Reaction of *N,N'*-Dimethyl-2-nitroethene-1,1-diamine with α,β-Unsaturated Acyl Isothiocyanates: Preparation of 1,3-Thiazin-4-one and 4-Nitro-1,2-thiazol-5(2*H*)-imine Derivatives[1])

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The reaction of *N,N'*-dimethyl-2-nitroethene-1,1-diamine (**8**) with α,β-unsaturated acyl isothiocyanates **9** affords 3,3-diamino-2-nitroacrylthioamides **10** (*Scheme 2*) in moderate-to-good yields. Cyclization of **10** under acidic conditions gives 1,3-thiazin-4-one derivatives of type **11**. Oxidative cyclization of **10** with diethyl azodicarboxylate leads to 4-nitro-1,2-thiazol-5(2*H*)-imine derivatives **12**.

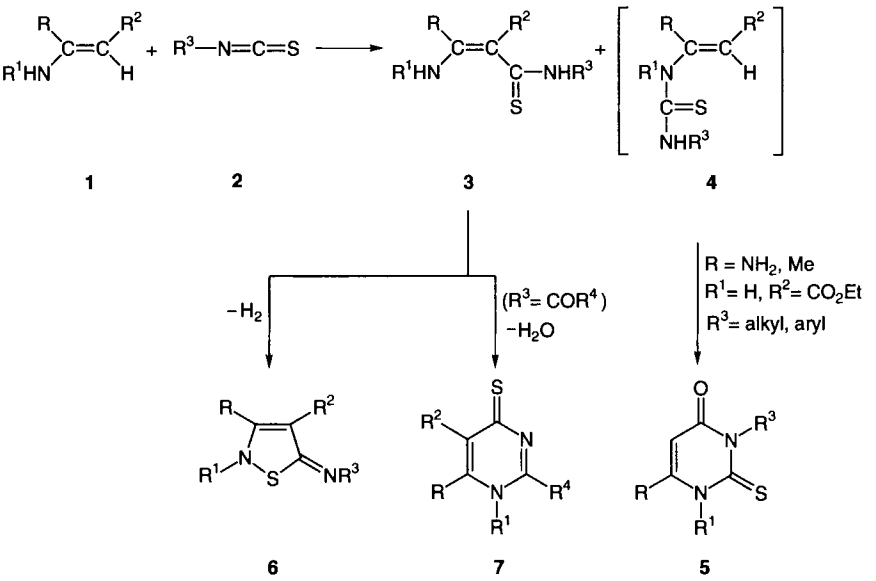
1. Introduction. – Enamines **1** with electron-withdrawing groups at the C(β)-atom easily add onto acyl isothiocyanates **2** (R^3 = acyl). The products of this reaction are suitable synthons in heterocyclic chemistry [1–11] (*Scheme 1*). In principle, this reaction can lead not only to the addition product at the C-atom (*C*-adduct, **3**), but also to the product of addition at the NHR^1 group (*N*-adduct, **4**). The *N*-adduct has never been isolated. However, its formation has been indicated indirectly by the isolation of its cyclization product **5**, a thiouracil derivative, from the reaction of **1** with alkyl and aryl isothiocyanates [10][12], but not with acyl isothiocyanates. Oxidative cyclization of the *C*-adduct **3** yields 1,2-thiazole derivatives **6**, and, in the case of the products of acyl isothiocyanates (R^3 = COR^4), pyrimidine-4(1*H*)-thiones of type **7** are formed *via* cyclization and dehydration.

In the case of α,β-unsaturated acyl isothiocyanates, the synthetic possibilities of the reaction with **1** should increase: in addition to 1,2-thiazole derivatives **6** and pyrimidine-4(1*H*)-thiones **7**, other heterocycles involving the C=C bond could be formed.

For the last few years, we have been studying reactions with nitroketenaminals of type **8** (2-nitroethene-1,1-diamines) and their use in the preparation of heterocyclic compounds [13–15] (*cf.* also [16]). In the present paper, we describe the results of the reaction of **8** with isothiocyanates **9** bearing an α,β-unsaturated acyl group (*cf. Scheme 2*).

[1]) Presented in preliminary form at the 'XII Seminario Cientifico', Centro Nacional de Investigaciones Cientificas, Habana, Cuba, 1995 (*M.I.G.T.*) and at the 'Tenth International Conference on Organic Synthesis', Bangalore, India, 1994 (*D.M.A.*).

Scheme 1



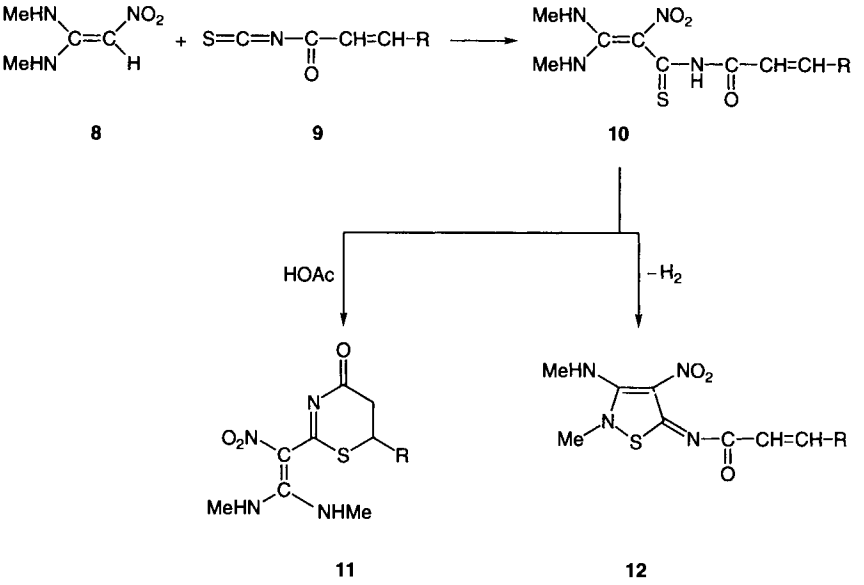
2. Results and Discussion. – The reaction of *N*,*N*′-dimethyl-2-nitroethene-1,1-diamine (**8**) with α,β-unsaturated acyl isothiocyanates **9**[2]) in acetone at room temperature yielded the corresponding 3,3-diamino-2-nitroacrylthioamides **10** (*Scheme 2* and *Table 1*) as the primary products in fair-to-good yields. As found in reactions of nitroketenaminals of type **8** with other isothiocyanates (*cf.* [17][18]), only the *C*-adduct was formed.

