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Reactions of Heterocumulenes with Organometallic Reagents: XVII.* One-Pot Synthesis of Alkoxy and (Alkylsulfanyl)-Substituted Pyrroles and 2,3-Dihydropyridines from Aliphatic Isothiocyanates and Lithiated Alkoxyallenes

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Abstract—A fundamentally new approach was developed to designing pyrrole and dihydropyridine rings from available allenes and isothiocyanates involving a single preparative stage. Applying the reaction of lithiated alkoxyallenes with aliphatic isothiocyanates we have synthesized previously unknown 1-alkyl(cycloalkyl) pyrroles and 2,3-dihydropyridines with rare alkoxy- and alkylsulfanyl substituents. It was proved that the five- and six-membered azaheterocycles formed as a result of competing reactions of direct intramolecular cyclization of S-alkylated adducts of lithiated alkoxyallenes with isothiocyanates (1-aza-1,3,4-trienes) into pyrroles and of [1,5]-sigmatropic rearrangement into conjugated 2-aza-1,3,5-trienes with subsequent closure into dihydropyridine ring (through 6π-electrocyclization).

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Acetylene and allene carbanions, for ages classed among unique and most promising synthons and building blocks for the fine organic synthesis [2], recently find developing application in the new strategy for creating C–C, C–N, C–O, and C–S bonds in the targeted heterocyclic synthesis [3–14] including the synthesis of fundamental nitrogen, oxygen, and sulfur heterocycles: pyrroles, thiophenes, furans, pyridines, quinolines, azepines, azetidines, pyrrolines, pyridazines, oxazines, imidazoles, thietanes, oxepanes etc., in particular, owing to the research of the authors of this study [4–11]. A special position in the metallopropadiene series belongs to the lithiated alkoxyallenes [first of all, to methoxyallene (**I**)] [4, 5, 9–13] due to their availability [13], high synthetic versatility [4, 5, 9–14], and regiospecificity of their generation [13]. However among diverse electrophiles (predominantly aldehydes, ketones, alkyl halides, oxiranes, more seldom, nitrones, nitriles, imides, imines and heterocumulenes like CO_2, CS_2, PhN=C=O, PhN=S=O), brought into reactions with polyunsaturated carbanions, organic isothiocyanates before our studies [4–11] were not practically explored [15].

At the same time the availability and high reactivity of isothiocyanates with respect to nucleophiles make them attractive starting compounds for the synthesis of heteropolyene systems, for instance, 1-aza-1,3,4-trienes of the type C=C=C–C=N– (which might be very active in heterocyclization reactions) by the reaction with such highly nucleophilic intermediates like carbanions of alkynes or 1,2-dienes easily generated from the corresponding substrates under the action of superbases [2, 13]. The systematic investigation of the reaction pair isothiocyanate–metalloalkyne of metallodiene that we started in 1995 led to the development of the conceptually new strategy of the synthesis of all the most important aza-

* For Communication XVI, see [1].

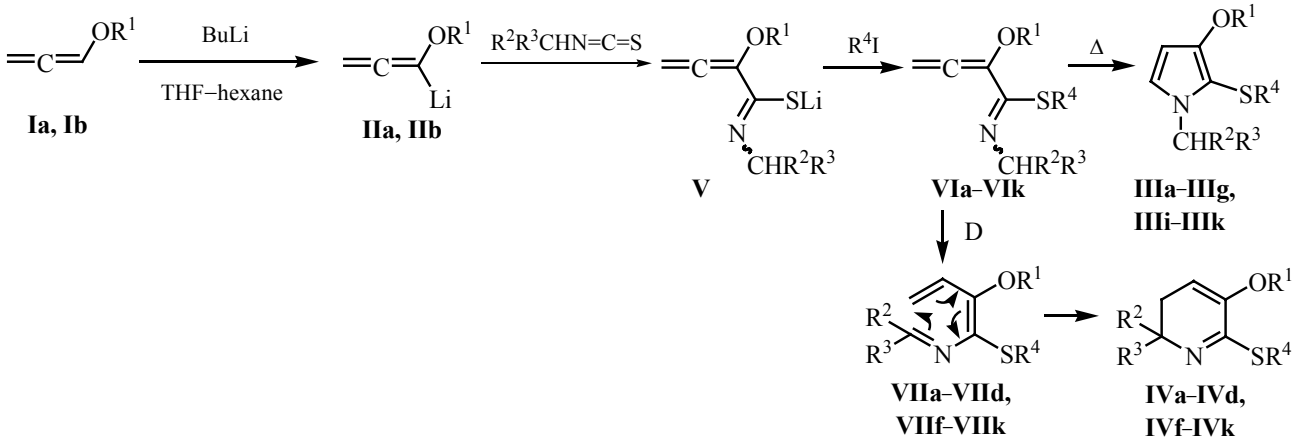
and thiaheterocycles (pyrroles, pyrrolines, pyridines, dihydropyridines, quinolines, azepines, dihydroazepines, thietanes, thiophenes, dihydrothiophenes, thiopyrans) [4, 5], and also of carbocycles (cyclobutenes, cyclobutanes) [8, 16] from the same precursors: adducts of metallated dienes and alkynes with isothiocyanates.

Thus we discovered for the first time [4, 5] that the reaction of lithiated alkoxyallenes **II** with aliphatic [methyl, ethyl, isopropyl, *sec*-butyl, methoxymethyl, 2-(vinyloxy) ethyl] and cycloaliphatic (cyclopropyl, cyclopentyl, cyclohexyl) isothiocyanates opened unexpectedly simple way to previously unknown and difficultly obtainable heterosubstituted pyrroles and 2,3-dihydropyridines: 1-alkyl(cycloalkyl)-2-(alkylsulfanyl)-3-alkoxypyrroles **IIIa–IIIg, IIIi–IIIk** and 6-(alkylsulfanyl)-5-alkoxy-2,3-dihydropyridines **IVa–IVd, IVf–IVk** (Scheme 1) as had been concisely reported (on single examples) in [10, 11]. Here these and new data are discussed in more detail.

We found that the deprotonation of methoxy- and *tert*-butoxyallene (**Ia, Ib**) with butyllithium in THF–hexane environment proceeded easily, fast (5–10 min) and regiospecifically (with the formation of α-lithiated intermediates **II**) even at very low temperature (–100…–60°C) [4, 10]. It was previously reported on the lithiation of alkoxyallenes with BuLi or EtLi in ether , mixtures Et_2O–THF, Et_2O–hexane and THF–hexane at –35…–15°C (10–25 min) [13]. It is reasonable to bring methoxyallene (**Ia**) into the reaction in some excess relative to BuLi (1.1–1.5 mol per 1 mol of BuLi) accounting for its high volatility under experimental conditions due to its relatively low boiling point, vigorous stirring, and a strong flow of the inert gas.

