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Pyrrole-2-Dithiocarboxylates: Synthesis of 2-(1-Alkylthio-2-Cyanoethenyl)Pyrroles

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Abstract. 2-(1-Alkylthio-2-cyanoethenyl)pyrroles were synthesized in good to high yields by reaction of pyrrole-2-dithiocarboxylates with active methylene nitriles in a KOH-DMSO medium. The condensation of 4,5,6,7-tetrahydroindole with cyanoacetate also leads to 1-ethylthio-2-cyano-4,5,6,7-tetrahydrocyclohexa-[c]-3H-pyrrolizin-3-one in 61% yield. The effect of substituent on the reaction course has been studied. The dipole moments and spectral characteristics of products are presented.

INDRODUCTION

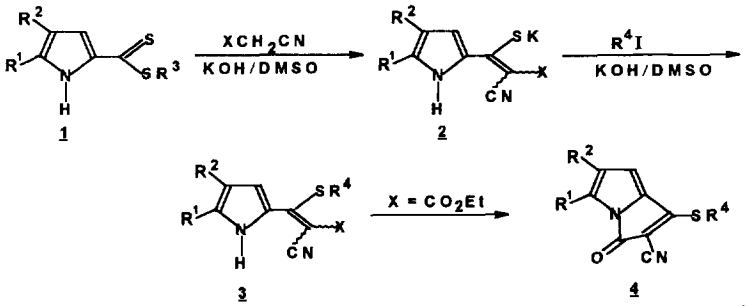
2-Vinylpyrroles having functional substituents at the vinyl group which present essential intermediates in the synthesis of annelated heterocycles, have not been well understood until now. Of most interest are those with a polarized "push-pull" vinyl group (an electron-donor substituent at the one carbon atom and an electron-acceptor substituent at the other carbon). A number of compounds of this type were obtained by reaction of pyrroledithiocarboxylates with tetracyanoethylene oxide[1] and of 1- pyrrolemagnesiumbromide with 2-cyano-3-ethoxy-3-ethylthioacrylonitrile.[2]

Earlier we briefly mentioned that the condensation of pyrrole-2-dithiocarboxylates **1** with some CH-acids in the presence of KOH-DMSO suspension followed by alkylation of enthiolates **2** provides a smoother and more general route to the corresponding functionalized 2-vinylpyrroles.[3]

RESULTS AND DISCUSSION

For further study of this reaction and to establish the limits of its applicability and selectivity as well as for the synthesis of novel functionally substituted 2-vinylpyrroles we have investigated the interaction of pyrrole-2-dithiocarboxylates **1** with active methylene nitriles, XCH_2CN such as malononitrile (X = CN), cyanacetamide ($X = CONH_2$), and cyanacetate ($X = CO_2Et$) in the KOH-DMSO system (**Scheme 1**).

The reaction is carried out by heating (100-110°C, 1.5 h) pyrroles **1** with the CH-acid anions formed by treatment (room temperature, 0.5 h) of active methylene nitriles with the KOH-DMSO system. The alkylation of the intermediate thiolate **2** with alkyl halides R^4I occurs at room temperature to afford 2-vinylpyrroles **3** (Table 1).



1 2 3 4

R^1 = *n*-Pr, *n*-Bu, Ph; R^2 = H, Et, *n*-Pr; R^1-R^2 = $(CH_2)_4$; R^3 = Et, *n*-Pr, *n*-Bu, Allyl; R^4 = Et, *n*-Bu, Allyl; X = CN, $CONH_2$, CO_2Et.

