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NOVEL [4+2] CYCLOADDITION REACTION OF ARYL-METHYLIDENEMALONONITRILES TO UNSATURATED CHALCOGEN AMIDES. SYNTHESIS, STRUCTURE, AND PROPERTIES OF TRIETHYLAMMONIUM 3,5,5-TRICYANO-1,4,5,6-TETRAHYDROPYRIDINE-2-SELENOLATES AND -THIOLATES

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Reaction of arylmethylidenemalononitriles with 3-aryl-2-cyanoprop-2-eneselenoamides in the presence of Et_3N gave triethylammonium 4,6-diaryl-3,5,5-tricyano-1,4,5,6-tetrahydropyridine-2-selenolates. A similar reaction with cyclohexylidenecyanothioacetamide yields triethylammonium 4-aryl-1,5,5-tricyano-3-azaspiro[5.5]undec-1-ene-2-thiolate. Alkylation of the obtained selenolates and thiolates gives 6-(alkylseleno)-2,4-diaryl-1,4-dihydropyridine-3,3,5(2H)-tricarbonitriles and 4-(alkylthio)-2-aryl-3-azaspiro[5.5]undec-4-ene-1,1,5-tricarbonitriles, respectivelly. The structure of 2,4-di(2-furyl)-6-{[2-(4-methylphenyl)-2-oxoethyl]seleno}-1,4-dihydropyridine-3,3,5(2H)-tricarbonitrile has been confirmed by the X-ray structural analysis.

Keywords: arylmethylidenemalononitriles, cyanoselenoacetamide, cyanothioacetamide, prop-2-ene-selenoamides, prop-2-enethioamides, 1,4,5,6-tetrahydropyridines, [4+2] cycloaddition, X-ray structural analysis.

Due to their availability and unusual chemical properties, α,β-unsaturated thioamides [1-3] and selenoamides [4] continue to attract the attention of investigators and are widely used in the synthesis of heterocyclic compounds. One of the most successful examples which demonstrates the unique synthetic potential of unsaturated thioamides is the preparation of 3,4-dihydro-2*H*-thiopyran and 4*H*-thiopyran derivatives through their reaction with electron deficient alkenes and alkynes [5-10].

Similar reaction has been discussed in the studies [11, 12] where a spontaneous dimerization of 3-aryl-2-cyanoprop-2-enethioamides **1** takes place through a [4+2] cycloaddition to give the thiopyrans **2**. There are known a series of examples of the cycloaddition of maleic anhydride to α,β-unsaturated selenoamides to

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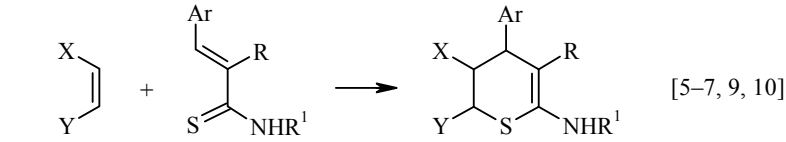
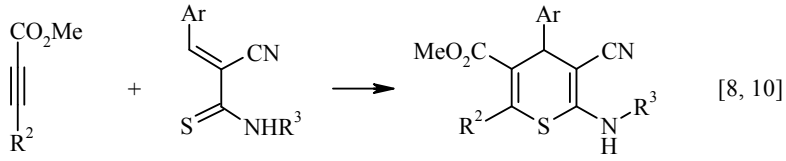
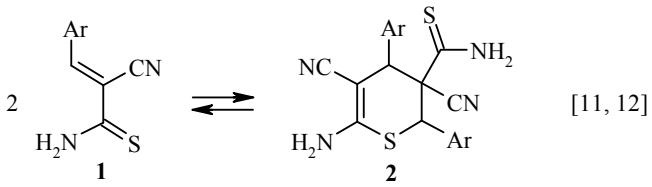


[5–7, 9, 10]



[8, 10]

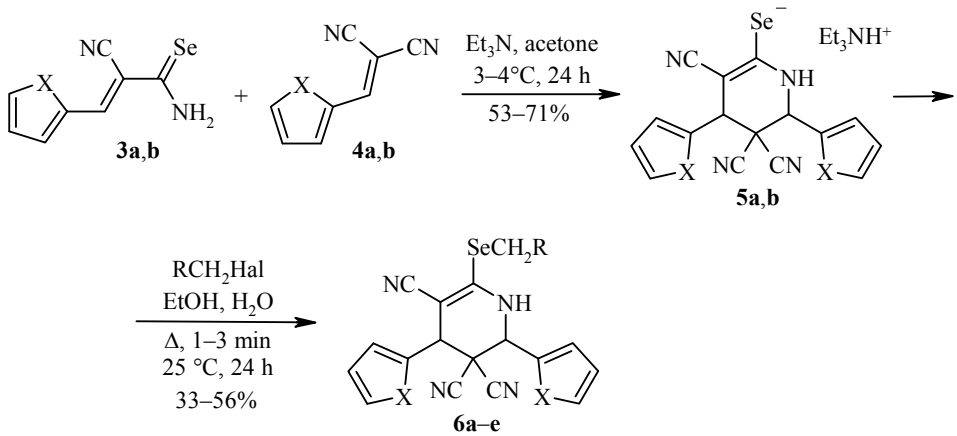


[11, 12]

1 **2**

X = NO_2, CN, CO_2Me, CO_2Et; Y = H, Ph, CO_2Me, or X + Y = CONRCO;
R = H, CN; R^1 = H, alkyl, acyl; R^2 = H, CO_2Me; R^3 = H, Me, cycloalkyl

form condensed 4*H*-selenopyrans [13, 14]. We have recently found that 3-(2-thienyl)-2-cyanoacrylselenoamide (**3a**) reacts readily with (2-thienyl)methylidenemalononitrile (**4a**) in the presence of Et_3N to form triethylammonium 3,5,5-tricyano-4,6-di(2-thienyl)-1,4,5,6-tetrahydropyridine-2-selenolate (**5a**) [15]. To the best of our knowledge this is the first example of a reaction in which an unsaturated selenoamide behaves as a C=C–C=N synthon/dienophile in a formal [4+2] cycloaddition.



3a,**b** **4a**,**b** **5a**,**b** **6a–e**

3–5 a X = S, **b** X = O; **6 a** X = S, R = PhNHCO; **b** X = S, R = 4-MeC_6H_4NHCO;
c X = O, R = PhCO; **d** X = O, R = 4-MeC_6H_4CO; **e** X = O, R = 4-MeC_6H_4NHCO

In continuation of our studies, we have decided to examine the scope and limitations of the novel reaction. It was found that this reaction is general for the use of α,β-unsaturated selenoamides **3**. Hence, the selenolate **5b** was obtained in 53% yield in the reaction of the selenoamide **3b** with furfurylidenemalononitrile (**4b**). The selenolates **5a**,**b** are readily alkylated by alkyl halides to give the 6-(alkylseleno)-2,4-diaryl-1,4-dihydropyridine-3,3,5(2*H*)-tricarbonitriles **6a-e** in 33-56% yields.