As known [15, 17] and as we have established [4–11] isothiocyanates add carbanions exclusively by the nucleophilic (carbophilic) mechanism. The formation of products of thiophilic addition in these reactions (in contrast to the other thiocarbonyl compounds [18]) was not observed up till now. For instance, 1-alkoxy-1-lithioallenes **II** reacted with alkyl, cycloalkyl, and heteroalkyl isothiocyanates exothermic at low temperature (–100... –30°C) and fast (5–15 min) giving the corresponding lithium allenylimidothioates **V** in the most cases in virtually quantitative yield. Usually the isothiocyanate or its solution in a small quantity of THF is added in one portion to the cooled to –100...–90°C solution of 1-alkoxy-1-lithioallene **II** generated in situ in the mixture THF–hexane The temperature is maintained at –60...–30°C (as a rule, about –60°C). Somewhat raised temperature (up to –35...–30°C) is feasible in reactions with secondary isothiocyanates that because of the stereoelectronic effects of the substituent react with carbanions **II** slower than the primary isothiocyanates. To compensate possible losses due to the presence of water traces or other active impurities in solvents, reagents or the atmosphere 1-lithio-1-methoxyallene (**IIa**) is used in slight excess with respect to isothiocyanate (1.01–1.35 mol per 1 mol of isothiocyanate). Moreover because it is easier to remove from the reaction products volatile methoxyallene and/or its alkyl derivatives (products of protolysis and alkylation of intermediate **IIa**) than unreacted isothiocyanate.

Scheme 1.



I, II, R^1 = Me (**a**), *t*-Bu (**b**); **III, IV, VI, VII**, $R^1 = R^4$ = Me: $R^2 = R^3$ = H (**a**), R^2 = H, R^3 = Me (**b**), $R^2 = R^3$ = Me (**c**), R^2 = Me, R^3 = Et (**d**), R^2, $R^3 = (CH_2)_n$, n = 2 (**e**), 4 (**f**); R^1 = Me, R^2,$R^3 = (CH_2)_5$, R^4 = Et (**g**); $R^1 = R^4$ = Me: R^2 = H, R^3 = OMe (**h**), R^2 = H, $R^3 = CH_2OCH{=}CH_2$ (**i**); R^1 = *t*-Bu, $R^2 = R^3$ = H, R^4 = Me (**j**), R^4 = Et (**k**).

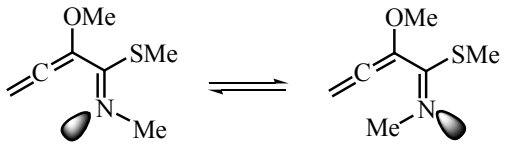
The examination of the potential energy surface of the reaction between methyl isothiocyanate and 1-lithio-1-methoxyallene **IIa** performed by methods of various levels in the basis 6-31G** showed that the formation of adduct **Va** proceeded in one stage through a four-center transition state [E_{act} 74.4 (HF) and 75.3 (B3LYP) kJ mol^{-1}] [19].

Further alkylation of adducts **V** at –80...20°C (10–30 min) by the addition to the reaction mixture of alkyl halide, e.g., MeI or EtI taken in excess (1.4–2.8 mol per 1 mol of adduct) for the completion of the reaction occurs exclusively at the sulfur atom and in virtually quantitative yield affords previously unknown and unavailable allenylimidothioates **VI**, 1-aza-1,3,4-trienes existing as a mixture of *syn*-(*Z*) and *anti*-(*E*)-isomers with respect to the carbon–nitrogen double bond. Their formation is unambiguously proved by IR and NMR spectra.

The vibrations of bonds C=N and C=C=C give rise in the IR spectrum of 1-aza-1,3,4-triene **VIa** (Scheme 1) to thw absorption bands at 1618 and 1946 cm^{-1} respectively. The presence of geometric isomers of 1-aza-1,3,4-trienes **VI** originating from the relative rigidity of the C=N bond and the nonlinear structures containing this bond [20] is revealed by NMR spectra: in the proton as well as carbon spectra of compound **VI** all signals are doubled with the shift from some thousandths to some ppm units. For instance, the difference in the chemical shifts (Δδ) for *syn*-(*Z*)- and *anti*-(*E*)-isomers of 1-aza-1,3,4-triene **VIa** in the ^{1}H NMR spectrum attains from 0.005 to 0.160 ppm, and in the ^{13}C NMR spectrum, fromt 0.32 to 3.74 ppm (taken from solutions in $CDCl_3$).

Recently the solution was found for the problem of identification of *syn*-(*Z*)- and *anti*-(*E*)-isomers observed in the NMR spectra of 1-aza-1,3,4-trienes **VI**. By an example of compound **VIa** constants J(C,C) in 1-aza-1,3,4-triene were measured for the first time, the ratio was determined of *syn*-(*Z*)- and *anti*-(*E*)-isomers (C_6D_6, –10°C, 35 : 65) (Scheme 2) [21], and the signals assignments to definite geometric isomers were made in the ^{1}H and ^{13}C NMR spectra. The experimental data were reliably confirmed by quantum-chemical calculations [21, 22]. It was also established that the ratio of *syn*-(*Z*)- and *anti*-(*E*)-isomers **VIa** very strongly depended on the nature of the solvent and changed, for instance, from ~1 : 2 in C_6D_6 [21] and in CCl_4 to ~1 : 1 in $CDCl_3$. And in proton-donor solvents (CD_3OD) the equilibrium concentration of *syn*-(*Z*)-isomer **VIa** even exceeded that of the *anti*-(*E*)-isomer. The quantum-chemical study of the mechanism of *syn*-(*Z*)/*anti*-(*E*)-isomerization in the allenylimidothioate series showed by the example of compound **VIa** that the most probble mechanisms were inversion (E_{act} 74.4 kJ mol^{-1}) and catalyzed by nucleophile (E_{ac} 61.6 kJ mol^{-1}) transition channels.

Scheme 2.



syn-(*Z*)-**VIa** (~35%, J_{CC} 86.1 Hz) ⇌ *anti*-(*E*)-**VIa** (~65%, J_{CC} 68.4 Hz)

At storage (even at low temperature) and at heating 1-aza-1,3,4-trienes **VI** unexpectedly rearrange into pyrroles **III** and/or 2,3-dihydropyridines **IV** [4]. It was established from the experimental data that the formation of the pyrrole **III** ring occurs as a result of a direct intramolecular cyclization of 1-aza-1,3,4-triene **VI**, and the formation of the ring of dihydropyridine **IV** is preceded by a sigmatropic rearrangement of 1-aza-1,3,4-triene **VI** into a conjugated 2-aza-1,3,5-triene system **VII** followed by the electrocyclization of the latter (Scheme 1). It should be stressed that none of this reaction was known before our research [4, 5, 10, 11] may be because were unknown and unavailable proper 1-aza-1,3,4-trienes of type **VI**.