Scheme 1

Table 1. 2-(1-Alkylthio-2-cyanoethenyl)pyrroles **3**

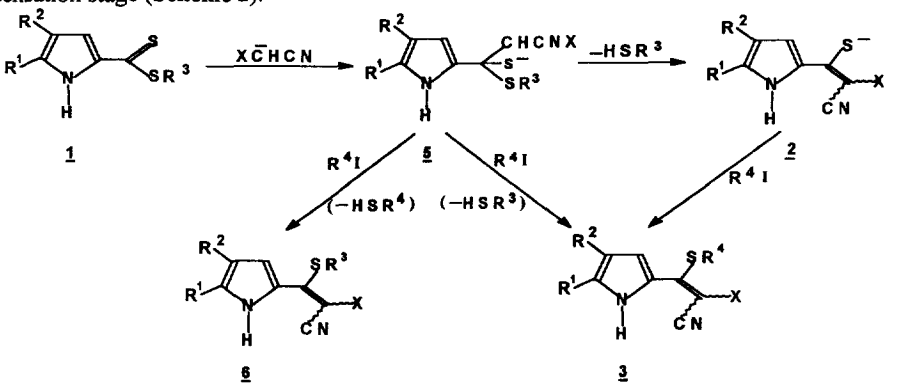
Pyrrole	R^1	R^2	R^4	X	M.p., °C	Yield, %
3a	$(CH_2)_4$		Et	CN	138-139	88
3b	$(CH_2)_4$		Et	$CONH_2$	134-135	85
3c	$(CH_2)_4$		Et	CO_2Et	95-96	29
3d	$(CH_2)_4$		*n*-Bu	CN	93-94	70
3e	$(CH_2)_4$		*n*-Bu	$CONH_2$	114	64
3f	$(CH_2)_4$		Allyl	CN	109-110	63
3g	$(CH_2)_4$		Allyl	$CONH_2$	129	52
3h	*n*-Bu	n-Pr	Et	CN	oil	51
3i	*n*-Bu	n-Pr	Et	$CONH_2$	79-80	91
3k	*n*-Pr	Et	Et	CN	54-55	48
3l	*n*-Pr	Et	Et	$CONH_2$	109-110	90
3m	Ph	H	Et	CN	90	78
3n	Ph	H	Et	$CONH_2$	148	82

*The data of elemental analysis (C, H, N, S) for all compounds correspond to their general formula.

The three reaction stages, i.e. , generation of the CH-acid anion, reaction of the latter with pyrrole-2-dithiocarboxylate **1** and alkylation of the thiolate **2**, can be conducted as a one-pot process.

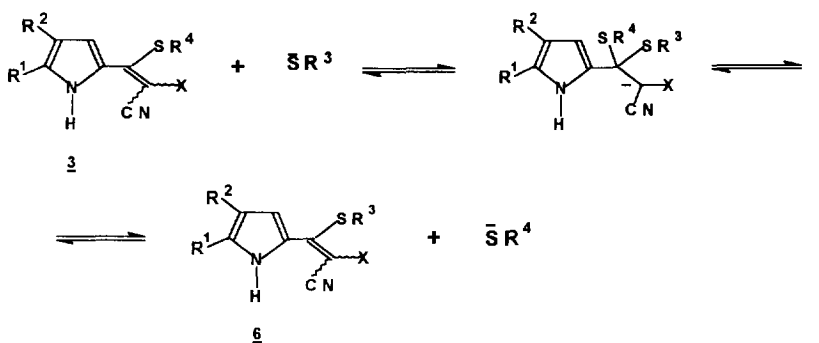
The reaction with malononitrile and cyanacetamide gives, along with 2-vinylpyrroles **3**, minor amounts (~ 5%) of the products of intramolecular cyclization of 2-vinylpyrroles **3**. With CH-acid possessing a carboxyl function (cyanacetate) the condensation is accompanied by annelation of vinylpyrrole **3c** to the corresponding pyrrolyzin-3-one **4** as a major product (**Scheme 1**, Table1). The ratio **3c** : **4** does not depend on the reaction conditions. Upon heating the reactants for 0.5, 1.5 and 3h the yield of the products is 15 and 29, 29 and 61, 15 and 36%, respectively. The lower total yield of **3c** and **4**, when the condensation is carried out for 0.5 h, is

explained by an incomplete conversion of pyrrole-2-dithiocarboxylate **1c**. When heating is increased up to 3 h resinification is increased. With $R^3 \neq R^4$, together with the vinylpyrroles **3** the vinylpyrroles **6** having an SR^3 group are also formed which can be explained by an incomplete abstraction of HSR^3 from the intermediate **5** at the initial condensation stage (**Scheme 2**).



