl acetate 5/1 as a viscid red oil, 0.28 g (8%); ^{1}H nmr: δ 2.12-2.19 (m, 2H, 5-H thiazine), 2.97-3.01 (t, 2H, 6-H thiazine, J = 7 Hz), 3.46-3.49 (t, 2H, 4-H thiazine, J = 7 Hz), 4.60 (s, 2H, C*H*$_2$-C$_6$H$_5$), 6.11 (s, 1H, C=C*H*-C$_6$H$_3$), 7.26-7.41 (m, 5H, C$_6$H$_5$), 7.98-8.02 (m, 1H, C$_6$H$_3$), 8.11-8.13 (m, 1H, C$_6$H$_3$), 8.70 ppm (s, 1H, C$_6$H$_3$); ^{13}C nmr: δ 25.4 (C-5 thiazine), 26.4 (C-6 thiazine), 48.6 (C-4 thiazine), 57.6 (*C*H$_2$-C$_6$H$_5$), 93.0 (C=*C*H-C$_6$H$_3$), 121.6-129.9 (C-3,5,6 C$_6$H$_3$, C-2,3,4,5,6 C$_6$H$_5$), 136.2 (C-1 C$_6$H$_5$), 140.8, 141.4, 144.7 (C-1, C-2, C-4 C$_6$H$_3$), 155.8 ppm (C-2 thiazine); ms: m/z 190 (20), 178 (28), 91 (100).

Anal. Calcd. for C$_{18}$H$_{17}$N$_3$O$_4$S (371.42): C, 58.21; H, 4.61; N, 11.31. Found: C 57.98; H, 4.55; N, 11.61.

2-(3-Benzylthiazolidine-2-ylidene)-2-(2-cyanophenyl)acetonitrile (**22**).

This compound was obtained from 0.81 g (0.005 mole) of 2-(2-cyanophenyl)acetonitrile (**21**) and 1.92 g (0.005 mole) of **1** after heating for 1 hour as yellow crystals (ethanol), 0.67 g (42%), mp 100°; ir: ν 2 CN 2220, 2180 cm^{-1}; ^{1}H mnr: δ 3.00-3.04 (t, 2H, 5-H thiazolidine, J = 7 Hz), 3.74-3.77 (t, 2H, 4-H thiazolidine, J = 7 Hz), 5.11 (s, 2H, C*H*$_2$-C$_6$H$_5$), 7.00-7.02, 7.26-7.67 ppm (m, m, 9H, phenyl protons); ^{13}C nmr: δ 27.7, 27.8 (C-5 thiazine, *E/Z*-isomeres), 53.2, 54.0 (C-4 thiazine, *E/Z*-isomeres), 55.4, 56.4 (*C*H$_2$-C$_6$H$_5$, *E/Z*-isomeres), 67.5, 70.1 (=*C*-CN, *E/Z*-isomeres), 112.7, 115.0, 117.9, 119.6, 122.1 (2x CN, *E/Z*-isomeres, C-2 C$_6$H$_4$, *E/Z*-isomeres), 127.0-133.3 (C-2,3,4,5,6 C$_6$H$_5$, *E/Z*-isomeres, C-3,4,5,6 C$_6$H$_4$, *E/Z*-isomeres), 135.3, 135.6 (C-1 C$_6$H$_5$, *E/Z*-isomeres), 139.0, 140.7 (C-1 C$_6$H$_4$, *E/Z*-isomeres), 164.9, 165.2 ppm (C-2 thiazolidine, *E/Z*-isomeres); ms: m/z 318 (14), 317 (59, M$^+$), 91 (100).

Anal. Calcd. for C$_{19}$H$_{15}$N$_3$S (317.42): C, 71.90; H, 4.76; N, 13.24 S, 10.10. Found: C, 71.86; H, 4.71; N, 13.33; S, 10.08.

2-(2-Cyanophenyl)-2-(5-methyl-3-phenethylthiazolin-2-ylidene)-acetonitrile (**23**).