Obviously the ratio of the heterocyclic reaction products, i.e., pyrrole **III** and 2,3-dihydropyridine **IV**, is governed by the ratio of the rates of two competing processes related to the thermally induced reorganization of 1-aza-1,3,4-triene **VI**: the intramolecular [1,5]-cyclization into pyrrole (with the formation of a new C–N bond) and the isomerization into 2-aza-1,3,5-triene **VII** (through [1,5]-H shift). It is also obvious that the kinetic parameters of the concurrent reactions alongside the thermodynamic characteristics of the reaction products should be or at least may be significantly affected by the stereoelectronic effects of the substituents in the starting 1-aza-1,3,4-triene **VI** and in the long run by the structure of the initial reagents (allene, isothiocyanate, and alkyl halide). From the data presented in the table it is seen that among three variables (substituents at the nitrogen, oxygen, and sulfur atoms) the strongest effect on the ratio of the cyclic reaction products and consequently on the reaction route produces the substituent at the nitrogen atom of 1-aza-1,3,4-triene **VI**, i.e., the structure of isothiocyanate [4].

Dependence of yield and ratio of cyclic reaction products on the structure of initial reagents : alkoxyallene ($R^1OCH=C=CH_2$), isothiocyanate ($R^2R^3CHN=C=S$), and alkyl iodide (R^4I)

R^1	R^2	R^3	R^4	Overall yield, %[a]	Content of reaction products in the mixture, %	
					pyrrole **III**	dihydropyridine **IV**
Me	H	H	Me	(79)	70–75	30–25
Me	H	Me	Me	91 (86)	20–25	80–75
Me	Me	Me	Me	89 (73)	15	85
Me	Me	Et	Me	87 (79)	10–15	85–90
Me	$(CH_2)_2$		Me	80	100	0
Me	$(CH_2)_4$		Me	98–100[b]	[c]	[d]
Me	$(CH_2)_5$		Et	75 (72)	12	88
Me	H	MeO	Me	100[e] (73)	0	100
Me	H	CH_2=CHOCH$_2$	Me	94 (70)	50	50
t-Bu	H	H	Me	86 (60)	83	17
t-Bu	H	H	Et	89 (73)	88	12

[a] Preparative yields (nonoptimized) of the mixture of "crude" and purified products (in parentheses).
[b] Yield of 2-aza-1,3,5-triene **VIIf** in a mixture with 1−8% (depending on conditions) of 1-aza-1,3,4-triene **VIf** and/or pyrrole **IIIf**.
[c] Identified in NMR spectra as a side product at the isomerization of 1-aza-1,3,4-triene **VIf** into 2-aza-1,3,5-triene **VIIf** and reorganization of the latter into dihydroazepine at treating with *t*-BuOK [23].
[d] Isolated in ~ 6% yield from polymerization products of 2-aza-1,3,5-triene **VIIf**.
[e] Yield of 2-aza-1,3,5-triene **VIIh.**

Thus, compound **VIa** (Scheme 1), the first member of the series of methoxy-substituted 1-aza-1,3,4-trienes, prepared from 1-lithio-1-methoxyallene (**IIa**), methyl isothiocyanate, and MeI, at moderate heating (30–40°C) and storage (under usual conditions and even in a freezer chamber) isomerized quantitatively into pyrrole **IIIa** and 2,3-dihydropyridine **IVa** in the ratio 2.2–2.5 : 1. Sometimes the heterocyclization of 1-aza-1,3,4-triene **VIa** starts spontaneously (practically at once after the removal of solvents from the reaction mixture on a rotary evaporator) and proceeds with a powerful exothermic effect that can be avoided if the solvent is removed in the presence, for example, of paraffin oil.

The attempt to shift the reaction to the side of formation of conjugated azatriene **VIIa** by adding (dropwise!) 1-aza-1,3,4-triene **VIa** to paraffin oil heated to 180–190°C resulted in the change of the ratio of cyclic products for benefit of 2,3-dihydropyridine **IVa (**from 25 to 54% in the mixture with C pyrrole **IIIa**). However we did not succeed to register (even in the NMR spectra) generated *in situ* thermodynamically unstable 2-aza-1,3,5-triene **VIIa**. It immediately cyclized into dihydropyridine **IVa**. At the addition of 1-aza-1,3,4-triene **VIa** to paraffin oil heated to 250–260°C the content of 2,3-dihydropyridine **IVa** grew to 58%, and that of pyrrole **IIIa** decreased respectively from 75 to 42%. Similar temperature effect on the ratio of heterocycles **IIIa** and **IVa** was also observed at the chromatography of azatriene **VIa** at different temperatures: The higher the temperature of the vaporizer and the column, the more the reaction was shifted to the side of the formation of 2,3-dihydropyridine **IVa** (up to 51–59% in the mixture with pyrrole **IIIa** whose content in these cases was 41–49%). At milder temperature mode of the chromatography the main heterocyclization product of 1-aza-1,3,4-triene **VIa** was always pyrrole **IIIa**.

1-Aza-1,3,4-triene **VIb** obtained from 1-lithio-1-methoxyallene (**IIa**) and ethyl isothiocyanate (Scheme 1), on the contrary, easily isomerized into 2-aza-1,3,5-triene **VIIb** (by NMR data), whose 6π-electrocyclization led to the formation of dihydropyridine **IVb**. Here pyrrole **IIIb** was the minor cyclic product (see the table). However also in this case it was not easy to stop the reaction at the stage of the formation of 2-aza-1,3,5-triene **VIIb**. For instance, 1-aza-1,3,4-triene **VIb** at storage in the freezer for a week approximately to 5% converted into purrole **IIIb** and nearly to 70%, into 2-aza-1,3,5-triene **VIIb** which partially (by ~20%) cyclized into dihydropyridine **IVb**. In the ^{1}H NMR spectrum of 1-aza-1,3,4-triene **VIb** after the

storage in the freezer for two weeks the main signals are those of 2,3-dihydropyridine **IVb** and 2-aza-1,3,5-triene **VIIb**. The intensity of signals of 1-aza-1,3,4-triene **VIb** and pyrrole **IIIb** is negligible.