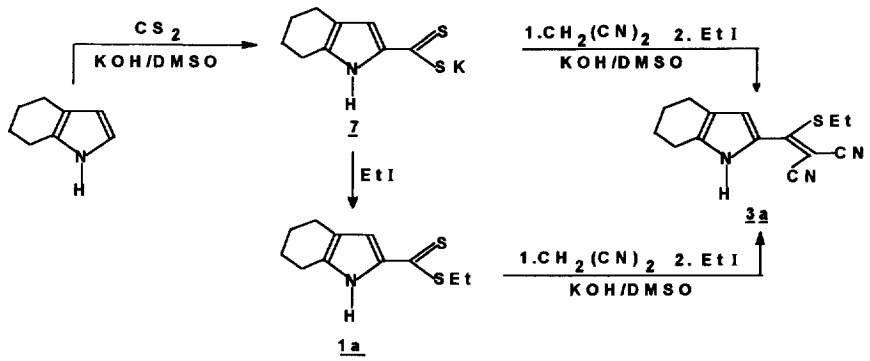
Scheme 2

A side formation of vinylpyrroles **6** bearing the SR^3 group can be avoided by increasing the time of heating (from 1.5 to 2 h) prior to the introduction of the alkylating agent. Thus, the condensation of ethyl 4,5,6,7-tetrahydroindole-2-dithiocarboxylate **1a** with cyanacetamide and allyl iodide affords a mixture of 2-(1-ethylthio-2-carbamoyl-2-cyanoethenyl)-4,5,6,7-tetrahydroindole **3b** and 2-(1-allylthio-2-carbamoyl-2-cyano-ethenyl)-4,5,6,7-tetrahydroindole **3g** in a 1:3 ratio (TLC and NMR spectroscopy). The pure pyrrole **3g** was



Scheme 3

prepared by condensation of the pyrrole **1a** with cyanacetamide and allyl iodide for 2 h as well as from the allyl 4,5,6,7-tetrahydroindole-2-dithiocarboxylate **1f** (100-110° C, 1.5 h). The side effect of prolonged heating is a decrease in the yield of vinylpyrroles **3** due to the formation of the products of their intramolecular cyclization (~15-20%). The fact that the SR^3 alkylthio group remains at the vinyl group can alternatively be explained by the exchange between the pyrroles **3** and the reaction mixture containing R^3S^- anions (**Scheme 3**). As the synthesis of the initial pyrrole-2-dithiocarboxylates **1**, like that of the 2-vinylpyrroles **3** is effected in the KOH-DMSO system,[4] it would be reasonable to carry out a one-pot reaction without isolation of the intermediate products. We have checked two versions (**A** and **B**) of this synthesis (**Scheme 4**).



Scheme 4

A. To the potassium salt of 4,5,6,7-tetrahydroindole-2-dithiocarboxylic acid 7, obtained at the first stage from tetrahydroindole and carbon disulfide, a mixture of malononitrile, KOH and DMSO (stirred for 0.5 h at room temperature prior to addition) was added, heated (100-110° C) and then alkylated at room temperature. Vinylpyrrole **3a** is formed in trace amounts in this case (TLC).

B. According to version **A** the salt 7 is alkylated at first and then is treated with malononitrile as described above.The yield of pure product 2-(1-ethylthio-2,2-dicyanoethenyl)-4,5,6,7-tetrahydroindole **3a** is 25% which