The structure of the 2,4-di(2-furyl)-6-{[2-(4-methylphenyl)-2-oxoethyl]seleno}-1,4-dihydropyridine-3,3,5(2*H*)-tricarbonitrile (**6d**) was studied by X-ray structural analysis (Fig. 1). The tetrahydropyridine ring exists in a "half chair" type conformation with a little twisted endocyclic C(1)–C(2) double bond (torsional angle N(1)–C(1)–C(2)–C(3) -8.1(2)º). The deviations of atoms C(4) and C(5) from the mean plane of the remaining atoms are -0.515(3) and

0.377(3) Å, respectively. The furan substituents and the cyano group C(21)–N(4) have an equatorial orientation (torsional angles C(1)–C(2)–C(3)–C(16) -142.16(14)º, C(1)–N(1)–C(5)–C(22) 176.39(13)º, and C(21)–C(4)–C(5)–N(1) 170.89(11)º), but the cyano group C(20)–N(3) is axial (torsional angle C(20)–C(4)–C(5)–N(1) 52.80(14)º). The furan substituent at the atom C(3) is disordered into the two positions A and B with relative population 0.485(10): 0.515(10) due to rotation around the C(3)–C(16) bond. In position A the oxygen atom of the furan ring has a *syn* orientation relative to the hydrogen atom at the C(3) atom (torsional angle O(2A)–C(16)–C(3)–H(3) -21º), but in position B (together with the furan substituent at the C(5) atom) it has the *anti* orientation (torsional angles O(2B)–C(16)–C(3)–H(3) 173º and O(3)–C(22)–C(5)–H(5) 163º). The Se(1)–C(6) bond deviates a little from the plane of the C(1)–C(2) double bond (torsional angle C(2)–C(1)–Se(1)–C(6) 161.97(12)º) which, along with the *gauche-gauche* conformation of the substituents at the methylene group (torsional angles C(1)–Se(1)–C(6)–C(7) 84.02(11)º and Se(1)–C(6)–C(7)–O(1) -88.78(18)º), sets up the conditions for formation of the intramolecular hydrogen bond N(1)–H(1)···O(1) (H···O 2.01 Å, N–H···O 159º). The tolyl substituent is coplanar with the carbonyl group (torsional angle O(1)–C(7)–C(8)–C(13) -0.6(3)º) despite the formation in such a conformation of the shortened intramolecular contact H(9)···H(6a) of 2.13 Å (sum of van der Waals radii 2.32 Å [16]). The molecules are bound as centrosymmetric dimers in the crystal *via* intermolecular hydrogen bonds C(23)–H(23)···O(1)^{i} [i: 1-*x*, -*y*, -*z*] (H···O 2.27 Å, C–H···O 153º).

The ^{1}H NMR spectra of compounds **6a-e** show signals for 4-CH protons as singlets at 5.06-5.24 ppm and 6-CH protons as doublets or broadened singlets with $J_{CH–NH}$ = 1.0-2.0 Hz at 5.45-5.74 ppm. The NH protons of the tetrahydropyridine ring appear as broadened singlets or as doublets at 8.16-9.06 ppm with $J_{CH–NH}$ = 1.0-2.0 Hz. It should be noted that the ^{1}H NMR spectra of compounds **5a**,**b** and **6a-e** are not doubled in signals, characteristic for a mixture of diastereomers, and this indicates the stereoselectivity of the cycloaddition process. Based on the X-ray analytical results the obtained compounds can be represented as a racemic mixture with a (2*S*,4*S*) and (2*R*,4*R*) configuration of the C-2 and C-4 optically active centers as indicated in the case of compounds **6a-e** (Fig 2). This result agrees well with the stereochemical configuration of the analogous thiopyran **2** cycloaddition product (Ar = 3-MeOC$_6$H$_4$) elucidated by the X-ray structural analysis [17].

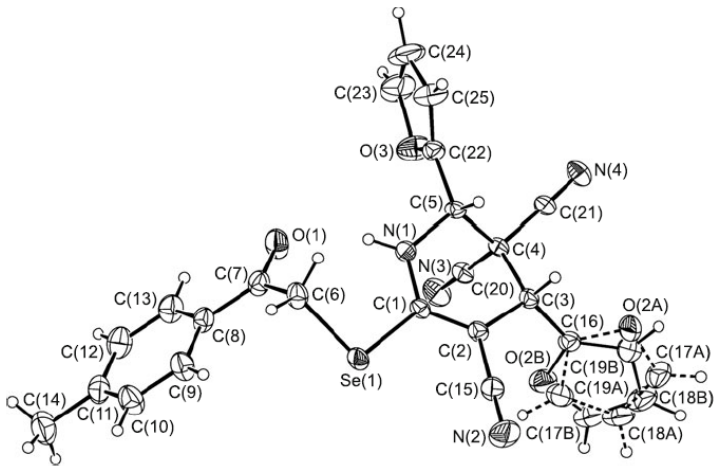


Fig. 1. Molecular structure of compound **6d** with representation of atoms with thermal vibration ellipsoids of 50% probability.

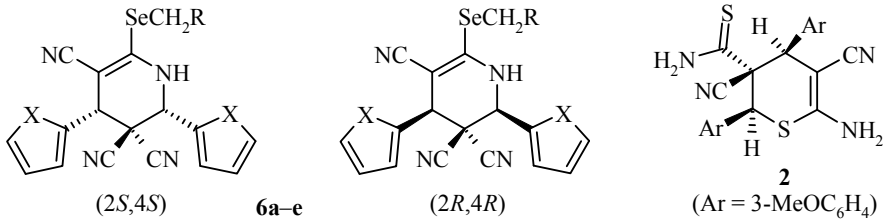
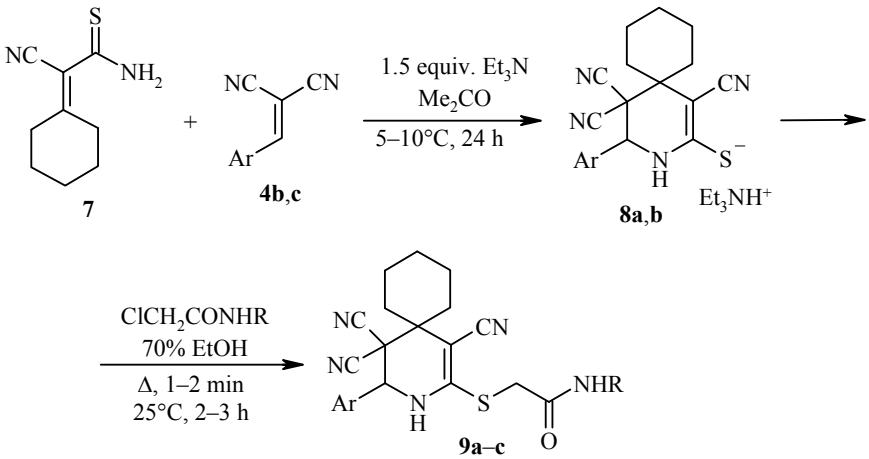


Fig. 2. Stereoisomers of compounds **6a-e** and **2.**

The IR spectra of pyridines **5b** and **6a-e** are characterized by the presence of strong absorption band at 2173-2198 cm^{-1} (3-C≡N) and a weak intensity absorption at 2231-2276 cm^{-1} (5-C≡N).