Inasmuch as 2-aza-1,3,5-trienes attract independent interest (as linear precursors both of 2,3-dihydropyridines [4] and, for example, of 3*H*-azepines and 4,5-dihydro-3*H*-azepines [7]) we with especial attention investigated the [1,5]-sigmatropic rearrangement of the synthesized 1-aza-1,3,4-trienes **VI**. The best result that was attained up till now by the variation of the isomerization conditions of N-ethyl-substituted azatriene was a mixture of 1-aza-1,3,4-triene **VIb** and 2-aza-1,3,5-triene **VIIb** (in the ratio ~3 : 2) containing traces of pyrrole **IIIb** and 2,3-dihydropyridine **IVb**. For 1-aza-1,3,4-trienes **VIc, VId, VIf** the conditions were found of the isomerization into 2-aza-1,3,5-trienes excluding or minimizing the thermally induced competing heterocyclization reactions of 1-aza-1,3,4-trienes **VI** into pyrroles **III** and of 2-aza-1,3,5-trienes **VII** into 2,3-dihydropyridines **IV**. The isomerization process was monitored by NMR spectroscopy.

Short (10–15 min) heating to 65–67°C of 1-aza-1,3,4-triene **VIc** obtained from 1-lithio-1-methoxyallene (**IIa**) and isopropyl isothiocyanate (Scheme 1) results in 2-aza-1,3,5-triene **VIIc** containing an impurity of 10% of pyrrole **IIIc**. At uncontrolled isomerization of 1-aza-1,3,4-triene **VIc** gives usually a mixture of 15% of pyrrole **IIIc** and 85% of 2,3-dihydropyridine **IVc** (see the table).

The isomerization of 1-aza-1,3,4-triene **VId** (Scheme 1) synthesized from 1-lithio-1-methoxyallene (**IIa**) and *sec*-butyl isothiocyanate into 2-aza-1,3,5-triene **VIId** was carried out under similar conditions (~60°C, 12–15 min) and also to 90%. The impurity of pyrrole **IIId** did not exceed 10%.

Materially pure 2-aza-1,3,5-triene **VIIf** (Scheme 1) [99% with traces (<1%) of pyrrole **IIIf**] was obtained in a quantitative yield by removing the solvents at the bath temperature not exceeding 25°C first on a rotary evaporator and then is a vacuum of oil pump (at 1 mm Hg) followed by the storage of the sample at –15°C (freezer chamber) for 18 h.

The transition of 1-aza-1,3,4-triene **VIg** obtained by adding 1-lithio-1-methoxyallene (**IIa**) to cyclohexyl isothiocyanate with the subsequent S-alkylation of the adduct with ethyl iodide into a stable structural isomer **VIIg** (Scheme 1) occurs in keeping with calculation data (HF/6-31G**) [19] in a sigle stage by [1,5]-migration of hydrogen through the flattening of the molecule skeleton (E_{act} 141.9 kJ mol^{-1}). Experimentally isolated 2-aza-1,3,5-triene **VIIg** contained an impurity of pyrrolea **IIIg** and 1-aza-1,3,4-triene **VI**g. The corresponding 2,3-dihydropyridines **IV** in the spectra of the isomerization products of compounds **VIc, IVd**, **VIf** were not identified.

At heating (in the course of removing the solvents on a hot water bath, at distillation, chromatography etc.) 1-aza-1,3,4-trienes **VIb–VId**, **VIg** or their mixtures with 2-aza-1,3,5-trienes **VII**, as was already mentioned, suffer quantitative heterocyclization with the predominant formation of 2,3-dihydropyridines **IV** (see the table). It unexpectedly turned out that the polymerization and/or tarring rate of 2-aza-1,3,5-triene **VIIf** was considerably larger than its electrocyclization rate into 2,3-dihydropyridine **IVf**. As a result the latter was isolated in 6% yield. All attempts to minimize the thermally induced polymerization of 2-aza-1,3,5-triene **VIIf** were unsuccessful. The polymerization proceds with notable rate even during th removal of solvents from the reaction products on a rotary evaporator at 50–60°C appearing in the growth of the viscosity of the oily substance and in the corresponding changes in the ^{1}H NMR spectrum. The same simple maintained at room temperature for 24 h practically lost the flowability, and in its ^{1}H NMR spectum only the unidentified signals of the polymer were present. At the short heating (for several seconds) in the flame of spirit lamp of the mixture with a little benzene of 2-aza-1,3,5-triene **VIIf** free of polymer (obtained by solvents removal at room temperature) a sharp temperature rise from 50 to 130°C was observed with boiling of the product (without external heating). However instead of expected 2,3-dihydropyridine **IVf**, the product of the exothermic electrocyclization of 2-aza-1,3,5-triene **VIIf** in this case also polymer was obtained whose formation was presumably related also to the low thermal stability of compound **IVf**.

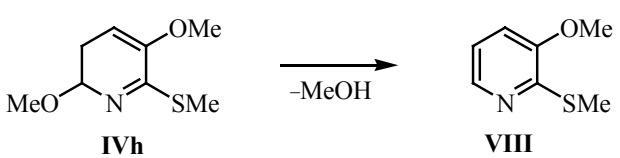
In contrast to compounds **VIf, VIg**, derivatives of cyclopentyl and cyclohexyl isothiocyanates respectively 1-aza-1,3,4-triene **VIe** obtained from 1-lithio-1-methoxyallene (**IIa**) and cyclopropyl isothiocyanate (Scheme 1), on the contrary, does not isomerize into the corresponding 2-aza-1,3,5-triene **VIIe** even at heating. As a result forms exclusively 1-cyclopropylpyrrole **IIIe** (see the table). The corresponding 2,3-dihydropyridine was not identified in NMR spectra.

The use in the reaction with 1-lithio-1-methoxy-allene (**IIa**) of methoxymethyl isothiocyanate gave an unexpect-

ed result. It turned out that after the alkylation of adduct **Vh** the formed 1-aza-1,3,4-triene **VIh** (Scheme 1) already under the conditions of the reaction at uncommonly low temperature (–70 × 0°C) for [1,5]sigmatropic rearrangements isomerized quantitatively into 2-aza-1,3,5-triene **VIIh** whose electrocyclization provided in high yield one more representative of previously unknown and unavailable 6-(alkylsulfanyl)-2,3-dihydropyridines, 2-methoxy-2,3-dihydropyridine **IVh** (see the table). The corresponding pyrrole **IIIh** was not identified among the reaction products. Moreover, dihydropyridine **IVh** was found to undergo very readily the aromatization with methanol liberation (Scheme 3) that occurred without catalyst at room temperature (1 month, conversion of compound **IVh** 85%). In the presence of hydrochloric acid the quantitative conversion of dihydropyridine **IVh** into previously unknown 2-(methylsulfanyl)-3-methoxypyridine (**VIII**) was attained in 1.5–2 h (Et_2O, ~30°C). It should be noted that no spontaneous or thermally induced aromatization of the other here described 2,3-dihydropyridines **IV** was observed.