In the ^{1}H-NMR spectra of compounds **10** in (D_6)DMSO at room temperature, the signal of the thioamide-N*H* appears at very low field (*ca.* 13 ppm). This fact can be explained by an intramolecular H-bond between this H-atom and one of the O-atoms of the NO_2 group (*cf.* crystal structure of **10a**, *Chapt. 3*) in addition to the influence of two neighboring electron-withdrawing groups. The ^{13}C-NMR studies of different nitroketeneaminals by *Rajappa* and *Nagarajan* [19] were used to assign all of the signals in the ^{13}C-NMR spectra of **10**. In the case of **10c**, the signal corresponding to =C(β)H appears at 129.4 ppm, *ca.* 13 ppm upfield compared to the =C(β)H signals of **10a** and **10b** (142.2 and 142.4 ppm, resp.). This points to a lower anisotropic and field effect of the furan ring compared to the Ph ring [20] and subsequently to a higher electron density at this C-atom in **10c**.

Under acidic conditions, derivatives of type **10** were cyclized to form 1,3-thiazin-4-one derivatives **11** (*Scheme 2*). Interestingly, the cyclization to **11** occurred readily when the crude reaction mixture of the *C*-adducts **10** was stirred in acetone for 2–3 days (*Method A*). However, suspensions of the isolated and purified *C*-adducts **10** in acetone showed no change despite longer reaction times. These results indicate a catalysis of the

[2]) The isothiocyanates **9** were prepared *in situ* by the addition of the corresponding acyl chloride to a solution of NH_4SCN in acetone.

Scheme 2[a])



[a]) X-Ray crystallography of compounds of type **10** showed that there is no C=C bond adjacent to the NO_2 group; a more likely presentation is a zwitterionic form (*cf.* also [15]).

Table 1. *Prepared* N-*Acyl-3,3-bis(methylamino)-2-nitroacrylthioamides* **10**

Compound	R	Yield [%]	M.p. [°]
10a	Ph	87	165.0–165.5
10b	4-MeO–C_6H_4	59	161.5–162.0
10c	2-Furyl	59	155.0–156.5

Table 2. *Prepared 2-[2-Bis(methylamino)-1-nitroethenyl]-5,6-dihydro-4*H-*1,3-thiazin-4-ones* **11**

Compound	R	Yield [%]		M.p. [°]
		Method A	*Method B*	
11a	Ph	61	89	208–209
11b	4-MeO–C_6H_4	52	81	183
11c	2-Furyl	–	72	178
11d	Me	42	–	227–228

cyclization reaction by acidic impurities in the reaction mixture[2]). This assumption has been confirmed by adding several drops of AcOH to a suspension of pure **10** in acetone: under these conditions, the formation of the cyclized product **11** could be observed. The reaction rate increased as a function of the acid concentration and reached its maximum value when glacial AcOH was employed as the solvent (*Method B*, *Table 2*).

Generally, **10** was obtained with sufficient purity to be used in the cyclization reactions without further purification. As an exception, **10d** (R = Me) could not be isolated; it cyclized rapidly under the conditions of its preparation to give 1,3-thiazin-4-one **11d**. This fact can be explained by comparing the influence of the substituents attached to the C(β)-atom on the C=C bond of the acyl group. Thus, in the case of **10d**, C(β) is more electrophilic than in **10a**, because of the missing conjugation of an aromatic group. As a consequence, the cyclization to **10d** occurs more readily.

On the other hand, the formation of **11c** seems to be rather difficult, as **10c** showed a remarkable tendency to be oxidized yielding 4-nitro-1,2-thiazol-5(2*H*)-imine **12c**. Thus, by stirring the crude mixture of **10c** for 1–2 days, **12c** precipitated instead of the expected **11c**, though the 1,3-thiazin-4-one was detected by TLC. This difficulty with the formation of **11c** can be explained by taking into account the higher electron density at the C(β)-atom of **10c** mentioned above (*cf.* ^{13}C-NMR spectrum), which disfavors the intramolecular *Michael* addition. The thiazine derivative **11c** was then obtained in 72% yield by stirring **10c** in AcOH. The formation of 1,2-thiazole **12c** can be explained by an oxidative cyclization with participation of atmospheric O_2. A similar behavior has been described by *Mishio et al.* [21] for the *C*-adduct of the reaction of 5-nitro-2-furoylisothiocyanate with β-aminocrotonates. *Junjappa* and co-workers [22] reported on the synthesis of related 1,2-thiazole derivatives in the reaction of nitroketenaminals with benzoyl isothiocyanate in boiling benzene. The *C*-adducts from nitroketenaminals and benzoyl isothiocyanate have also been cyclized to yield 1,2-thiazol-5(2*H*)-imines by using Br_2 as the oxidizing reagent [18][22][23].

We were able to improve the yield of 4-nitro-1,2-thiazol-5(2*H*)-imines **12** by treatment of the adducts **10** with diethyl azodicarboxylate (DEAD) in DMF as a dehydrogenation reagent (*Table 3*; *cf.* also [15]).