This compound was obtained from 0.70 g (0.005 mole) of **21** and 1.82 g (0.005 mole) of **4** by stirring 12 hours at room temperature and flash chromatography with dichloromethane as yellow crystals, 0.10 g (6%), mp 120°; ir: ν 2 CN 2220, 2160 cm^{-1}; ^{1}H nmr: δ 1.97 (s, 3H, CH$_3$), 3.16-3.20 (t, 2H, C*H*$_2$-C$_6$H$_5$, J = 7 Hz), 4.28-4.31 (t, 2H, CH$_2$-N, J = 7 Hz), 5.97-5.98 (s, 1H, 4H thiazoline), 7.21-7.71 ppm (m, 9H, phenyl protons); ^{13}H nmr: δ 11.8 (CH$_3$), 35.1 (*C*H$_2$-C$_6$H$_5$), 51.4 (CH$_2$-N), 62.8 (=*C*-CN), 114.2 (C-2 C$_6$H$_4$), 116.0, 118.0 (2x CN), 121.1 (C-5 thiazoline), 126.9 (C-4 thiazoline), 127.8-133.9 (C-2,3,4,5,6 C$_6$H$_5$, C-3,4,5,6 C$_6$H$_4$), 137.3 (C-1 C$_6$H$_5$), 140.8 (C-1 C$_6$H$_4$), 163.5 ppm (C-2 thiazoline); ms: m/z 344 (9, M$^+$), 104 (100).

Anal. Calcd. for C$_{21}$H$_{17}$N$_3$S (343.45): C, 73.45; H, 4.99; N, 12.23; S, 9.34. Found: C, 73.18; H, 4.97; N, 12.18; S, 9.24.

2-(2-Cyanophenyl-2-(3-methyltetrahydro-2*H*-1,3-thiazin-2-ylidene)acetonitrile (**24a**).

This compound was obtained from 0.81 g (0.005 mole) of **21** and 1.45 g (0.005 mole) of **7a** by heating for 2.5 hours as yellow crystals (ethanol), 0.59 g (46%), mp 110°; ir: ν 2 CN 2220, 2160 cm^{-1}; ^{1}H nmr: δ 2.12-2.37 (m, 2H, 5-H thiazine), 2.89-2.97, 3.04-3.13 (t, 2H, 6-H thiazine, s, 3H, CH$_3$), 3.44-3.57 (t, 2H, 4-H thiazine), 7.16-7.33 (m, 1H, C$_6$H$_5$), 7.42-7.66 (m, 3H, C$_6$H$_5$), ms: m/z 256 (17), 255 (100, M$^+$).

Anal. Calcd. for C$_{14}$H$_{13}$N$_3$S (255.34): C, 65.85; H, 5.13; N, 16.46; S, 12.56. Found: C, 65.94; H, 5.11; N, 16.48; S, 12.60.

2-(3-Benzyltetrahydro-2*H*-1,3-thiazin-2-ylidene)-2-(2-cyanophenyl)acetonitrile (**24b**).

This compound was obtained from 1.62 g (0.010 mole) of **21** and 3.65 g (0.010 mole) of **7b** by heating for 3 hours as greenish-yellow crystals (ethanol), 1.6 g (49%), mp 129°; ir: ν 2 CN 2220, 2180 cm^{-1}; ms: m/z 332 (11), 331 (44, M$^+$) 91 (100).

Anal. Calcd. for C$_{20}$H$_{17}$N$_3$S (331.44): C, 72.48; H, 5.17; N, 12.68; S, 9.67. Found: C, 72.40; H, 5.14; N, 12.79; S, 9.58.

REFERENCES AND NOTES

[1] Iminium Carbonic Acid Derivative Salts. **XI**. W. Hanefeld, M. Naeeni and M. Schlitzer, *J. Heterocyclic Chem.*, **33**, 1903 (1996).

[2] Iminium Carbonic Acid Derivative Salts. **VIII**. W. Hanefeld and H. Harms, *J. Heterocyclic Chem.*, submitted.

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[4] K. Peseke, H. Feist, W. Hanefeld, J. Kopf and H. Schulz, *J. Carbohydr. Chem.*, **14**, 317 (1995).

[5] W. Hanefeld, M. Naeeni and M. Schlitzer, *J. Heterocyclic Chem.*, **33**, 1785 (1996).

[6] W. Hanefeld, H. Harms and M. Schlitzer, *Arch Pharm. (Weinheim)*, **328**, 431 (1995).

[7] W. Hanefeld, M. Schlitzer and J. v. Gösseln, *Arch Pharm. (Weinheim)*, **318**, 185 (1985).