Whereas the replacement of the hydrogen atom in methyl isothiocyanate by a heteroatomic substituent (methoxy group) favors the fast and quantitative isomerization of the obtained therefrom 1-aza-1,3,4-triene **VIh** into 2-aza-1,3,5-triene **VIIh** and thus completely "inhibiting" the pyrrole channel of compound **VIh** transformation (in the case of 1-aza-1,3,4-triene **VIa** the main reaction product is pyrrole **IIIa**, up to 75% in the mixture with 2,3-dihydropyridine **IVa**) (see the table), the analogous replacement of a hydrogen atom in the methyl group of ethyl isothiocyanate (for vinyloxy group) provides an opposite effect. Unlike 1-aza-1,3,4-triene **VIb** whose thermally induced conversion provides as the main product 2,3-dihydropyridine **IVb** [up to 80% in the mixture with pyrrole **IIIb** (see the table)], the distillation of 1-aza-1,3,4-triene **VIi** obtained from 1-lithio-1-methoxyallene (**IIa**) and 2-(vinyloxy)ethyl isothiocyanate (Scheme 1) afforded approximately equimolar mixture of 1-[2-(binyloxy)ethyl]pyrrole **IIIi** and 2-[(vinyloxy) methyl]-2,3-dihydropyridine **IVi**. This experiment shows that the introduction of the vinyloxy group into the ethyl isothiocyanate, on the contrary, essentially facilitates the closure of 1-aza-1,3,4-triene **VIi** obtained therefrom into the pyrrole ring hence partially "inhibiting" the [1,5]-H shift. The presence in compounds **IIIi, IVi, VIi** of the highly reactive vinyloxy group essentially extends their synthetic potential [24], in particular as monomers (it is well known [25] that the most important application field for vinyl ethers is the industry of synthetic polymers).

Scheme 3.



IVh **VIII**

The effect of the structure of alkoxyallene **Ia, Ib** on the ratio of cyclic products proved to be less important than the effect of isothiocyanates structure, although in going from 1-aza-1,3,4-triene **VIa** obtained from methyl isothiocyanate and 1-lithio-1-methoxy-allene (**IIa**) to 1-aza-1,3,4-trienes **VIj**, **VIk** prepared from methyl isothiocyanate and 1-(*tert*-butoxy)-1-lithioallene (**IIb**) the content of pyrroles in the mixture with 2,3-dihydropyridines somewhat grew, from 70–75% (for pyrrole **IIIa**) to 83–88% (for pyrroles **IIIj**, **IIIk**) (see the table).

By an example of α-lithiated methoxyallene **IIa** and methyl isothiocyanate the effect was studied on the overall yield and the products ratio of reaction conditions [the solvent nature (THF–hexane, Et_2O–hexane), the order (the isothiocyanate addition to the solution of lithiated allene, the solution of lithiated allene addition to the isothiocyanate solution) and velocity of reagents introduction (by one portion, by small portions, dropwise) temperature and duration of various stages of the process] and of the workup of the reaction mixture (with water with ice, cold water or saturated solution of ammonium chloride; extraction of reaction products with pentane and/or ether, drying with K_2CO_3 or $MgSO_4$). The strong influence of reaction conditions on its result was not observed.

Two most probable cyclization routes of 1-aza-1,3,4-trienes **VI** into pyrroles **III** are postulated in [4, 11]: through the protonated form of 3-alkoxy-1-aza-1,3,4-triene (Scheme 4) or through the carbenoid cyclic intermediate (Scheme 5).

The formation of pyrrole structures through the protonation of 3-alkoxy-1-aza-1,3,4-triene **VI** recently was confirmed by calculations [19]. The most favorable for the cyclization is the proton attack on the π-orbital localized on the C_β–C_γ centers of the allene fragment. This results in the activation of the *p*-orbital of atom C_γ and its coupling with the π-orbital of the nitrogen atom. The calculations demonstrate that whereas the [1,5]-H shift (**VIa**)→(**VIIa**) and the subsequent electrocyclic rearrangement of 2-aza-1,3,5-triene **VIIa** into 2,3-dihydropyridine **IVa** have activation energies

114.3 and 90.1 kJ mol^{-1} respectively, the formation of the pyrrole ring **IIIa** through the protonated structures **A** and **B** occurs with the activation barrier 44.9 kJ mol^{-1} (HF/6-31G**).

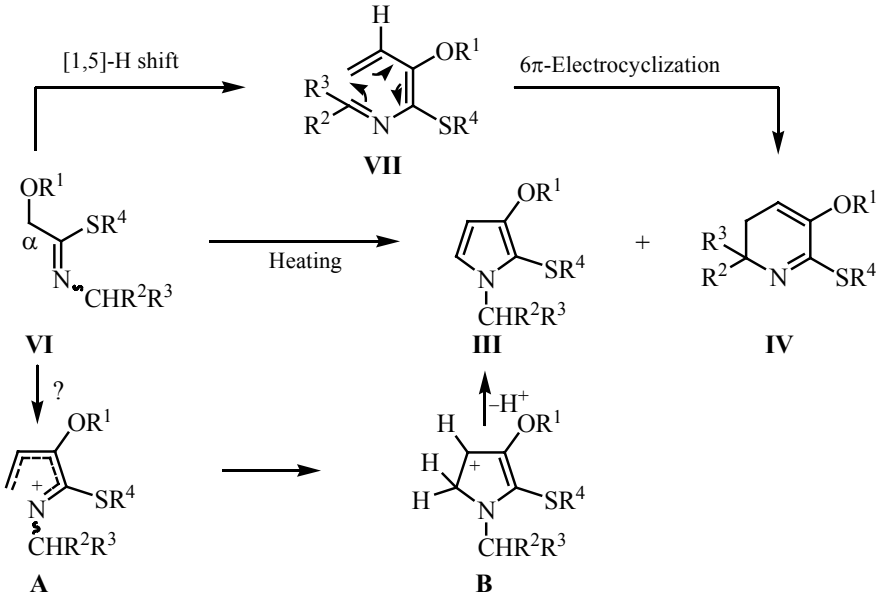
Obviously, the presence of an alkoxy group in 1-aza-1,3,4-triene **VI** should facilitate the protonation due to the stabilization of the carbenium center with oxygen atom in agreement with the fact that neither from 1-lithio-1-methylallene nor from 3-(*tert*-butyl)-1-lithio-allene under identical conditions pyrroles were formed. The only reaction products in these cases were the corresponding 2,3-dihydropyridines [26, 27] (independent of the structure of aliphatic isothiocyanate) and/or pyridines [27]. Yet this mechanism has not up till now obtained a reliable experimental proof.