Table 2. Spectral Characteristics of the Pyrroles **3a-n**, **4**

Pyr-role	IR, cm^{-1}	^1H NMR, δ, ppm, ($CDCl_3$)			
		R^1	R^2	R^4	H-3
3a	520, 625, 700, 800, 820, 900, 1000, 1120, 1170, 1200, 1265, 1300, 1340, 1430, 1490, 1565, 2200, 2845, 2910, 3250	1.75	2.64	1.28 (Me) 3.11(SCH_2)	7.12
3b	625, 700, 800, 820, 920, 1000, 1120, 1170, 1220, 1265, 1300, 1415, 1485, 1570, 1635, 2190, 2845, 2910, 3180, 3370	1.75	2.64	1.28(Me) 3.02 (SCH_2)	7.06
3c	820, 915, 1000, 1015, 1120, 1155, 1200, 1225, 1300, 1350, 1410, 1490, 1570, 1673, 2190, 2830, 2910, 3255	1.76	2.67	1.32 (Me) 3.11 (SCH_2)	7.10
3d	520, 600, 625, 700, 800, 820, 900, 1000, 1050, 1120, 1170, 1200, 1300, 1340, 1430, 1565, 2200, 2830, 2910, 2950, 3256	1.81	2.64	0.94 (Me) 1.55 (SCH_2) 3.13 (SCH_2)	7.18
3e	550, 600, 625, 800, 820, 1000, 1060, 1120, 1170, 1220, 1260, 1300, 1330, 1430, 1490, 1570, 1600, 1640, 2190, 2830, 2910, 3150, 3350	1.80	2.64	0.89 (Me) 1.53 (CH_2) 3.05 (SCH_2)	7.13
3f	520, 620, 700, 800, 820, 900, 1000, 1065, 1120, 1170, 1200, 1300, 1345, 1430, 1480, 1560, 1625, 2200, 2840, 2910, 3270	1.79	2.61	3.72 (SCH_2) 5.15 (=CH_2) 5.70 (CH=)	7.17
3g	550, 590, 630, 700, 750, 780, 800, 820, 900, 920, 960, 1000, 1030, 1060, 1120, 1130, 1230, 1265, 1300, 1345, 1415, 1585, 1600, 1635, 1650, 2190, 2845, 2920, 3075, 3180, 3280, 3375, 3420	1.79	2.61	3.68 (SCH_2) 5.15 (=CH_2) 5.84 (CH=)	7.10

Table 2. Continued

Pyr-role	IR, cm^{-1}	^1H NMR, δ, ppm, ($CDCl_3$)			
		R^1	R^2	R^3	H-3
3h	820, 900, 1000, 1050, 1180, 1260, 1330, 1420, 1485, 1550, 1620, 2200, 2850, 2910, 2940, 3385	0.95(Me) 1.57(CH_2) 2.03(CH_2)	0.95 (Me) 1.57(CH_2) 2.63(CH_2)	1.34(Me) 3.14(SCH_2)	7.17
3i	720, 750, 820, 870, 1000, 1100, 1150, 1200, 1300, 1320, 1330, 1410, 1480, 1595, 1640, 2190, 2850, 2910, 2945, 3190, 3310, 3380	0.93(Me) 1.53(CH_2) 2.36(CH_2)	1.30(Me) 1.53(CH_2) 2.62(CH_2)	1.30 (Me) 3.08(SCH_2)	7.16
3k	805, 910, 980, 1020, 1100, 1145, 1205, 1270, 1305, 1350, 1420, 1445, 1475, 1550, 1630, 2195, 2850, 2900, 2945, 3265	0.99 (Me) 1.63(CH_2) 2.44 (CH_2)	1.22(Me) 2.63(CH_2)	1.34(Me) 3.17(SCH_2)	7.20
3l	515, 550, 565, 765, 810, 845, 1000, 1105, 1145, 1180, 1195, 1275, 1300, 1330, 1350, 1415, 1445, 1490, 1598, 1625, 2180, 2850, 2905, 2950, 3180, 3300, 3350	0.95(Me) 1.63(CH_2) 2.36 (CH_2)	1.22(Me) 2.58(CH_2)	1.28(Me) 3.07(SCH_2)	7.16
3m	650, 690, 740, 780, 1000, 1060, 1080, 1245, 1270, 1310, 1395, 1450, 1490, 1510, 1565, 2210, 2875, 2970, 3300	7.65	6.76	1.37(Me) 3.20(SCH_2)	7.38
3n	480, 510, 670, 690, 750, 790, 800, 875, 1020, 1050, 1080, 1150, 1265, 1290, 1310, 1365, 1400, 1435, 1485, 1490, 1530, 1595, 1634, 1655, 2190, 2870, 2910, 2965, 3200, 3440	7.58	6.65	1.26(Me) 3.06 (OCH_2)	7.35
4*	630, 710, 730, 1015, 1220, 1345, 1415, 1475, 1710, 2200, 2840, 2910, 2965, 3100	1.70	2.60	1.38(Me) 3.45(SCH_2)	6.76

* Solution in DMSO.

is considerably lower than that of this compound obtained by the two-step procedure (total yield 63%).