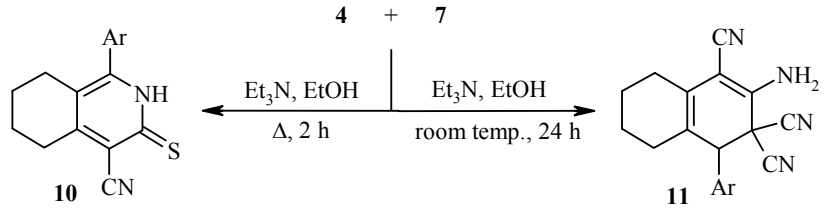
To further expand scope of the reaction, the reaction of arylmethylidenemalononitriles **4** with other cyanothioacetamide derivatives has been studied.

It was found that the reaction of the thioacrylamide **7** with unsaturated dinitriles **4b**,**c** in cold acetone in the presence of Et_3N (1.5 equiv.) gave the cycloaddition products **8a**,**b** in 68-72% yields. The obtained thiolates **8a**,**b** were readily alkylated in aqueous alcohol as shown in the scheme below to form *S*-alkylation products **9a-c**. Compounds **8a**,**b** are beige, amorphous powders, poorly soluble in acetone and ether but soluble in DMSO and hot aqueous EtOH. The ^1H NMR spectra of the 4-aryl-1,5,5-tricyano-3-azaspiro[5.5]undec-1-ene-2-thiolates **8a**,**b** show 4-CH protons at 4.85-4.96 ppm and signals for the NH protons at high field in the region 5.80-5.84 ppm. In the spectra of the alkylation products **9a-c** a downfield shift is seen for the 4-CH protons observed at 5.14-5.34 ppm and for the NH protons at 8.83-9.08 ppm. The structure of the triethylammonium 1,5,5-tricyano-4-phenyl-3-azaspiro[5.5]undec-1-ene-2-thiolate (**8b**) is also confirmed by ^{13}C NMR spectroscopic results with the use of the attached proton test (APT).



4b, **8a** Ar = 2-furyl, **4c**, **8b** Ar = Ph; **9 a** Ar = 2-furyl, R = 4-MeC_6H_4;
b Ar = Ph, R = 4-MeC_6H_4; **c** Ar = Ph, R = 3-Cl-4-MeC_6H_3

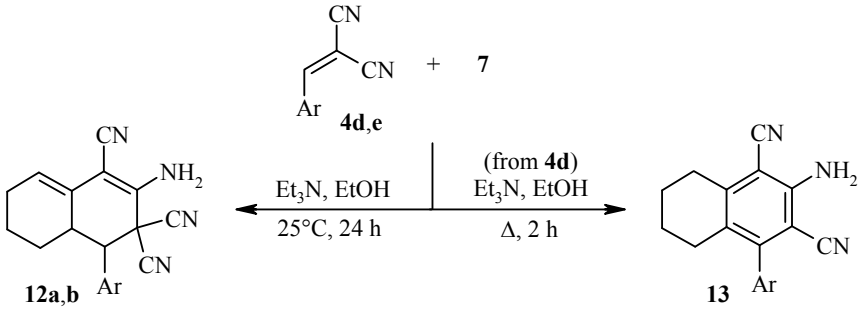
It is interesting to note that the literature data [18] proposes that the Et_3N-catalyzed reaction of the thioacrylamide **7** with the unsaturated nitriles **4** takes place differently, and depending on the conditions produces either the isoquinolinethiones **10** or the 3,4,5,6,7,8-hexahydronaphthalenes **11**.



[18]

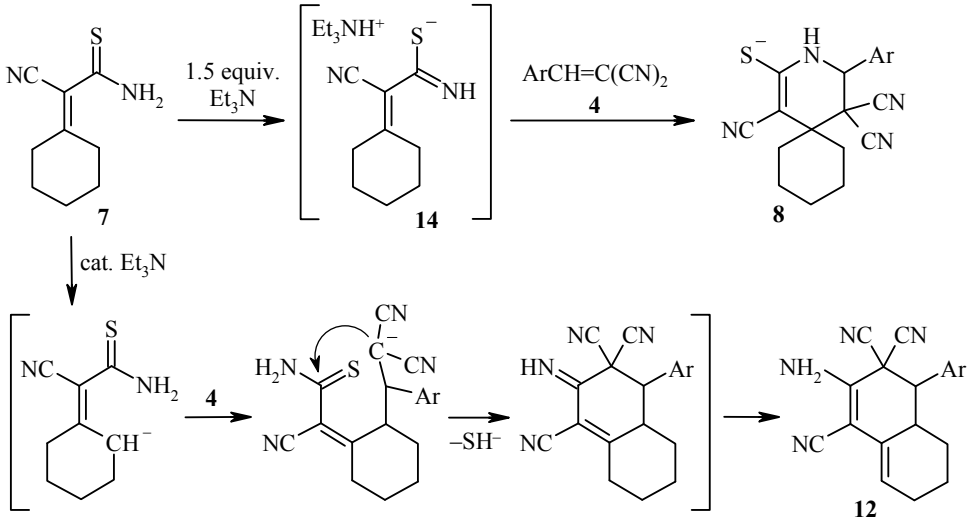
Upon reproduction of the reported method it was found that the reaction of thioamide **7** with unsaturated nitriles **4d**,**e** at 25ºC in alcohol in the presence of catalytic amounts of Et_3N gives products which physicochemical and spectroscopic parameters proved to be identical to the hexahydronaphthalenes **11** as reported in the work [18]. However, the yields after purification (20-22%) proved to be markedly lower than reported (55-76%). The first compounds of this type **11** were reported by Gewald and Schill [19] as the products of a three-component condensation of cyclohexanone with malononitrile and benzaldehyde and also as

the products of cross dimerization of cyclohexylidenemalononitrile with the unsaturated dinitriles **4**. However in later work [20-25] it was shown (including the involvement of the X-ray structural analysis [26, 27]) that the structure **11** were assigned wrong and that these compounds should be assigned the structure of the isomeric heteroannular 2-amino-4a,5,6,7-tetrahydronaphthalene-1,3,3(4*H*)-tricarbonitriles **12**. Analysis of the ^{1}H NMR and ^{13}C NMR (APT) spectroscopic data confirmed that the products of the reaction of thioamide **7** with dinitriles **4d**,**e** under the conditions reported above are compounds **12a**,**b**. We also were unable to reproduce the method for synthesis of the isoquinolines **10**. Refluxing thioamide **7** with one equivalent of unsaturated dinitrile **4d** in the presence of catalytic amounts of Et_3N gave the tetrahydronaphthalene **13** as the known product of aromatization of compounds **12** [20, 21].