The second hypothetical route of the [1,5]-cyclization of 1-aza-1,3,4-trienes **VI** into pyrroles **III** assumes a direct nucleophilic attack of the nitrogen atom on the terminal carbon atom of the allene fragment leading to the formation of σ-bond C–N and a cyclic carbine **C** (Scheme 5). The activation energy of this stage for 1-aza-1,3,4-triene **VIa** equals 96.2 kJ mol^{-1} [28] and is ~2 times greater than the activation barrier (44.9 kJ mol^{-1}) [19] of the pyrrole ring **IIIa** formation through the protonated structures (Scheme 4). [1,2]-Hydride shift in intermediate **C** occurs with overcoming the activation barrier of 61.5 kJ mol^{-1} (transition state **D**). The overall heat balance of the reaction attains 156.6 kJ mol^{-1} [28].

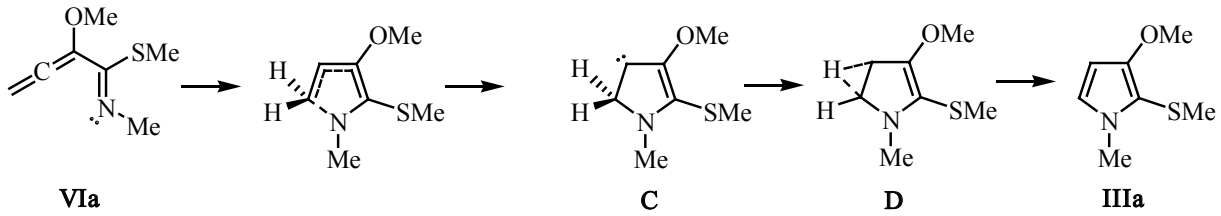
Note that in [29] quantum-chemical methods were applied to the study of various mechanisms of the opening of pyrrole ring at the thermolysis of unsubstituted 1*H*-pyrrole [30], and it was established that the most preferable was the inverted mechanism of the direct nucleophilic attack (Scheme 6).

We developed a simple and convenient method of isolation of the synthesized pyrroles and dihydropyridines in the individual state consisting in the treatment of their mixture first with pentane and then with the cold ~1 M

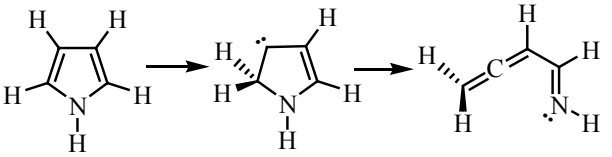
Scheme 4.



Scheme 5.



Scheme 6.



solution of HCl. After the separation of layers and the removal of solvent from the organic phase pyrrole **III** is obtained. Dihydropyridine **IV** is extracted from the water phase after the neutralization of the latter with the concn. solution of KOH. Compounds **III** and **IV** were isolated in good overall yields (up to 85%). Their composition and structure were confirmed by elemental analysis, IR, ^{1}H, ^{13}C NMR, and mass spectra [31].

Hence we demonstrated for the first time that alkoxyallenes and aliphatic isothiocyanates are fundamentally new starting compounds for the simple and convenient synthesis of previously unknown 2-(alkylsulfanyl)-3-alkoxypyrroles and 6-(alkylsulfanyl)-5-alkoxy-2,3-dihydropyridine in high yield in one preparative stage. The reported experimental data allow a conclusion that the approach we found and the synthetic method based thereon for preparation of versatile pyrroles and 2,3-dihydropyridines proceeding from isothiocyanates and α-lithiated alkoxyallenes possess the general character and wide preparative prospects.

EXPERIMENTAL

IR spectra were recorded on spectrophotometers Bruker IFS-25, Perkin Elmer-283, and Specord 75-IR from thin layers, in pellets with KBr, and in films obtained by evaporation of CCl_4 solutions. NMR spectra were registered on spectrometers Bruker DPX-400 [400.13 (^{1}H) and 100.62 MHz (^{13}C)], Bruker AC-300 [300 (^{1}H) and 75 MHz (^{13}C)], Bruker DPX-250 [250 (^{1}H) and 62.9 MHz (^{13}C)] from ~5–10% solutions in $CDCl_3$, internal reference HMDS, and Varian EM-390 [90 MHz (^{1}H)] for ~20% solutions in CCl_4, internal reference TMS. To prove the structure and to provide the complete assignments of signals in ^{1}H and ^{13}C NMR spectra a series of 2D NMR experiments was carried out (COSY-^{1}H, HSQC-^{13}C, and HMBC-^{13}C) on a spectrometer Bruker AV-400. GLC analysis was performed on a chromatograph Varian 3400 (flame-ionization detector, capillary column 15 m × 0.53 mm, stationary phase DB-5 1.5 μm, carrier gas nitrogen). Mass spectra were measured on spectrometer Jeol AX 505 (accelerating voltage 3 kV, emission current 100 mA, ionizing electrons energy 70 eV, carrier gas helium).

All operations were carried out under nitrogen or argon atmosphere. Cooling was performed with liquid nitrogen. THF was purified by dispersed KOH (~50 g l^{-1}) and distillation over $LiAlH_4$ or sodium in the presence of benzophenone under the inert atmosphere. Methoxyallene (**Ia**) and *tert*-butoxyallene (**Ib**) were synthesized by procedure [13], isopropyl, *sec*-butyl, 2-(vinyloxy)ethyl, cyclopropyl, cyclopentyl, and cyclohexyl isothiocyanates were obtained by condensation of the corresponding triethylammonium N-monosubstituted dithiocarbamates with acetic anhydride or acetyl chloride [4], methoxymethyl isothiocyanate, by boiling methoxy(chloro)methane with potassium thiocyanate in pentane [32]. Butyllithium (1.6 and 2.5 M hexane solutions) and the other reagents and solvents used in the study were commercial products. The individuality of initial reagents was checked by NMR spectra. The lithiation was predominantly performed using 1.6 M hexane solution of BuLi and only in special cases (marked in the description of the experiment) 2.5 M solution was applied. The yields of all reaction products were calculated on the theoretically possible with respect to isothiocyanate.

Methyl-*N*-methyl-2-methoxybuta-2,3-dienimidothioate (VIa), 1-methyl-2-(methylsulfanyl)-3-methoxypyrrole (IIIa), and 6-(methylsulfanyl)-5-methoxy-2,3-dihydropyridine (IVa). *a*. To a solution of 104 mmol of BuLi in 65 ml of hexane and 65 ml of THF at –90°C was added by one portion 9.1 g (130 mmol) of allene **Ia** (the reaction proceeded with powerful exothermic effect and required efficient cooling). The reaction mixture was stirred for 10 min at –65...–60°C, cooled to –100°C and a solution of 7.35 g (100.7 mmol) methyl isothiocyanate in ~20 ml of THF was added by one portion. The temperature quickly raised to –60°C (at cooling). The reaction mixture was stirred for 10 min at –65...–60°C and to the formed bright yellow dispersion was added 22 g (154.9 mmol) of MeI. After warming the reaction mixture to 0°C it was treated with 100 ml of ice water at vigorous stirring. The reaction product was extracted into pentane (4 × 50 ml), the extracts were thrice washed with water and dried with K_2CO_3. The solvent was divided in two equal parts.