Table 3. *Prepared 2-Methyl-3-(methylamino)-4-nitro-1,2-thiazol-5(2*H*)-imines* **12**

Compound	R	Yield [%]	M.p. [°]
12a	Ph	91	267–268
12b	4-MeO–C_6H_4	85	285–286
12c	2-Furyl	82	236–238

It is worth mentioning that **11** was transformed into **12** by heating in DMF for *ca.* 15 min, *e.g.*, during recrystallization from DMF. Evidently, this transformation takes place *via* ring opening (*retro-Michael* addition to give **10**) and subsequent oxidative cyclization.

3. Crystal-Structure Determination of 10a[3]). – A crystal of **10a** · Me_2CO, obtained from acetone, was used for a low-temperature X-ray crystal-structure determination. All measurements were made on a *Rigaku AFC5R* diffractometer using graphite-

[3]) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-101067. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: + 44-(0)1223-336033 or e-mail: deposit(*a*)ccdc.cam.ac.uk).

monochromated MoK_α radiation (λ = 0.71069 Å) and a 12-kW rotating anode generator. The $\omega/2\theta$ scan mode was employed for data collection. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. Data collection and refinement parameters are given in *Table 4*. The structure was solved by direct methods using SHELXS86 [24], which revealed the positions of all non-H-atoms. The asymmetric unit also contains one molecule of acetone, which is not disordered. The non-H-atoms were refined anisotropically. All of the H-atoms bonded to N-atoms were placed in the positions indicated by a difference electron-density map, and their positions were allowed to refine together with individual isotropic displacement parameters. The H-atoms bonded to C-atoms were fixed in geometrically calculated positions (d(C–H) = 0.95 Å), and they were assigned fixed isotropic displacement parameters with a value equal to 1.2 U_{eq} of the parent C-atom. The orientations of the Me-group H-atoms were based on peaks located in a difference electron-density map. Refinement of the structure was carried out on F using full-matrix least-squares procedures, which minimized the function $\sum w(|F_o| - |F_c|)^2$. A correction for secondary extinction was not applied. Neutral-atom scattering factors for non-H-atoms were taken from [25a] and the scattering factors for H-atoms from [26]. Anomalous dispersion effects were included in F_{calc} [27]; the values for f' and f'' were those of [25b]. All calculations were performed using the TEXSAN crystallographic software package [28]. Data collection and refinement parameters are listed in *Table 4*; a view of the molecule is shown in *Fig. 1*.

Table 4. *Crystallographic Data of* **10a**

Crystallized from	acetone
Empirical formula	$C_{14}H_{16}N_4O_3S \cdot Me_2CO$
Formula weight	378.44
Crystal color, habit	red, prism
Crystal dimensions [mm]	0.25 × 0.42 × 0.48
Temp. [K]	173(1)
Crystal system	orthorhombic
Space group	$Pna2_1$
Z	4
Reflections for cell determination	25
2θ Range for cell determination [°]	35–39
Unit cell parameters a [Å]	11.737(1)
b [Å]	14.454(1)
c [Å]	11.388(1)
V [Å^3]	1931.9(3)
D_x [g cm^{-3}]	1.301
μ(MoK_α) [mm^{-1}]	0.197
$2\theta_{(max)}$ [°]	60
Total reflections measured	3693
Symmetry independent reflections	3204
Reflections used [$I > 2\sigma(I)$]	2530
Parameters refined	246
Final R	0.0392
wR ($w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$)	0.0322
Goodness of fit	1.569
Final Δ_{max}/σ	0.0003
$\Delta\rho$ (max; min) [e Å^{-3}]	0.27; −0.25
Range of $\sigma(d$(C–C)) [Å]	0.003–0.005

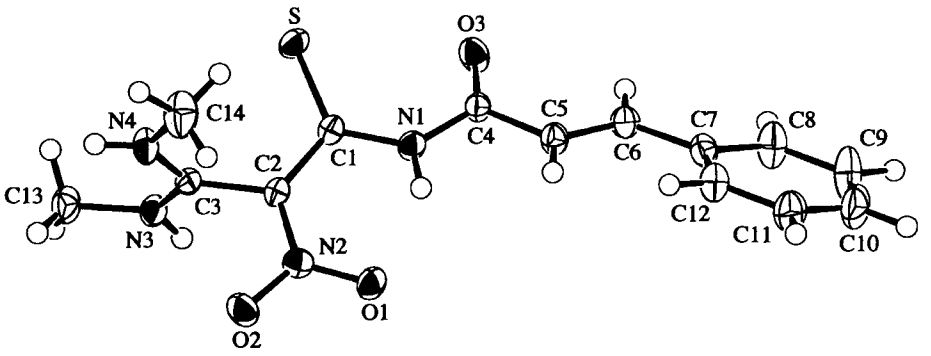


Fig. 1. *ORTEP Plot* [29] *of the molecular structure of* **10a** (with 50% probability ellipsoids)

As is usually found for these compounds (*cf.* [15][16][30]), the C(2),C(3) bond (*Table 5*) displays single-bond character, and the C(13)–N(3)–C(3)–N(4)–C(14) plane makes an angle of 89.3(3)° with the N(2)–C(2)–C(1) plane. Other bond lengths suggest that delocalized π-bonding occurs from the NO_2 group to at least N(1), and this is supported by the relative planarity of this region. The C(3),N(3) and C(3),N(4) bonds are also quite short, which suggests some double-bond character for these bonds, possibly due to the formation of a zwitterion (*cf.* [15]). It is interesting that the five atoms of the bis(methylamino)methylidene group are completely planar, which may be a further indication that the C,N bonds have double-bond character.