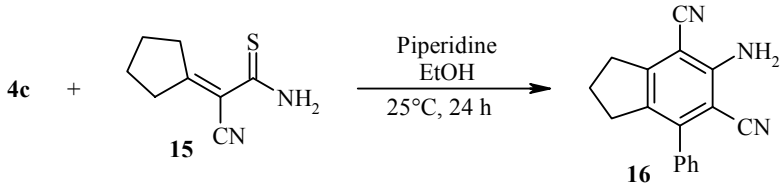
4d, **12a**, **13** Ar = 4-$MeOC_6H_4$; **4e**, **12b** Ar = 4-MeC_6H_4

Such major differences in the reaction course were due to the amount of base used, which allowed us to make several proposals regarding the mechanism for the formation of compound **8**. The key intermediate necessary for the cycloaddition reaction is likely the 1-azabutadiene-2-thiolate **14**. In the case of insufficient base an alternative Michael addition/carbocyclization process becomes possible for the thioamide **7** and leads to the naphthalenes **12**.

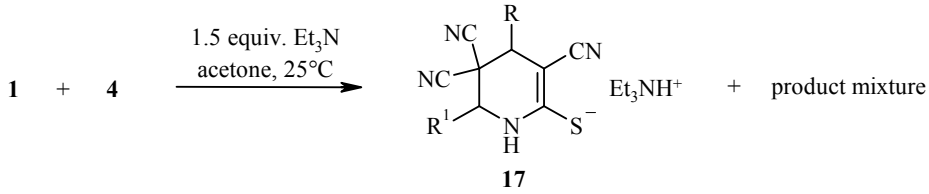


Treatment of the cyclopentylidenecyanothioacetamide (**15**) with dinitriles **4b**,**c** (acetone, 1.5 equiv. Et_3N, 25ºC) causes tarring of the reaction mixture. However, using the excess of piperidine in alcohol the thioamide **15** and benzylidenemalononitrile (**4c**) gave the indane derivative **16** in 47% yield.

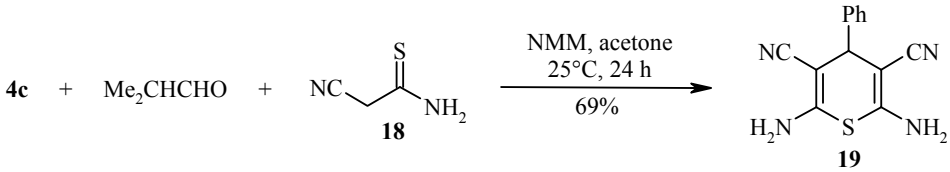
The 3-aryl-2-cyanothioacrylamides **1** react readily with the unsaturated nitriles **4** in the presence of 1.5 equiv. of Et_3N to give white or light-yellow, finely crystalline powders insoluble in acetone. However, in contrast to thioamide **7** and selenoamides **3a**,**b** reaction products were complex mixtures. We propose



that, along with the expected triethylammonium 3,5,5-tricyano-1,4,5,6-tetrahydropyridine-2-thiolates **17** there are side products of a concurrent process of dimerization of thioamides **1** are being formed. A detailed analysis on the course of the reaction of thioacrylamides **1** with the arylmethylidenemalononitriles **4** will be the subject of our further research.

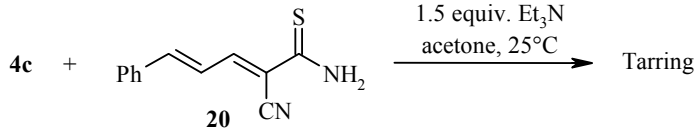


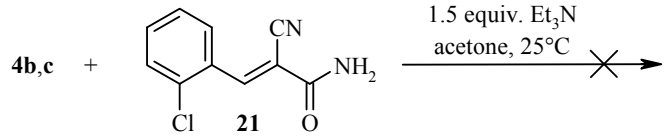
An attempt to synthesize compounds of type **11** by reacting isobutyral, cyanothioacetamide (**18**), and benzylidenemalononitrile (**4c**) was unsuccessful, the product being a 69% yield of the 4*H*-thiopyran **19** (a known product of the reaction of thioamide **18** with the dinitrile **4c** [28, 29]).



NMM = *N*-methylmorpholine

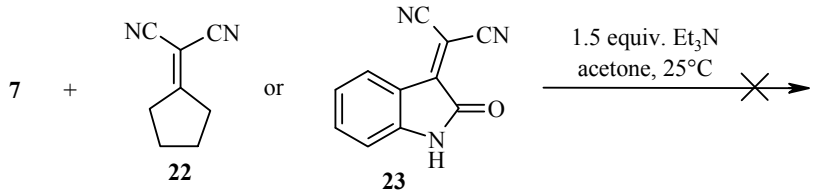
Treatment of the penta-2,4-dienethioamide **20** with benzylidenemalononitrile (**4c**) in acetone in the presence of excess Et_3N led to tarring of the reaction mixture. It was also impossible to utilize cyanoacetamide derivatives in the reaction, the starting acrylamide **21** being isolated in 40 and 21% yields after reaction with the unsaturated dinitriles **4b**,**c**.





However, it was possible to identify several limitations in relation to the structure of the dienophile reaction component. The unsaturated dinitriles **22** and **23** did not react with the thioacrylamide **7**, likely as a result of steric hindrance.

In conclusion, the reaction of 3-aryl-2-cyanoselenoacrylamides with arylmethylidenemalononitriles in the presence of a excess of Et_3N in acetone occurs as a formal [4+2] cycloaddition to yield the corresponding



triethylammonium 3,5,5-tricyano-1,4,5,6-tetrahydropyridine-2-selenolates. Under the similar conditions the cyclohexylidenecyanothioacetamide gives triethylammonium 4-aryl-1,5,5-tricyano-3-azaspiro[5.5]undec-1-ene-2-thiolates. However, in the presence of catalytic amounts of Et_3N, a carbocyclization occurs to yield 2-amino-4a,5,6,7-tetrahydronaphthalene-1,3,3(4*H*)-tricarbonitriles. It was possible to establish several limitations of this novel reaction which were determined by the structure of the starting reagents. The structure of 2,4-di(2-furyl)-6-{[2-(4-methylphenyl)-2-oxoethyl]seleno}-1,4-dihydropyridine-3,3,5(2*H*)-tricarbonitrile was studied using X-ray structural analysis.