The vinylpyrroles (**3a**-**3g**, **3i**-**3n**) are bright-colored (yellow and orange) crystals. The vinylpyrrole **3h** is a yellow oil (due to this color it was not possible to determine their refraction index). The pyrrolizine **4** was obtained as violet crystals. The yield and constants of the products are presented in Table 1.

The structure of the compounds synthesized is proved by IR and ^1H NMR spectroscopy (Table 2). In the ^1H NMR spectra of the adducts **3** there are no signals for the pyrrole ring protons at the α-position; the proton at the β-position appears as a doublet in the 7.1-7.7 ppm region, whereas the SCH_2-group proton signals occur in the 3.0-3.1 ppm region. The character and integral intensities of the signals are in full agreement with the structure of vinylpyrroles **3**.

In the IR spectra of all the pyrroles **3**, the stretching vibration band corresponding to the NH bond of pyrrole ring, is observed in the 3250-3270 cm^{-1} region (in compound **4** this band is absent). In the spectra of compounds (**3b**, **3e**, **3g**, **3i**, **3l**, **3n**, X = $CONH_2$), together with the above band in the 3200-3500 cm^{-1} range there are bands corresponding to symmetric and asymmetric vibrations of the N-H bonds of the amide group. .In all the compounds examined the CN stretching vibration occurs as a single band at 2190 cm^{-1} (for compounds with X = $CONH_2$, CO_2Et) and at 2200 cm^{-1} (for compounds where X = CN). According to Hartke et al.,[2] in 2-(1-methylthio-2,2-dicyanoethenyl)pyrrole this band manifests itself as a doublet. The pyrrole skeletal vibrations are present at 1490, 1335 cm^{-1}. The high-frequency band of the pyrrole skeleton is difficult to identify due to the presence in this region of the stretching vibration of the C=CS double bond at 1565-1570 cm^{-1} (1546, 1476 cm^{-1} as defined in ref. 2).

The pyrroles, where X = CN (**3a**, **3d**, **3f**, **3m**), show high dipole moments, characteristic of compounds containing cyano groups (Table 3).

Table 3. Dipole Moments of 2-Vinylpyrroles **3** (Benzene, 25°C)

Pyrrole	**3a**	**3d**	**3f**	**3m**	**3b**	**3e**	**3i**	**3n**
Dipole moment, μ, D	7.14	6.77	6.66	6.18	3.81	3.92	3.60	3.13

Introduction of the phenyl group into the pyrrole ring position 5 decreases the μ value as was the case with NH-pyrroles.[5] The dipole moments calculated by vector-additive scheme are much lower than the experimental values (Table 4).

Table 4. Calculated Dipole Moments of the 2-(1-Ethylthio-2,2-dicyanoethenyl)pyrrole

Conformation	Orientation of the Et-S bond with respect to C=C			
	cis	*trans*	*gauche*	
Planar	1.2	3.3	2.6	
60° (a)	2.4	4.2	4.0(b)	2.0(b)
90° (a)	2.9	4.7	4.5(b)	3.4(b)

(a) The angle between the pyrrole ring and the double bond.

(b) Two values correspond to parallel and antiparallel orientations of the Z-component of the pyrrole ring and Et-S dipole moment.

The most polar form (4.7 D) is that with the *trans* -orientation of the C_{SP^3}-S bond relative to the vinyl group and with displacement of the latter out of the pyrrole ring plane. In this case the dipole moment component in the XY plane points to the double bond at an angle of approximately 14° and is 4.3 D. For a planar molecule this component points to the double bond at an angle of 36° and is equal to 3.3 D.

The difference between the experimental and calculated dipole moments can be explained by a considerable contribution of the π-conjugation effect. The substitution of a nitrile group by an amide group decreases the dipole moment (compounds **3b**, **3e**, **3i**, **3n**, **Table 3**). The introduction of the phenyl group in the pyrrole ring position 5 (compound **3n**) produces an effect analogous to that in compound **3m**. Assuming that for compounds (**3b**, **3e**, **3i**, **3n**) the π-moment will also be of significant value, it is difficult to draw a conclusion on the molecule structure from calculations using just a vector-additive scheme.