The carbonyl O-atom lies on the same side of the chain as the S-atom, but the chain is twisted slightly so as to minimize steric interactions between these two atoms. This conformation is probably also stabilized by the intramolecular H-bond between the amide H-atom and an O-atom of the NO_2 group. The thioacrylamide chain deviates

Table 5. *Selected Bond Lengths* [Å] *and Angles* [deg] *for* **10a**

S–C(1)	1.663(3)	N(3)–C(13)	1.456(4)
O(1)–N(2)	1.278(3)	N(4)–C(3)	1.316(3)
O(2)–N(2)	1.265(3)	N(4)–C(14)	1.462(4)
O(3)–C(4)	1.220(3)	C(1)–C(2)	1.434(3)
N(1)–C(1)	1.375(3)	C(2)–C(3)	1.490(3)
N(1)–C(4)	1.392(3)	C(4)–C(5)	1.482(4)
N(2)–C(2)	1.363(3)	C(5)–C(6)	1.327(4)
N(3)–C(3)	1.318(3)	C(6)–C(7)	1.471(4)
C(1)–N(1)–C(4)	130.3(2)	N(2)–C(2)–C(3)	113.8(2)
O(1)–N(2)–O(2)	118.9(2)	C(1)–C(2)–C(3)	119.8(2)
O(1)–N(2)–C(2)	122.5(2)	N(3)–C(3)–N(4)	121.7(2)
O(2)–N(2)–C(2)	118.6(2)	N(3)–C(3)–C(2)	117.9(2)
C(3)–N(3)–C(13)	122.9(2)	N(4)–C(3)–C(2)	120.4(2)
C(3)–N(4)–C(14)	124.0(3)	O(3)–C(4)–N(1)	124.8(3)
S–C(1)–N(1)	124.1(2)	O(3)–C(4)–C(5)	123.8(2)
S–C(1)–C(2)	119.6(2)	N(1)–C(4)–C(5)	111.4(2)
N(1)–C(1)–C(2)	116.3(2)	C(4)–C(5)–C(6)	121.9(3)
N(2)–C(2)–C(1)	126.3(2)	C(5)–C(6)–C(7)	125.3(3)

more significantly from planarity, compared with related compounds. The bonds mostly responsible for this deviation are the C(1)–N(1) (15° twist), N(1)–C(4) (7°), and C(4)–C(5) (12°) bonds.

Each of the MeNH groups of the molecule acts as a donor for intermolecular H-bonds. The corresponding acceptor atoms are the amide O-atom and the O-atoms of the NO_2 group of a neighboring molecule with each amino group interacting with a different neighboring molecule. H–N(4) forms bifurcated H-bonds to both O-atoms of the NO_2 group. One of the intermolecular H-bonds links the molecules into infinite one-dimensional chains running parallel to the *x*-axis. The bifurcated interaction links the molecules into infinite one-dimensional chains running parallel to the *z*-axis. The combination of intermolecular interactions links the molecules into a three-dimensional network (*Fig. 2*). The amide H-atom forms an intramolecular H-bond with O(1) of the NO_2 group so that this O-atom is accepting two H-bonds.

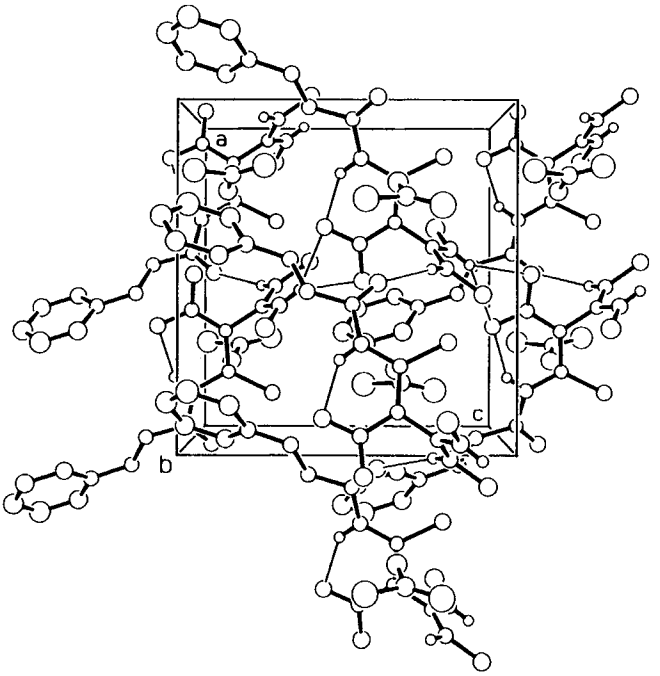


Fig. 2. *Molecular packing of* **10a** *showing the H-bonding scheme* (arbitrary spheres for atoms; uninvolved H-atoms omitted for clarity)

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Experimental Part

1. *General.* See [16]. TLC: Silica-gel-*60-*F_{254}-precoated plates (0.25 mm; *Merck*); $CHCl_3$/MeOH 10:2 as eluent. Acetone was dried with anh. $CaCl_2$. M.p.: on a *Boetius* hot plate, uncorrected. IR Spectra: in KBr on a

Perkin-Elmer-297 apparatus. ^{1}H-NMR (300 MHz) and ^{13}C-NMR spectra (50.4 MHz): in (D_6)DMSO on a *Bruker AC-300* instrument and a *Varian XL-200* instrument, respectively; TMS as internal standard. EI-MS: on a *JEOL JMS DX 300* instrument (70 eV) or on a *Finnigan SSQ-700* apparatus; CI-mode with NH_3 as ionization gas. Peaks (> 10%) are given in *m/z*. The starting materials were synthesized according to described procedures: N,N'-*dimethyl-2-nitroethene-1,1-diamine* (**8**) [31][32], cinnamoyl chloride [33], 4-methoxycinnamoyl chloride [34], 2-(2-furyl)prop-2-enoyl chloride [34], and but-2-enoyl chloride [35]. Diethyl azodicarboxylate (DEAD) was purchased from *Merck*.