EXPERIMENTAL

IR spectra were recorded on an IRS-29 (LOMO) spectrophotometer using vaseline oil. ^{1}H NMR spectra were recorded on Bruker DPX-400 (400 MHz, compounds **5b**, **6a-e**, **8a**,**b**, **9a-c**, **19**) or Bruker Avance 500 (500 MHz, compounds **12a**,**b**, **13**, **16**) spectrometers using DMSO-d_6 with TMS as internal standard. APT ^{13}C NMR spectra were recorded on a Bruker Avance 500 spectrometer (125 MHz) using DMSO-d_6 with TMS as internal standard. HPLC-MS was performed on a Agilent 1100 liquid chromatograph with a diode array detector (215, 254, and 265 nm) and an Agilent LC/MSD SL mass selective detector. Column Zorbax SB-C18, solvents: A – MeCN–H_2O, 95:5 + 0.1% CF_3COOH, B – H_2O + 0.1% CF_3COOH, flow rate 3 ml/sec, electrospray ionization at atmospheric pressure. Elemental analysis was carried out on a Carlo-Erba 1106 Elemental Analyzer. Melting points were determined on a Kofler heating stage and are not corrected. Monitoring of the purity of the products was carried out by TLC on Silufol UV-254 plates in the system acetone–hexane (1:1) and visualized using iodine vapor and a UV detector. 2-Cyano-3-(2-thienyl)-selenoacrylamide (**3a**) and 2-cyano-3-(2-furyl)acrylselenoamide (**3b**) were prepared by condensation of cyanoselenoacetamide with the corresponding aldehydes [30]. Triethylammonium 3,5,5-tricyano-4,6-di-(2-thienyl)-1,4,5,6-tetrahydropyridine-2-selenolate (**5a**) [15], cyclohexylidenecyanothioacetamide (**7**) [31], cyclopentylidenecyanothioacetamide (**15**) [31], and cyanothioacetamide (**18**) [32] were prepared by a known methods.

Triethylammonium 3,5,5-Tricyano-4,6-di(2-furyl)-1,4,5,6-tetrahydropyridine-2-selenolate (5b). A mixture of 2-cyano-3-(2-furyl)acrylselenoamide (**3b**) (450 mg, 2.0 mmol), (2-furyl)methylidenemalononitrile (**4b**) (290 mg, 2.0 mmol), and an excess of Et_3N (0.41 ml, 3.0 mmol) in acetone (3 ml) was stirred under an argon stream with cooling in an ice bath (3-4ºC) to dissolution of the starting reagents (2-3 min), and left for 24 h at the indicated temperature under an argon atmosphere. The precipitate formed was filtered off and washed with acetone and hexane. Yield 500 mg (53%), beige powder, mp 129-131ºC. IR spectrum, ν, cm^{-1}: 3431, 3212 (N–H), 2260 (5-C≡N), 2173 (3-C≡N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.13 (9H, t, ^3J = 7.1, $N(CH_2C\underline{H}_3)_3$); 2.79 (6H, q, ^3J = 7.1, $N(C\underline{H}_2CH_3)_3$); 4.98 (1H, s, 4-CH); 5.37 (1H, br. s, 6-CH); 6.48-6.52 (2H, m, H-3,4 Fur); 6.59 (1H, d, ^3J = 3.2, H-3' Fur); 6.72-6.73 (1H, m, H-4' Fur); 7.63-7.64 (1H, m, H-5 Fur); 7.69-7.70 (1H, m, H-5' Fur). The signals for the NH and NH^+ protons were not observed as a result of deuterium exchange. Found, %: C 56.27; H 5.41; N 15.02. $C_{22}H_{25}N_5O_2Se$. Calculated, %: C 56.17; H 5.36; N 14.89.

6-(Alkylseleno)-2,4-diaryl-1,4-dihydropyridine-3,3,5(2*H*)-tricarbonitriles 6a-e (General Method). A mixture of the selenolate **5a**,**b** (0.30 mmol) and the corresponding alkyl halide (0.30 mmol) in 70% EtOH (20 ml) was refluxed under an argon stream to full dissolution of the starting reagents (1-3 min), rapidly filtered through a paper filter, and left for 24 h at 25ºC in an argon atmosphere. The precipitate formed was filtered off and washed with EtOH and hexane to give the selenides **6a-e**, samples of which were purified from a suitable solvent for analytical purposes.

2-{[3,5,5-Tricyano-4,6-di(2-thienyl)-1,4,5,6-tetrahydropyridin-2-yl]seleno}-*N*-phenylacetamide (6a). Yield 90 mg (56%), colorless crystals, mp 205-207ºC (EtOH–AcOH, 1:1). IR spectrum, ν, cm^{-1}: 3411, 3302, 3210 (N–H), 2231, 2190 (C≡N), 1708 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.85 (1H, d, ^2J = 13.5) and 3.90 (1H, d, ^2J = 13.5, $SeCH_2$); 5.24 (1H, s, 4-CH); 5.74 (1H, d, ^3J = 1.0, 6-CH); 7.05 (1H, t, ^3J = 7.5, H-4 Ph); 7.10-7.11 (1H, m, H-4 thienyl); 7.17-7.18 (1H, m, H-4' thienyl); 7.25-7.29 (3H, m, H Ar); 7.49-7.59 (5H, m, H Ar); 8.99 (1H, d, ^3J = 1.0, NH); 10.34 (1H, s, CONH). Found, %: C 53.72; H 3.24; N 13.21. $C_{24}H_{17}N_5OS_2Se$. Calculated, %: C 53.93; H 3.21; N 13.10.

2-{[3,5,5-Tricyano-4,6-di(2-thienyl)-1,4,5,6-tetrahydropyridin-2-yl]seleno}-*N*-(4-methylphenyl)acetamide (6b). Yield 55 mg (33%), beige powder, mp 212-214ºC (EtOH–AcOH, 1:1). IR spectrum, ν, cm^{-1}: 3476, 3391, 3300 (N–H), 2249, 2194 (C≡N), 1710 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.29 (3H, s, $ArC\underline{H}_3$); 3.81 (1H, d, ^2J = 13.5) and 3.86 (1H, d, ^2J = 13.5, $SeCH_2$); 5.22 (1H, s, 4-CH); 5.73 (1H, d, ^3J = 1.0, 6-CH); 7.05 (2H, d, ^3J = 8.3, H Ar); 7.10 (1H, dd, ^3J = 5.1, ^3J = 3.4, H-4 thienyl); 7.15-7.16 (1H, m, H-4' thienyl); 7.27 (1H, d, ^3J = 3.4, H-3 thienyl); 7.38 (2H, d, ^3J = 8.3, H Ar); 7.47-7.49 (2H, m, H Ar); 7.56 (1H, d, ^3J = 5.1, H-5 thienyl); 9.07 (1H, d, ^3J = 1.0, NH); 10.25 (1H, s, CONH). Found, %: C 54.72; H 3.53; N 12.91. $C_{25}H_{19}N_5OS_2Se$. Calculated, %: C 54.74; H 3.49; N 12.77.

2,4-Di(2-furyl)-6-{[2-oxo-2-phenylethyl]seleno}-1,4-dihydropyridine-3,3,5(2*H*)-tricarbonitrile (6c). Yield 75 mg (51%), colorless crystals, mp 185-187ºC (EtOH). IR spectrum, ν, cm^{-1}: 3379, 3273 (NH), 2252, 2192 (C≡N), 1660 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.70 (2H, br. s, $SeCH_2$); 5.08 (1H, s, 4-CH); 5.45 (1H, br. s, 6-CH); 6.49-6.50 (1H, m, H-4 Fur); 6.53-6.55 (1H, m, H-4' Fur); 6.60 (1H, d, ^3J = 3.2, H-3 Fur); 6.80 (1H, d, ^3J = 3.2, H-3' Fur); 7.49-7.53 (2H, m, H Ar); 7.60-7.63 (2H, m, H Ar); 7.70-7.72 (1H, m, H-5 Fur); 8.00 (2H, d, ^3J = 8.1, H Ar); 8.16 (1H, br. s, NH). Found, %: C 58.86; H 3.39; N 11.63. $C_{24}H_{16}N_4O_3Se$. Calculated, %: C 59.15; H 3.31; N 11.50.