EXPERIMENTAL

IR Spectra of pyrroles were recorded on a Specord IR-75 spectrometer in film (compound **3h**) or in KBr pellets. ^{1}H NMR spectra were run on a Tesla BS 567 A spectrometer (100 MHz) in $CDCl_3$. Dipole moments were measured on an Epsilon instrument (1 MHz) in a 20 pF platinum cell, benzene, 25°C, and calculated using the Higasi formula. The reaction course and the product purity were monitored by TLC on a Silufol UV-254 in a 1:1 hexane-ether system.

2-(1-Ethylthio-2,2-dicyanoethenyl)-4,5,6,7-tetrahydroindole 3a. *1.* KOH (1 g, 15 mmol), malononitrile (1 g, 15 mmol) and 50 ml of DMSO are stirred for 0.5 h at room temperature, then ethyl 4,5,6,7-tetrahydroindole-2-dithiocarboxylate **1a** (2.26 g, 10 mmol) is added and the mixture is heated for 1.5 h at 108-110°C. After cooling the reaction mixture to room temperature, ethyl iodide (2.34 g, 15 mmol) is added and stirred for 2 h. The reaction mixture is diluted with water (1:3), the crystals are filtered off. The crystal weight after drying is 0.2 g, m.p. 152-153°C. The aqueous layer is extracted with ether, and the water-washed ether extracts are dried with $MgSO_4$. After removal of ether the residue is recrystallized from methanol to give 2.26 g (88%) of compound **3a**. ^{13}C NMR Spectrum ($CDCl_3$, δ, ppm): 22.21 - 23.21 (cyclohexane ring), 14.46 (Me), 31.01 (SCH_2), 125.74, 124.75 (pyrrole ring C^4, C^5), 120.26 (pyrrole ring C^3), 141.84 (pyrrole ring C^2), 155.55 (CO), 116.43 (CN), 159.38 (C^1), 67.37 (C^2). The IR and ^1H NMR spectra of **3a** are presented in Table 2.

The pyrroles **3h, 3k** and **3m** were obtained in a similar manner.

2. 4,5,6,7-Tetrahydroindole (1.2 g, 10 mmol), KOH (1.2 g, 20 mmol) and 20 ml of DMSO are stirred for 0.5 h at room temperature, then carbon disulfide (1.52 g, 20 mmol) is added. The reaction mixture is allowed to stand at room temperature for 2 h, then a mixture of KOH (1g, 15 mmol), malononitrile (1g, 15 mmol) and 50 ml of DMSO stirred before the addition for 0.5 h at room temperature, is added. The reaction is performed at 108-110° C for 1.5 h. After cooling the reaction mixture to room temperature, ethyl iodide (2.34 g, 15 mmol) is added and the mixture is stirred for 2 h. After the treatment described in *1*, 1.9 g of a resinous liquid was isolated from which it was not possible to isolate pyrrole **3a** in spite of its presence according to TLC.

3. 4,5,6,7-Tetrahydroindole (1.2 g, 10 mmol), KOH (1.2 g, 20 mmol) and 20 ml of DMSO are stirred for 0.5 h at room temperature, then carbon disulfide (1.52 g, 20 mmol) is added. The reaction mixture is allowed to stand at room temperature for 2 h, ethyl iodide (2.34 g, 15 mmol) is added, then a mixture of KOH (1g, 15 mmol), malononitrile (1g, 15 mmol) and 50 ml of DMSO stirred prior to addition for 0.5 h at room temperature, is added. The reaction mixture is heated (108-110°C, 1.5 h), cooled to room temperature, then ethyl iodide (2.34 g, 15 mmol) is added and the mixture is stirred for 2 h. After the treatment described in procedure *1*, 0.64 g (25%) of the pyrrole **3a** was obtained.

2-(1-Ethylthio-2-carbamoyl-2-cyanoethenyl)-4,5,6,7-tetrahydroindole 3b. By procedure *1* described for the synthesis of the pyrrole **3a**, 2.2 g (84.8%) of the pyrrole **3b** was prepared from KOH (1 g, 15 mmol), cyanacetamide (1.26 g, 15 mmol), 50 ml of DMSO, pyrrole **1a** (2.26 g, 10 mmol) and (2.34 g, 15 mmol) ethyl iodide; ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 22.59 - 23.85 (cyclohexane ring), 14.72 (Me), 32.57 (SCH_2), 127.70, 124.75 (pyrrole ring C^4, C^5), 125.03 (pyrrole ring C^3), 142.40 (pyrrole ring C^2), 166.21 (CO), 121.10 (CN), 151.81 (C^1), 94.04 (C^2) and 0.2 g of red crystals, m.p. 189-190° C.