2. *Synthesis of* N-*Acyl-3,3-bis(methylamino)-2-nitroprop-2-enethioamides* **10**. *General Procedure*. A soln. of the corresponding acyl chloride (20 mmol) in dried acetone (15 ml) was added dropwise at r.t. to a stirred soln. of NH_4SCN (1.52 g, 20 mmol) in dried acetone (5 ml). After 30 min, the precipitated NH_4Cl was filtered, and the soln. of the acyl isothiocyanate **9** was slowly added at r.t. to a stirred suspension of **8** (1.96 g, 15 mmol) in dried acetone (15 ml). The adduct **10** precipitated as a red solid and the mixture was stirred for 1 h. The product was filtered, and washed with H_2O and a small amount of acetone. Anal. pure samples of **10** were obtained by recrystallization from EtOH.

2.1. *3,3-Bis(methylamino)-2-nitro*-N-*(3-phenylpropenoyl)prop-2-enethioamide* (**10a**): 4.17 g (87%). Red-orange crystals. M.p. 165.0–165.5°. IR: 3220*m*, 3120*m*, 2980*m*, 1690*m*, 1660*s*, 1630*s*, 1575*m*, 1545 (sh), 1520*s*, 1500 (sh), 1450*m*, 1420*s*, 1390 (sh), 1345*s*, 1325*s*, 1285*s*, 1270*s*, 1230*m*, 1200*m*, 1185*m*, 1155*m*, 1120*s*, 1050*m*, 1040*m*, 1020*m*, 985*m*, 900*m*, 755*m*. ^{1}H-NMR: 13.15 (*s*, NHCO); 9.58, 8.81 (2 br. *s*, 2 MeN*H*); 7.70 (*m*, 2 arom. H); 7.61 (*d*, *J* = 15.8, H–C(β)^4)); 7.44 (*m*, 3 arom. H); 7.33 (*d*, *J* = 15.8, H–C(α)^4)); 2.83, 2.80 (2*s*, 2 *Me*NH). ^{13}C-NMR: 179.3 (*s*, C=S); 164.9 (*s*, C=O); 161.0 (*s*, $(MeNH)_2C$); 142.2 (*d*, C(β)^4)); 134.5 (*s*, 1 arom. C); 130.3, 129.0, 128.2 (3*d*, 5 arom. C); 122.4 (*d*, C(α)^4)); 118.2 (*s*, $=C(NO_2)$); 29.7, 29.0 (2*q*, 2 MeNH). CI-MS[5]): 149 (16), 132 (100). Anal. calc. for $C_{14}H_{16}N_4O_3S$ (320.37): C 52.49, H 5.03, N 17.49, S 10.01; found: C 52.55, H 5.21, N 17.22, S 10.27.

2.2. N-*[3-(4-Methoxyphenyl)propenoyl]-3,3-bis(methylamino)-2-nitroprop-2-enethioamide* (**10b**): 3.09 g (59%). Red-orange crystals. M.p. 161.5–162.0°. IR: 3460 (br.), 3260 (br.), 3030*m*, 1695*m*, 1650*s*, 1625*s*, 1604*s*, 1575*m*, 1515*s*, 1465*m*, 1425*s*, 1360*s*, 1335 (sh), 1310*s*, 1290*s*, 1255*s*, 1230 (sh), 1195 (sh), 1175*s*, 1150*s*, 1115*s*, 1030*m*, 1020*m*, 985*m*, 905*m*, 825*m*. ^{1}H-NMR: 13.13 (*s*, NHCO); 9.52, 8.75 (2 br. *s*, 2 MeN*H*); 7.61 (*AA'* of *AA'BB'*, J_{AB} = 8.8, 2 arom. H); 7.55 (*d*, *J* = 15.2, H–C(β)^4)); 7.19 (*d*, *J* = 15.2, H–C(α)^4)); 6.99 (*BB'* of *AA'BB'*, J_{AB} = 8.8, 2 arom. H); 3.80 (*s*, MeO); 2.83, 2.80 (2*s*, 2 *Me*NH). ^{13}C-NMR: 179.4 (*s*, C=S); 165.0 (*s*, C=O); 161.0 (*s*, $(MeNH)_2C$, MeO–*C*); 142.4 (*d*, C(β)^4)); 130.1 (*d*, 2 arom. C); 127.1 (*s*, 1 arom. C); 119.7 (*d*, C(α)^4)); 118.1 (*s*, $=C(NO_2)$); 114.5 (*d*, 2 arom. C); 55.4 (*q*, MeO); 29.7, 29.1 (2*q*, 2 MeNH). CI-MS[5]): 132 (100).