2,4-Di(2-furyl)-6-{[2-(4-methylphenyl)-2-oxoethyl]seleno}-1,4-dihydropyridine-3,3,5(2*H*)-tricarbonitrile (6d). Yield 75 mg (50%), colorless crystals, mp 201-203ºC (AcOH). IR spectrum, ν, cm^{-1}: 3212, 3131 (NH), 2276, 2193 (C≡N), 1660 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.44 (3H, s, $ArC\underline{H}_3$); 4.67 (2H, br. s, $SeCH_2$); 5.09 (1H, s, 4-CH); 5.46 (1H, d, ^3J = 2.0, 6-CH); 6.50-6.51 (1H, m, H-4 Fur); 6.54-6.56 (1H, m, H-4' Fur); 6.60 (1H, d, ^3J = 3.0, H-3 Fur); 6.81 (1H, d, ^3J = 3.0, H-3' Fur); 7.31 (2H, d, ^3J = 8.1, H Ar); 7.64-7.65 (1H, m, H-5 Fur); 7.73-7.74 (1H, m, H-5' Fur); 7.89 (2H, d, ^3J = 8.1, H Ar); 8.17 (1H, d, ^3J = 2.0, NH). Found, %: C 59.61; H 3.66; N 11.24. $C_{25}H_{18}N_4O_3Se$. Calculated, %: C 59.89; H 3.62; N 11.17.

3,5,5-Tricyano-2-{[4,6-di(2-furyl)-1,4,5,6-tetrahydropyridin-2-yl]seleno}-*N*-(4-methylphenyl)acetamide (6e). Yield 56 mg (36%), beige powder, mp 211-213ºC (AcOH). IR spectrum, ν, cm^{-1}: 3432, 3301, 3180 (NH), 2251, 2198 (C≡N), 1650 (C=O, C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.30 (3H, s, $ArC\underline{H}_3$); 3.80 (1H, d, ^3J = 13.5) and 3.87 (1H, d, ^3J = 13.5, $SeCH_2$); 5.07 (1H, s, 4-CH); 5.53 (1H, d, ^3J = 1.7, 6-CH); 6.48-6.49 (1H, m, H-4 Fur); 6.54-6.55 (1H, m, H-4' Fur); 6.58 (1H, d, ^3J = 3.4, H-3 Fur); 6.84 (1H, d, ^3J = 3.4, H-3' Fur); 7.06 (2H, d, ^3J = 8.3, H Ar); 7.41 (2H, d, ^3J = 8.3, H Ar); 7.61 (1H, d, ^3J = 1.0, H-5 Fur); 7.68 (1H, d, ^3J = 1.2, H-5' Fur); 8.93 (1H, d, ^3J = 1.7, NH); 10.24 (1H, s, CONH). Found, %: C 57.91; H 3.79; N 13.68. $C_{25}H_{19}N_5O_3Se$. Calculated, %: C 58.15; H 3.71; N 13.56.

Triethylammonium 4-Aryl-1,5,5-tricyano-3-azaspiro[5.5]undec-1-ene-2-thiolates 8a,b (General Method). Et_3N (0.35 ml, 2.5 mmol) was added to a mixture of the cyclohexylidenecyanothioacetamide **7** (300 mg, 1.66 mmol) and the corresponding arylmethylidenemalononitrile **4a**,**b** (1.70 mmol) in a minimum volume of cold acetone (1.5-2.0 ml). The solution obtained was stirred at 5ºC, and formation of a precipitate began after 3-5 min. The reaction mixture was stirred for a further 2 h and left for 24 h in a fridge. The precipitate was filtered off and washed successively with acetone and ether.

Triethylammonium 1,5,5-Tricyano-4-(2-furyl)-3-azaspiro[5.5]undec-1-ene-2-thiolate (8a). Yield 480 mg (68%), beige powder, mp 108-110ºC. IR spectrum, ν, cm^{-1}: 3160 (NH), 2250 (5-C≡N), 2168 (1-C≡N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.20 (9H, t, ^3J = 7.1, $N(CH_2C\underline{H}_3)_3$); 1.50-2.37 (10H, m, $(CH_2)_5$); 2.99-3.02 (6H, m, $N(C\underline{H}_2CH_3)_3$); 4.96 (1H, br. s, 4-CH); 5.80 (1H, br. s, 1-NH); 6.48-6.49 (1H, m, H-4 Fur);

6.64-6.65 (1H, m, H-3 Fur); 7.63-7.64 (1H, m, H-5 Fur). The signals for the NH^+ proton were not observed likely as a result of deuterium exchange. Found, %: C 65.16; H 7.46; N 16.44. $C_{23}H_{31}N_5OS$. Calculated, %: C 64.91; H 7.34; N 16.46.

Triethylammonium 1,5,5-Tricyano-4-phenyl-3-azaspiro[5.5]undec-1-ene-2-thiolate (8b). Yield 521 mg (72%), beige powder, mp 126-128ºC. IR spectrum, ν, cm^{-1}: 3180 (NH), 2248 (5-C≡N), 2160 (1-C≡N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.19 (9H, t, ^3J = 7.3, $N(CH_2C\underline{H}_3)_3$); 1.56-1.79 (8H, m) and 2.33-2.47 (2H, m, $(CH_2)_5$); 3.02 (6H, q, ^3J = 7.3, $N(C\underline{H}_2CH_3)_3$); 4.85 (1H, br. s, 4-CH); 5.84 (1H, br. s, NH); 7.44-7.45 (2H, m, H Ph); 7.54-7.57 (3H, m, H Ph). The signals for the NH^+ proton were not observed likely as a result of deuterium exchange. ^{13}C NMR spectrum, δ, ppm: 8.8 ($N(CH_2\underline{C}H_3)_3$); 21.1*, 21.7* (C-3,5 cyclohexylidene); 24.9* (C-4 cyclohexylidene); 33.4*, 35.0* (C-2,6 cyclohexylidene); 43.2* (C-4); 45.7* ($N(\underline{C}H_2CH_3)_3$); 51.7* (C-5); 57.8 (C-6); 70.7* (C-3); 113.2* (5-C≡N); 114.7* (5-C≡N); 126.7* (3-C≡N); 128.1 (C-2,3,5,6 Ph); 129.3 (C-4 Ph); 136.5* (C-1 Ph); 173.5 (C-2). Mass spectrum, *m*/*z*: 102.2 $[Et_3NH^+]^+$, 352.0 $[M\text{-}Et_3N+H_2O]^+$. Found, %: C 69.13; H 7.76; N 16.10. $C_{25}H_{33}N_5S$. Calculated, %: C 68.93; H 7.64; N 16.08.