From the first part the solvent was removed on a rotary evaporator at the bath temperature not exceeding 30°C. We obtained as a residue 7.8 g (99%) of 1-aza-1,3,4-triene **VIa** (mixture of *E*- and *Z*-isomers). IR spectrum (thin

layer), ν, cm^{-1}: 436, 589, 622, 667, 699, 903, 958, 975, 998, 1050, 1088, 1140, 1173, 1211, 1267, 1310, 1396, 1435, 1448, 1459, 1547, 1618, 1946 (=C=), 2771, 2831, 2861, 2919, 2957, 3005, 3214, 3289. ^{1}H NMR spectrum (90 MHz, CCl_4), δ, ppm, ratio of *E*- and *Z*-isomers ~2 : 1: 2.20 s, 2.35 s (3H, SMe), 3.17 s, 3.25 s (3H, NMe), 3.45 s (3H, OMe), 5.63 s (2H, CH_2=). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm, ratio of *E*- and *Z*-isomers ~1 : 1: 2.27 s, 2.43 s (3H, SMe), 3.327 s, 3.331 s (3H, NMe), 3.46 s, 3.51 s (3H, OMe), 5.69 s, 5.74 s (2H, CH_2=). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 12.84, 15.13 (SMe), 40.86, 41.38 (NMe), 55.86, 56.18 (OMe), 93.06, 93.56 (CH_2=), 128.21, 131.95 (O–C=), 158.43, 160.08 (C=N), 198.81, 200.52 (=C=). ^{13}C NMR spectrum (100 MHz, C_6D_6, –10°C), δ, ppm, *E*-isomer: 13.48 (SMe), 41.97 (NMe), 56.37 (OMe), 94.52 (CH_2=), 129.14 (O–C=), 155.72 (C=N), 199.60 (=C=); *Z*-isomer: 14.96 (SMe), 40.77 (NMe), 56.50 (OMe), 93.56 (CH_2=), 132.27 (O–C=), 161.66 (C=N), 200.27 (=C=).

To the second part of the organic fraction 40 ml of paraffin oil was added, and the solvent was removed on the rotary evaporator at the bath temperature 60–70°C. The residue was distilled in a vacuum to obtain 6.25 g (79%) of the mixture of pyrrole **IIIa** and 2,3-dihydropyridine **IVa** in the ratio ~7 : 3 (according to ^{1}H NMR and GLC data), bp 115–117°C (15 mm Hg), n_D^{20} 1.5515. The distillate was dissolved in 50 ml of pentane, the solvent was vigorously shaken with cold (0°C) 1 M hydrochloric acid (20% excess), and the layers were separated. The water layer was extracted with pentane (4 × 50 ml), the combined organic fraction was treated with a small quantity of concn. solution of KOH (till neutral reaction), the layers were separated. The organic fraction was dried with K_2CO_3, the solvents were removed under a reduced pressure to obtain in the residue pyrrole **IIIa**. Yield 4.2 g (53%), content of the main substance 99% (by GLC data), colorless fluid, bp 84–85°C (2 mm Hg), n_D^{20} 1.5470. At room temperature and on cooling pyrrole **IIIa** crystallized. IR spectrum (film), ν, cm^{-1}: 700, 970, 1100, 1320, 1370, 1400, 1410, 1460, 1550, 2830, 2920–2940, 3000, 3100–3120. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 2.14 s (3H, SMe), 3.59 s (3H, NMe), 3.79 s (3H, OMe), 5.82 d (1H, 4-CH=, ^3J 3.2 Hz), 6.53 d (1H, 5-CH=, ^3J 3.2 Hz). ^{13}C NMR spectrum (J mod, 100 MHz, $CDCl_3$), δ, ppm: 20.32 (SMe), 33.83 (NMe), 58.09 (OMe), 94.32 (4-CH=), 106.19 (2-C=), 120.99 (5-CH=), 151.29 (3-C=). For correct assignment of signals in the ^{13}C NMR spectrum 2D HMBC NMR experiment was performed. Mass spectrum, *m/z* (I_{rel}, %): 157 (100) $[M]^{+\cdot}$, 142, 98, 81, 73, 53, 42, 39. Found, %: C 53.54; H 7.36; N 8.41; S 20.13. $C_7H_{11}NOS$. Calculated, %: C 53.47; H 7.05; N 8.91; S 20.39. *M* 157.23.

The "acidic" water layer was treated with concn. KOH, extracted with ether (4 × 50 ml), the solution was dried with K_2CO_3 and on removing the solvent under a reduced pressure 2,3-dihydropyridine **IVa** was obtained. Yield 1.8 g (23%), nearly colorless fluid, bp 90–93°C (2 mm Hg), n_D^{20} 1.5444. IR spectrum (thin layer), ν, cm^{-1}: 540, 690, 790, 800, 960–970, 1025, 1050, 1100, 1170, 1210, 1250, 1310, 1350, 1400–1430–1450, 1570, 1640, 1690, 2830, 2900, 2930, 3000, 3070, 3140. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 2.19 m (2H, 3-CH_2), 2.26 s (3H, SMe), 3.56 m (2H, NCH_2), 3.58 s (3H, OMe), 5.10 t (1H, 4-CH=, ^3J 4.7 Hz). ^{13}C NMR spectrum (*J* mod, 100 MHz, $CDCl_3$), δ, ppm: 11.42 (SMe), 21.14 (3-CH_2), 48.12 (NCH_2), 54.48 (OMe), 98.83 (4-CH=), 147.85 (5-C=), 161.67 (6-C=). Mass spectrum, *m/z* (I_{rel}, %): 157 (100) $[M]^{+\cdot}$, 142, 124, 114, 95, 80, 69, 55, 41, 39, 27, 26, 18. Found, %: C 53.22; H 7.40; N 8.65; S 20.15. $C_7H_{11}NOS$. Calculated, %: C 53.47; H 7.05; N 8.91; S 20.39. *M* 157.23.