2.3. N-*[2-(Furan-2-yl)propenoyl]-3,3-bis(methylamino)-2-nitroprop-2-enethioamide* (**10c**): 2.74 g (59%). Red-orange crystals. M.p. 155.0–156.5°. IR: 3220 (br.), 3130*m*, 3060*m*, 1700*w*, 1650*s*, 1630*s*, 1525*m*, 1480*m*, 1445 (sh), 1425*m*, 1355*s*, 1285*s*, 1270*s*, 1230*m*, 1205*m*, 1155*m*, 1115*m*, 1075*w*, 1040*w*, 1020*m*, 980*m*, 750*m*. ^{1}H-NMR: 13.12 (*s*, NHCO); 9.56, 8.81 (2 br. *q*, 2 MeN*H*); 7.87 (*d*, *J* = 1.8, H–C(5) of furan); 7.44 (*d*, *J* = 15.5, H–C(β)^4)); 7.06 (*d*, *J* = 15.5, H–C(α)^4)); 6.95 (*d*, *J* = 3.8, H–C(3) of furan); 6.66 (*dd*, *J* = 3.8, 1.8, H–C(4) of furan); 2.83, 2.79 (2 br. *d*, 2 *Me*NH). ^{13}C-NMR: 179.2 (*s*, C=S); 164.8 (*s*, C=O); 161.0 (*s*, $(MeNH)_2C$); 150.8 (*s*, C(2) of furan); 145.9 (*d*, C(5) of furan); 129.4 (*d*, C(β)^4)); 118.9 (*s*, $=C(NO_2)$); 118.2 (*d*, C(α)^4)); 116.1 (*d*, C(3) of furan); 112.9 (*d*, C(4) of furan); 29.7, 29.1 (2*q*, 2 MeNH). CI-MS: 197 (31), 180 (29), 156 (45), 155 (18), 149 (11), 138 (30), 133 (22), 132 (100)[5]), 121 (27). Anal. calc. for $C_{12}H_{14}N_4O_4S$ (310.34): C 46.44, H 4.55, N 18.05, S 10.33; found: C 46.23, H 4.25, N 18.35, S 10.50.

3. *Synthesis of 2-[2-Bis(methylamino)-1-nitroethenyl]-5,6-dihydro-4*H-*1,3-thiazin-4-ones* **11**. *General Procedures. Method A*: The crude reaction mixture obtained after the preparation of **10** was stirred at r.t. for 2–3 d. Thiazine **11** precipitated as yellow solid, which was filtered, washed with H_2O and acetone, and recrystallized from the appropriate solvent. *Method B*: A soln. of **10** (3.2 mmol) in glacial AcOH (11 ml) was stirred at r.t. When the reaction was complete (TLC), the solvent was removed *i.v.*, and the oily residue was scratched in the presence of acetone. The precipitated **11** was purified by recrystallization.

3.1. *2-[2,2-Bis(methylamino)-1-nitroethenyl]-5,6-dihydro-6-phenyl-4*H-*1,3-thiazin-4-one* (**11a**): 0.91 g (89%, *Method B*). Pale-yellow solid (from EtOH). M.p. 208–209°. IR: 3240*m*, 3125*m*, 1665*s*, 1630*s*, 1580*m*, 1560 (sh), 1540 (sh), 1500 (sh), 1465*s*, 1430 (sh), 1415*s*, 1395*m*, 1345*s*, 1330 (sh), 1305 (sh), 1290*s*, 1240*s*, 1225*s*, 1195*s*, 1155*s*, 1150*s*, 1125*s*, 1040*m*, 1020*m*, 695*m*, 680*m*. ^{1}H-NMR: 9.57 (br. *q*, MeN*H*); 8.88 (br. *s*, MeN*H*); 7.4–7.32

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[4]) α and β refer to the C=O group.

[5]) The molecule underwent fragmentation even under CI-MS conditions; *m/z* 132 corresponds to the fragment ion $[(MeN)_2CCH(NO_2) + 1]^{+\cdot}$

(*m*, 5 arom. H); 4.61 (*dd*, *J* = 12.1, 3.5, H–C(6)); 2.86 (br. *d*, *Me*NH); 2.76 (*s* + *dd*, *J* = 14.5, 12.1, *Me*NH, H_{ax} of CH_2(5)); 2.65 (*dd*, *J* = 14.5, 3.5, H_{eq}, of CH_2(5)). ^{13}C-NMR: 176.9 (*s*, C=N); 169.9 (*s*, C=O); 160.4 (*s*, $(MeNH)_2C$); 139.0 (*s*, 1 arom. C); 128.9, 128.1, 127.8 (3*d*, 5 arom. C); 114.9 (*s*, $=C(NO_2)$); 42.7 (*d*, C(6)); 37.1 (*t*, C(5)); 29.9, 28.9 (2*q*, 2 MeNH). CI-MS: 321 (< 1, $[M+1]^+$), 149 (33), 132 (100). EI-MS: 320 (4, $M^{+\cdot}$), 215 (18), 148 (21), 147 (19), 132 (18), 131 (100), 104 (12), 103 (80), 102 (32), 77 (71). Anal. calc. for $C_{14}H_{16}N_4O_3S$ (320.37): C 52.49, H 5.03, N 17.49, S 10.27; found: C 52.48, H 5.68, N 16.88, S 10.42.

3.2. *2-[2,2-Bis(methylamino)-1-nitroethenyl]-5,6-dihydro-6-(4-methoxyphenyl)-4*H*-1,3-thiazin-4-one* (**11b**): 0.91 g (81%, *Method B*). Pale-yellow solid (from DMF/EtOH). M.p. 183°. IR: 3200*m*, 1670*s*, 1620*s*, 1610 (sh), 1580 (sh), 1570*s*, 1540 (sh), 1515*s*, 1490 (sh), 1460*s*, 1440*m*, 1420*s*, 1410*s*, 1390*m*, 1370 (sh), 1355*s*, 1345*s*, 1280*s*, 1260 (sh), 1235*s*, 1200 (sh), 1190*s*, 1180*s*, 1155*s*, 1140*s*, 1115 (sh), 1040*s*, 1030*s*, 1015*m*, 910*m*, 835*s*, 685*m*. ^{1}H-NMR: 9.55, 8.87 (2 br. *q*, 2 MeN*H*); 7.32 (*AA'* of *AA'BB'*, J_{AB} = 8.6, 2 arom. H); 6.95 (*BB'* of *AA'BB'*, J_{AB} = 8.6, 2 arom. H); 4.53 (*dd*, *J* = 12.3, 3.3, H–C(6)); 3.75 (*s*, MeO); 2.85, 2.77 (2 br. *d*, 2 *Me*NH); 2.75 (covered by MeNH signal, H_{ax} of CH_2(5)); 2.60 (*dd*, *J* = 14.5, 3.3, H_{eq} of CH_2(5)). ^{13}C-NMR: 176.8 (*s*, C=N); 169.9 (*s*, C=O); 160.5 (*s*, $(MeNH)_2C$); 159.0 (*s*, arom. MeO–*C*); 130.7 (*s*, 1 arom. C); 129.0 (*d*, 2 arom. C); 114.8 (*s*, $=C(NO_2)$); 114.2 (*d*, 2 arom. C); 55.2 (*q*, MeO); 42.2 (*d*, C(6)); 37.5 (*t*, C(5)); 29.8, 28.9 (2*q*, 2 MeNH). EI-MS: 350 (4, $M^{+\cdot}$), 178 (13), 161 (100), 133 (28), 118 (12), 89 (13), 77 (12). Anal. calc. for $C_{15}H_{18}N_4O_4S$ (350.40): C 51.42, H 5.18, N 15.99, S 9.15; found: C 51.29, H 4.90, N 15.71, S 9.40.