4-(Alkylthio)-2-aryl-3-azaspiro[5.5]undec-4-ene-1,1,5-tricarbonitriles 9a-c (General Method). The starting thiolate **8a**,**b** (0.35 mmol) was dissolved with heating in 70% EtOH (5-7 ml), and a solution of the corresponding *N*-substituted chloroacetamide (0.35 mmol) in EtOH (2-3 ml) was added. The mixture was refluxed with vigorous stirring for 1-2 min (precipitation of the product usually began) and then stirred for 2-3 h at 25ºC. After 24 h, the precipitate was filtered off and washed with 70% EtOH, Et_2O, and petroleum ether to give compounds **9a-c** in an analytically pure state.

2-{[1,5,5-Tricyano-4-(2-furyl)-3-azaspiro[5.5]undec-1-en-2-yl]thio}-*N*-(4-methylphenyl)acetamide (9a). Yield 99 mg (60%), fine, yellow-pink crystals, mp 234-236ºC. IR spectrum, ν, cm^{-1}: 3300-3270 (NH), 2242 (5-C≡N), 2190 (1-C≡N), 1660 (C=O, C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.22-2.11 (10H, m, $(CH_2)_5$); 2.29 (3H, s, $ArC\underline{H}_3$); 3.87 (2H, br. s, SCH_2); 5.34 (1H, br. s, 4-CH); 6.53-6.54 (1H, m, H-4 Fur); 6.81-6.82 (1H, m, H-3 Fur); 7.07 (2H, d, ^3J = 7.8, H Ar); 7.41 (2H, d, ^3J = 7.8, H Ar); 7.71-7.72 (1H, m, H-5 Fur); 9.08 (1H, br. s, NH); 10.31 (1H, s, CONH). Found, %: C 66.18; H 5.46; N 14.90. $C_{26}H_{25}N_5O_2S$. Calculated, %: C 66.22; H 5.34; N 14.85.

2-{[1,5,5-Tricyano-4-phenyl-3-azaspiro[5.5]undec-1-en-2-yl]thio}-*N*-(4-methylphenyl)acetamide (9b). Yield 111 mg (66%), white powder, mp 262-264ºC. IR spectrum, ν, cm^{-1}: 3280-3255 (NH), 2250 (5-C≡N), 2190 (1-C≡N), 1640 (C=O, C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.22-2.10 (10H, m, $(CH_2)_5$); 2.28 (3H, s, $ArCH_3$); 3.92 (1H, d, ^2J = 15.0) and 3.99 (1H, d, ^2J = 15.0, SCH_2); 5.24 (1H, br. s, 4-CH); 7.09 (2H, d, ^3J = 8.5, H Ar); 7.41 (2H, d, ^3J = 8.5, H Ar); 7.45-7.50 (3H, m, H Ph); 7.63-7.65 (2H, m, H Ph); 8.96 (1H, br. s, NH); 10.30 (1H, s, CONH). Found, %: C 69.98; H 5.70; N 14.50. $C_{28}H_{27}N_5OS$. Calculated, %: C 69.83; H 5.65; N 14.54.

***N*-(3-Chlorophenyl-4-methyl-)-2-{[1,5,5-tricyano-4-phenyl-3-azaspiro[5.5]undec-1-en-2-yl]thio}acetamide (9c)**. Yield 112 mg (62%), fine, colorless needles, mp 245-247ºC. IR spectrum, ν, cm^{-1}: 3240 (NH), 2250 (5-C≡N), 2193 (1-C≡N), 1655 (C=O, C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.22-2.10 (10H, m, $(CH_2)_5$); 2.30 (3H, s, $ArC\underline{H}_3$); 3.89 (1H, d, ^2J = 15.1) and 3.95 (1H, d, ^2J = 15.1, SCH_2); 5.14 (1H, br. s, 4-CH); 7.16 (1H, d, ^3J = 8.2, H Ar); 7.29 (1H, d, ^3J = 8.2, H Ar); 7.46-7.47 (3H, m, H Ph); 7.60-7.62 (2H, m, H Ph); 7.67 (1H, s, H Ar); 8.83 (1H, br. s, NH); 10.42 (1H, s, CONH). Found, %: C 65.26; H 5.11; N 13.60. $C_{28}H_{26}ClN_5OS$. Calculated, %: C 65.17; H 5.08; N 13.57.

2-Amino-4-acyl-4a,5,6,7-tetrahydronaphthalene-1,3,3(4*H*)-tricarbonitriles 12a,b were prepared by the reported method [18] for the synthesis of the isomeric compounds **11**. A mixture of the cyclohexylidenecyanothioacetamide **7** (300 mg, 1.66 mmol), the corresponding arylmethylidenemalononitrile **4d**,**e** (1.66 mmol), and Et_3N (0.2 ml) in abs. EtOH (5 ml) was stirred for 24 h at 25ºC. An equal volume of iced water was added, and the product was stirred. The resinous precipitate was separated and recrystallized from EtOH. The obtained products were spectroscopically identical to the compounds prepared by Gewald and Schill [19] and have a tetrahydronapthalene structure **12**.

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*Asterisks indicate out of phase signals here and subsequently in the Experimental.

2-Amino-4-(4-methoxyphenyl)-4a,5,6,7-tetrahydronaphthalene-1,3,3(4*H*)-tricarbonitrile (12a). Yield 111 mg (20%), pale-yellow crystals, mp 248-250ºC (sublimes, mp 229ºC) [18], 253-254ºC [21], 239 (22)). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.80-0.87 (1H, m), 1.40-1.48 (2H, m), 1.63-1.70 (1H, m), 2.05-2.20 (2H, m) and 2.71-2.79 (1H, m, 4a-CH, 5,6,7-CH_2); 3.45 (1H, d, ^3J = 12.5, 4-CH); 3.78 (3H, s, OCH_3); 5.70 (1H, s, 8-CH); 6.98-7.05 (2H, m, H Ar); 7.32-7.49 (4H, m, NH_2, H Ar). ^{13}C NMR spectrum, δ, ppm: 21.0 (CH_2); 24.9 (CH_2); 27.0 (CH_2); 34.0* (C-4a); 43.1 (C-3); 50.1* (C-4); 55.1* (OCH_3); 81.6 (C-1); 112.5 (3-C≡N); 112.6 (3-C≡N); 113.6*, 114.3* (C-3,5 Ar); 116.1 (1-C≡N); 120.2* (C-8); 126.3 (C-8a); 128.0*, 133.5* (C-2,6 Ar); 128.9 (C-*i* Ar); 143.5 (C-2); 159.5 (C-4 Ar). Mass spectrum, *m*/*z*: 331.2 $[M+H]^+$. Found, %: C 72.78; H 5.50; N 16.90. $C_{20}H_{18}N_4O$. Calculated, %: C 72.71; H 5.49; N 16.96.