The pyrroles **3i, 3l, 3n** were prepared in a similar way.

2-(1-Ethylthio-2-carbethoxy-2-cyanoethenyl)-4,5,6,7-tetrahydroindole 3c and 1-ethylthio-2-cyano-4,5,6,7-tetrahydrocyclohexa- [c]-3H-pyrrolizin-3-one 4. *1.* By procedure *1* described for the synthesis of pyrrole **3a** (108-110° C, 1.5 h), from KOH (1g, 15 mmol), cyanacetate (1.7 g, 15 mmol), 50 ml of DMSO, pyrrole **1a** (2.26 g, 10 mmol) and ethyl iodide (2.34 g, 15 mmol) 2.8 g of crystals were obtained. By heating in hexane, only part of the crystals were solubilized. After cooling of the hot hexane solution, 0.75 g (29%) of indole **3c** was isolated. The crystals not solved in hot hexane, after recrystallization from ethanol, gave 1.85 g (61%) of pyrrolizine **4**, m.p. 163-164° C. ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 21.72 - 22.55 (cyclohexane ring),

14.35 (Me), 26.54 (SCH_2), 127.01, 130.33 (pyrrole ring C^4, C^5), 116.23 (pyrrole ring C^3), 135.82 (pyrrole ring C^2), 163.85 (CO), 113.48 (CN), 160.53 (C^1), 91.94 (C^2). The IR and ^1H NMR spectra of **3c** and **4** are presented in Table 2.

2. An analogous reaction carried out for 0.5 h affords 0.4 g (15%) of pyrrole **3c** and 0.9 g (29%) of pyrrolizine **4**.

3. An analogous reaction carried out for 3.0 h affords 0.4 g (15%) of pyrrole **3c** and 1.1 g (36%) of pyrrolizine **4**.

2-(1-Allylthio-2-carbamoyl-2-cyanoethenyl)-4,5,6,7-tetrahydroindole 3g. *1*. KOH (1 g, 15 mmol), cyanacetamide (1.26 g, 15 mmol) and 50 ml of DMSO are stirred for 0.5 h at room temperature, then ethyl 4,5,6,7-tetra- hydroindole-2-dithiocarboxylate **1a** (2.26 g, 10 mmol) is added and the mixture is heated for 1.5 h at 108-110° C. After cooling the reaction mixture to room temperature allyl iodide (2.52 g, 15 mmol) is added and stirred for 2 h. The reaction mixture is diluted with water (1:3), the crystals (0.01 g) are filtered off. The crystals (1.7 g) remained after the removal of ether are a mixture of compounds **3b** and **3g**, (1:3); ^1H NMR spectrum ($CDCl_3$, δ, ppm): 1.30 (Me, 3H), 1.78, 2.60 (m, protons of cyclohexane ring, 8H), 3.11 (q, SCH_2 in SCH_2CH_3, 2H), 3.70 (d, SCH_2 in $SCH_2CH{=}CH_2$, 2H), 5.15 (d, $=CH_2$, 2H), 5.84 (CH=, 1H), 7.1 (d, H-3, 1H).

2. Analogously, by procedure *1* described for the synthesis of pyrrole **3g** (cooling time to room temperature 1.5 h) 1.6 g (52%) of pyrrole **3g** was prepared from pyrrole **1a**, cyanacetamide and allyl iodide.

3. Analogously, by procedure *1* described for the synthesis of pyrrole **3g** (108-110°C, 2 h) 0.5 g of bright-red unidentified crystals and 1.1 g (40%) of pyrrole **3g** were obtained from pyrrole **1a**, cyanacetamide and allyl iodide.

Analogously to procedure *1* presented for the synthesis of pyrrole **3g** from allyl 4,5,6,7-tetrahydroindole-2-carboxylate **1f**, malononitrile and allyl iodide the pyrrole **3f** was prepared. From the pyrrole **1a**, butyl iodide, malononitrile and cyanacetamide it was possible to obtain the pyrroles **3d** and **3e**, respectively.

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