3.3. *2-[2,2-Bis(methylamino)-1-nitroethenyl]-6-(furan-2-yl)-5,6-dihydro-4*H*-1,3-thiazin-4-one* (**11c**): 0.71 g (72%, *Method B*). Yellow solid. M.p. 178°. IR: 3220*m*, 3110*m*, 1670*s*, 1655*s*, 1605*m*, 1570*m*, 1545 (sh), 1505 (sh), 1480*s*, 1465 (sh), 1430 (sh), 1410*m*, 1370*m*, 1325 (sh), 1285*s*, 1265*s*, 1240*s*, 1195*m*, 1155*m*, 1125*m*, 1060*w*, 1015*m*, 875*m*, 690*w*. ^{1}H-NMR: 9.53, 8.85 (2 br. *q*, 2 MeN*H*); 7.64 (*d*, *J* = 1.8, H–C(5) of furan); 6.43 (*m*, H–C(3) of furan); 6.31 (*d*, *J* = 3.3, H–C(4) of furan); 4.75 (*dd*, *J* = 12.2, 3.3, H–C(6)); 2.85 (br. *d*, *Me*NH); 2.71 (br. *s*, *Me*NH); 2.85–2.65 (covered by *Me*NH signal, CH_2(5)). ^{13}C-NMR: 175.9 (*s*, C=N); 168.5 (*s*, C=O); 160.3 (*s*, $(MeNH)_2C$); 152.3 (*s*, C(2) of furan); 143.4 (*d*, C(5) of furan); 114.9 (*s*, $=C(NO_2)$); 110.7 (*d*, C(4) of furan); 107.1 (*d*, C(3) of furan); 35.7 (*d*, C(6)); 33.9 (*t*, C(5)); 29.3, 28.3 (2*q*, 2 MeNH). EI-MS: 310 (< 1, $M^{+\cdot}$), 138 (30), 121 (100), 94 (24), 71 (17), 65 (83), 59 (30), 44 (34), 39 (94). Anal. calc. for $C_{12}H_{14}N_4O_4S$ (310.34): C 46.44, H 4.55, N 18.05, S 10.33; found: C 46.45, H 4.37, N 17.80, S 10.52.

3.4. *2-[2,2-Bis(methylamino)-1-nitroethenyl]-5,6-dihydro-6-methyl-4*H*-1,3-thiazin-4-one* (**11d**): 1.62 g (42%, *Method A*). Pale-yellow solid (from EtOH). M.p. 227–228°. IR: 3230*m*, 3120*m*, 1665*s*, 1610*m*, 1565*m*, 1480*m*, 1475*m*, 1430*m*, 1410 (sh), 1395*m*, 1365*m*, 1320 (sh), 1270 (br.), 1225 (sh), 1180*s*, 1150*m*, 1085*w*, 680*w*. ^{1}H-NMR: 9.50, 8.79 (2 br. *s*, 2 MeN*H*); 2.83, 2.72 (2*s*, 2 *Me*NH); 2.85–2.75 (covered by *Me*NH signal, CH(6)); 2.6–2.5 (covered by DMSO signal, H_{eq} of CH_2(5)); 2.15 (*dd*, *J* = 10.9, 10.5, H_{ax} of CH_2(5)); 1.26 (*d*, *J* = 6.8, Me–C(6)). ^{13}C-NMR: 176.6 (*s*, C=N); 169.8 (*s*, C=O); 160.6 (*s*, $(MeNH)_2C$); 114.7 (*s*, $=C(NO_2)$); 33.8 (*d*, C(6)); 33.4 (*t*, C(5)); 29.8, 28.9 (2*q*, 2 MeNH); 20.3 (*q*, *Me*–C(6)). EI-MS: 258 (12, $M^{+\cdot}$), 153 (26), 138 (17), 124 (22), 111 (21), 98 (17), 86 (13), 85 (13), 82 (12), 81 (20), 80 (14), 71 (22), 69 (100). Anal. calc. for $C_9H_{14}N_4O_3S$ (258.30): C 41.85, H 5.46, N 21.69; found: C 41.43, H 5.37, N 21.67.

4. *Synthesis of 2-Methyl-3-(methylamino)-4-nitro-1,2-thiazol-5(*2H*)-imines* **12**. *General Procedure*. To a stirred soln. of **10** (3.1 mmol) in DMF (6.2 ml), DEAD (3.3 mmol, 0.52 ml) was added at r.t. After 15 min, the precipitated yellow **12** was filtered and washed with DMF and Et_2O. Recrystallization from DMF afforded pure **12**.