2-Amino-4-(4-methylphenyl)-4a,5,6,7-tetrahydronaphthalene-1,3,3(4*H*)-tricarbonitrile (12b). Yield 114 mg (22%), white powder, mp 268-270ºC (sublimes, mp 278-280ºC [18], 245-247ºC [33]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.79-0.87 (1H, m), 1.40-1.48 (2H, m), 1.63-1.68 (1H, m), 2.04-2.19 (2H, m), and 2.73-2.78 (1H, m, 4a-CH, 5,6,7-CH_2); 2.33 (3H, s, Ar$C\underline{H}_3$); 3.45 (1H, d, ^3J = 12.5, 4-CH); 5.71 (1H, s, 8-CH); 7.21-7.45 (6H, m, NH_2, H Ar). ^{13}C NMR spectrum, δ, ppm: 20.7* (Ar$\underline{C}H_3$); 21.0 (CH_2); 24.8 (CH_2); 27.0 (CH_2); 33.9* (C-4a); 43.0 (C-3); 50.4* (C-4); 81.6 (C-1); 112.4 (3-C≡N); 112.5 (3-C≡N); 116.1 (1-C≡N); 120.3* (C-8); 126.7*, 129.0*, 129.1*, 132.2* (C Ar); 128.9 (C-8a); 131.5 (C-4 Ar); 138.3 (C-*i* Ar); 143.6 (C-2). Mass spectrum, *m*/*z*: 315.1 $[M+H]^+$. Found, %: C 76.48; H 5.80; N 17.72. $C_{20}H_{18}N_4$. Calculated, %: C 76.41; H 5.77; N 17.82.

2-Amino-4-(4-methoxyphenyl)-5,6,7,8-tetrahydronapthalene-1,3-dicarbonitrile (13) was prepared according to the reported method [18] for the synthesis of the isoquinolinethiones **10**. A mixture of cyclohexylidenecyanothienoacetamide **7** (300 mg, 1.66 mmol), 4-(methoxyphenyl)methylidenemalononitrile **4d** (306 mg, 1.66 mmol) and Et_3N (0.2 ml) in 96% EtOH (8 ml) was refluxed for 2 h and left overnight (in the case of the isoquinolinethione **10** it did not form a precipitate). The solution was diluted with iced water, held for 1 day at 0ºC, and the mother liquor was decanted, and the resinous precipitate was triturated with ether. The obtained product was filtered off and recrystallized from EtOH. Yield 166 mg (33%), dark-yellow powder, mp 170-175ºC (decomp.) which was about 89% pure according to HPLC data. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.55-1.59 (2H, m) and 1.70-1.75 (2H, m, 6,7-CH_2); 2.18-2.21 (2H, m, 5-CH_2); 2.83-2.86 (2H, m, 8-CH_2); 3.83 (3H, s, OCH_3); 6.36 (2H, br. s, NH_2); 7.05 (2H, d, ^3J = 8.3, H Ar); 7.21 (2H, d, ^3J = 8.3, H Ar). Mass spectrum, *m*/*z*: 304.2 $[M+H]^+$.

5-Amino-7-phenylindane-4,6-dicarbonitrile (16). Piperidine (0.27 ml, 2.7 mmol) was added to a suspension of the cyclopentylidenecyanothioacetamide (**15**) (300 mg, 1.8 mmol), benzylidenemalononitrile **4c** (278 mg, 1.8 mmol), and 96% EtOH (3 ml), and the mixture was stirred for 0.5 h and left for 24 h at 25ºC. The precipitated crystals were filtered off and washed with EtOH. Yield 220 mg (47%), bright-yellow crystals, mp 211-213ºC (mp 220ºC [34], 226-228ºC [35], 148-149ºC [36]). ^{1}H NMR spectrum, δ, ppm: 1.96-1.99 (2H, m, 2-CH_2); 2.58-2.61 (2H, m, 1-CH_2); 2.99-3.02 (2H, m, 3-CH_2); 6.52 (2H, br. s, NH_2); 7.39-7.51 (5H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 24.0 (C-2); 31.3 (C-1); 33.5 (C-3); 92.2, 94.1 (C-4,6); 115.4 (C≡N); 116.2 (C≡N); 128.3*, 128.4* (C-2,3,5,6 Ph); 128.8* (C-4 Ph); 130.9 (C-7a); 136.7 (C-*i* Ph); 145.7 (C-3a); 152.3 (C-7); 154.8 (C-5). Mass spectrum, *m*/*z*: 260.1 $[M+H]^+$. Found, %: C 78.68; H 5.10; N 16.22. $C_{17}H_{13}N_3$. Calculated, %: C 78.74; H 5.05; N 16.20.

Reaction of Cyanothioacetamide (18) with Isobutyral and Benzylidenemalononitrile (4c). A mixture of the cyanothioacetamide (**18**) (200 mg, 2.0 mmol), isobutyral (0.18 ml, 2.0 mmol), and *N*-methylmorpholine (1 drop) was stirred in acetone (4 ml). After 5 min, the unsaturated nitrile **4c** (308 mg, 2.0 mmol) and *N*-methylmorpholine (0.33 ml, 3.0 mmol) were added, and the mixture was stirred for 1 h at 25ºC. The precipitate formed was filtered off after 24 h to give the pure 2,6-diamino-4-phenyl-4*H*-thiopyran-3,5-dicarbonitrile (**19**). Yield 351 mg (69%), pale-yellow powder, mp 183-185ºC (mp 184ºC [28]). ^{1}H NMR spectrum, δ, ppm: 4.25 (1H, s, 4-CH); 6.90 (4H, br. s, $2NH_2$), 7.22-7.27 (3H, m, H Ar); 7.32-7.36 (2H, m, H Ar).

X-ray Structural Analysis of Compound 6d. Crystals of compound **6d** are triclinic ($C_{25}H_{18}N_4O_3Se$, *M* 501.39). At 298 K: *a* 8.6829(2), *b* 10.6183(2), *c* 13.2165(3) Å; α 110.158(2), β 92,622(2), γ 92.0710(18)º; *V* 1140.95(5) Å^3; *Z* 2; space group $P\bar{1}$, d_{calc} 1.46 g/cm^3, μ(MoKα) 1.68 mm^{-1}; *F*(000) 508. The unit cell parameters and intensities of 38694 reflections (7759 independent, R_{int} 0.027) were measured on an Xcalibur 3 automatic, four-circle diffractometer (MoKα, graphite monochromator, CCD detector, ω-scanning, $2\theta_{max}$ 65.34º). The structure was solved by the direct method using the SHELX-97 program package [37]. The positions of the hydrogen atoms were calculated geometrically and refined using the "rider" model with $U_{iso} = nU_{eq}$ for the attached atom (n = 1.5 for a methyl group and n = 1.2 for remaining hydrogen atoms). The structure was refined using F^2 full-matrix least-squares analysis in the anisotropic approximation for non-hydrogen atoms to wR_2 = 0.082 for 7759 reflections (R_1 0.032 for 6150 reflections with $F > 4\sigma(F)$, *S* 1.02). For refinement of the structure, limits were placed on the bond lengths in the disordered furan ring as follows: C–O 1.37(1), C(–C)=C(–H) 1.34(1), C(–H)=C(–H) 1.32(1), and C–C 1.42(1). The full crystallographic data for the structure of compound **6d** has been placed at the Cambridge Crystallographic Data Center (deposit CCDC 948637).

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