4.1. *N-[2,5-Dihydro-2-methyl-3-(methylamino)-4-nitro-1,2-thiazol-5-ylidene]-3-phenylprop-2-enamide* (**12a**): 0.96 g (91%). Yellow solid (from EtOH). M.p. 267–268°. IR: 3290*s*, 1615*s*, 1570*m*, 1525*s*, 1470*s*, 1450*s*, 1420*s*, 1395*s*, 1345*s*, 1300*s*, 1285 (sh), 1250*s*, 1230*s*, 1220*s*, 1205 (sh), 1190*s*, 1180*s*, 1155*s*, 1120 (sh), 1070*m*, 1050*m*, 1030*m*, 1015*m*, 1000*m*, 970*m*, 845*m*, 815*m*, 765*s*, 720*m*, 690*m*. ^{1}H-NMR: 8.46 (br. *s*, MeN*H*); 7.80 (*d*, *J* = 15.9, H–C(β)^4)); 7.7–7.65 (*m*, 2 arom. H); 7.45–7.4 (*m*, 3 arom. H); 6.92 (*d*, *J* = 15.9, H–C(α)^4); 3.56 (*s*, MeN); 2.89 (br. *s*, *Me*NH). ^{13}C-NMR: 176.9 (*s*, S–C=N); 166.5 (*s*, MeNH*C*); 153.3 (*s*, C=O); 142.4 (*d*, C(β)^4)); 134.4 (*s*, 1 arom. C); 129.5, 128.4, 127.7 (3*d*, 5 arom. C); 122.5 (*d*, C(α)^4)); 116.5 (*s*, $=C(NO_2)$); 34.3 (*q*, MeN); 30.9 (*q*, MeNH). EI-MS: 318 (8, $M^{+\cdot}$), 301 (14), 272 (13), 162 (14), 131 (100), 103 (60), 77 (90). Anal. calc. for $C_{14}H_{14}N_4O_3S$ (318.36): C 52.82, H 4.43, N 17.60, S 10.07; found: C 52.83, H 4.27, N 17.65, S 10.31.

4.2. *N-[2,5-Dihydro-2-methyl-3-(methylamino)-4-nitro-1,2-thiazol-5-ylidene]-3-(4-methoxyphenyl)prop-2-enamide* (**12b**): 0.98 g (85%). Yellow solid (from DMF). M.p. 285–286°. IR: 3285*m*, 1620*s*, 1605*s*, 1565*m*, 1530*s*, 1510*s*, 1470*s*, 1445*m*, 1425*s*, 1405 (sh), 1385*s*, 1340*s*, 1305 (sh), 1295*s*, 1255*s*, 1230*s*, 1215*s*, 1195*s*, 1170*s*, 1120*m*, 1110*m*, 1035*m*, 1015*m*, 970*m*, 820*m*, 765*m*. ^{1}H-NMR: 8.48 (br. *s*, MeN*H*); 7.77 (*d*, *J* = 15.9, CH(β)^4)); 7.64 (*AA'* of *AA'BB'*, J_{AB} = 8.8, 2 arom. H); 6.99 (*BB'* of *AA'BB'*, J_{AB} = 8.8, 2 arom. H); 6.79 (*d*, *J* = 15.9, H–C(α)^4)); 3.83 (*s*, MeO); 3.55 (*s*, MeN); 2.90 (br. *s*, *Me*NH). CI-MS: 348 (7, $M^{+\cdot}$), 330 (13), 192 (12), 161 (100), 133 (28). Anal. calc. for $C_{15}H_{16}N_4O_4S$ (348.32): C 51.72, H 4.63, N 16.08, S 9.20; found: C 51.53, H 4.84, N 16.33, S 9.42.

4.3. *N-[2,5-Dihydro-2-methyl-3-(methylamino)-4-nitro-1,2-thiazol-5-ylidene]-3-(furan-2-yl)prop-2-enamide* (**12c**): 0.83 g (82%). Yellow solid (from DMF). M.p. 236–238°. IR: 3290*s*, 1630*s*, 1615*s*, 1565*s*, 1525 (sh), 1515*s*, 1485*s*, 1470*s*, 1430*s*, 1405*s*, 1385*s*, 1360*s*, 1325*s*, 1295*s*, 1285 (sh), 1270*s*, 1250*s*, 1230 (sh), 1205 (sh), 1190*s*, 1175*s*, 1160*s*, 1150*s*, 1050*s*, 1015*s*, 985*m*, 970*s*, 930*m*, 890*m*, 880*m*, 870*m*, 850*m*, 830*m*, 780*s*, 760*s*, 715*m*, 665*m*, 650*m*, 615*s*. ^{1}H-NMR: 8.47 (br. *s*, MeN*H*); 7.61 (*d*, *J* = 15.6, H–C(β)^4)); 7.56 (*d*, *J* = 1.7, H–C(5) of furan); 6.92 (*d*, *J* = 3.4, H–C(3) of furan); 6.64 (*d*, H–C(α)^4)); 6.60 (*dd*, *J* = 3.4, 1.7, H–C(4) of furan); 3.55 (*s*, MeN); 2.90 (br. *s*, *Me*NH). ^{13}C-NMR: 176.7 (*s*, S–C=N); 166.3 (*s*, MeNH*C*); 153.3 (*s*, C=O); 150.7 (*s*, C(2) of furan); 145.2 (*d*, C(5) of furan); 129.1 (*d*, C(β)^4)); 119.8 (*d*, C(α)^4)); 114.3 (*d* + *s*, C(3) of furan =C(NO_2)); 112.2 (*d*, C(4) of furan); 34.3 (*q*, MeN); 31.0 (*q*, MeNH). EI-MS: 308 (14, $M^{+\cdot}$), 122 (17), 121 (100), 71 (34), 65 (74). Anal. calc. for $C_{12}H_{12}N_4O_4S$ (308.32): C 46.75, H 3.92, N 18.17, S 10.40; found: C 46.61, H 4.15, N 18.37, S 10.44.

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