b To a solution of 112 mmol of BuLi in 70 ml of hexane and 80 ml of THF while stirring at –90°C was added in one portion cooled solution of 9.1 g (130 mmol) of allene **Ia** in 20 ml of THF. The reaction mixture was stirred for 5 min at –65...–60°C, cooled to –90°C and quickly was added thereto the solution of 7.35 g (100.7 mmol) of methyl isothiocyanate in 20 ml of THF. The reaction mixture was stirred for 5 min at –60°C, 22 g (154.9 mmol) of MeI was added, and the cooling was removed. After natural warming to 5°C the mixture was heated for 1 h at 30–40°C, then it was cooled and treated with the saturated water solution of NH_4Cl (at vigorous stirring). The reaction products were extracted into ether (4 × 50 ml), the extracts were dried with $MgSO_4$, the solvents were removed on a rotary evaporator at the bath temperature 30–40°C; the last drops of solvent were removed at the bath temperature ~70°C and cooling of the collector with liquid nitrogen. After removing the water bath the residue (13.25 g, 84%) unexpectedly started to boil (a vigorous exothermic reaction began), it was quickly cooled with liquid nitrogen. Analysis of crude product by GLC and NMR methods showed that it contained pyrrole **IIIa** (67%) and 2,3-dihydropyridine **IVa** (20%). By distillation in a vacuum 9.52 g (60%) of a mixture of compounds **IIIa** and **IVa** was isolated, bp ~75°C (~0.5 mm Hg), content of main substances 91% (by GLC data). The products

were separated with the use of dilute hydrochloric acid as described above.

c. To a solution of 10 g (137 mmol) methyl isothiocyanate in 50 ml of THF cooled to −50°C was added with a syringe in three portions a solution of 1-lithio-1-methoxyallene (**IIa**) prepared in another flask in a nitrogen flow from 120 mmol of BuLi in 75 ml of hexane and 9 g (128.6 mmol) of allene **Ia** in 50 ml of THF at −80°C. The solution turned into a bright yellow dispersion. The reaction mixture was allowed to warm to –35°C and 20 g (140.8 mmol) of MeI was added. After 30 min (when the temperature rose to 15°C) to the reaction mixture (transparent dark-brown solution) was poured in 150 ml of ice water. The reaction products were extracted into pentane (2 × 50 ml), the extracts were dried with K_2CO_3. The solvents were removed at a reduced pressure, the residue (17.5 g, 93%) was distilled in a vacuum. We obtained 12.4 g (66%) of a mixture of pyrrole **IIIa** and 2,3-dihydropyridine **IVa** in a ratio 3.3 : 1. The products were separated with the use of dilute hydrochloric acid as described above.

Methyl-2-methoxy-*N*-ethylbuta-2,3-dienimidothioate (VIb), 1-(methylsulfanyl)-2-methoxy-*N*-ethyl-idenebuta-1,3-dien-1-amine (VIIb), 2-(methylsulfanyl)-3-methoxy-1-ethylpyrrole (IIIb), 2-methyl-6-(methylsulfanyl)-5-methoxy-2,3-dihydropyridine (IVb). *a*. To a solution of 59.2 mmol of BuLi in 37 ml of hexane and 50 ml of THF at –100°C was added 4.5 g (64.3 mmol) of allene **Ia**. The temperature rose to –75°C. The reaction mixture was stirred for 10 min at –80...–75°C, cooled to –95°C, and 4.35 g (50 mmol) of ethyl isothiocyanate was added. The temperature rose to –65°C. The reaction mixture was stirred for 15 min at –65...–60°C (golden-yellow dispersion), 16 g (112.7 mmol) of MeI was added, the temperature was allowed to rise to 10°C, then the mixture was cooled to –10°C , and 80 ml of water solution of NH_4Cl was added at vigorous stirring. The reaction products were extracted into ether (3 × 20 ml), the extracts were washed with water (3 × 10 ml), and dried with $MgSO_4$. On removing the solvents at a reduced pressure and the bath temperature 20–30°C 8.6 g (100%) of thick brown fluid was obtained, n_D^{20} 1.4982 (mixture of 93% of 1-aza-1,3,4-triene **VIb**, 6% of 2-aza-1,3,5-triene **VIIb**, and 1% of pyrrole **IIIb** according to ^{1}H NMR data). ^{1}H NMR spectrum of 1-aza-1,3,4-triene **VIb** (mixture of *E*- and *Z*-isomers) (400 MHz, $CDCl_3$), δ, ppm: 1.22 t, 1.30 t (3H, $NCH_2C\underline{H}_3$, ^3J 7.2 Hz), 2.29 s, 2.43 s (3H, SMe), 3.46 s, 3.52 s (3H, OMe), 3.56 m (2H, NCH_2), 5.67 s, 5.74 s (2H, CH_2=). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 11.18, 13.44 (SMe), 13.50, 14.61 (Me), 46.44, 46.85 (NCH_2), 54.15, 54.44 (OMe), 91.34, 91.70 (CH_2=), 126.13, 126.75 (O–C=), 154.60, 156.49 (C=N), 197.00, 198.49 (=C=).

b. To a solution of 104 mmol of BuLi in 65 ml of hexane and 80 ml of THF at –100°C was added 9 g (128.6 mmol) of allene **Ia** in 10 ml of THF. The temperature rose to –50°C. The reaction mixture was stirred for 10 min at –55...–50°C, cooled to–100°C, and 9 g (103.4 mmol) of ethyl isothiocyanate was added. After the warming of the mixture to –55°C to the formed bright yellow dispersion was added 21.6 g (152.1 mmol) of MeI. At 0°C the reaction mixture was treated with 150 ml of cold water at vigorous stirring. The reaction products were extracted into pentane (2 × 50 ml), extracts were dried with K_2CO_3, then solvents were removed on the rotary evaporator at the bath temperature 60–70°C. Yield of reaction products 16.1 g (91%), content of the main products 98%: 21% of pyrrole **IIIb**, 77% of 2,3-dihydropyridine **IVb** (by GLC data). No signals of azatrienes **VIb** and **VIIb** were observed in the ^{1}H NMR spectrum. After separation of the reaction products like described above and the removal of the solvent from the organic fraction we obtained 3.65 g (21%) of pyrrole **IIIb**, content of the main substance 97% (by GLC data), light fluid, bp 82–83°C (1 mm Hg), n_D^{20} 1.5322. IR spectrum (thin layer), ν, cm^{-1}: 470, 600, 650, 700, 800, 940, 960, 980, 1035, 1080, 1090, 1110, 1170, 1220, 1250, 1330, 1380, 1400, 1450, 1460, 1540, 1640, 1680, 1710, 2830, 2940, 2975, 3100, 3120. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.33 t (3H, $NCH_2C\underline{H}_3$, ^3J 7.2 Hz), 2.14 s (3H, SMe), 3.77 s (3H, OMe), 3.97 q (2H, NCH_2, ^3J 7.2 Hz), 5.84 d (1H, 4-CH=, ^3J 3.2 Hz), 6.57 d (1H, 5-CH=, ^3J 3.2 Hz). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 16.92 (Me), 20.64 (SMe), 41.72 (NCH_2), 58.32 (OMe), 95.04 (4-CH=), 105.00 (2-C=), 119.40 (5-CH=), 151.64 (3-C=). Found, %: C 56.23; H 7.40; N 8.09; S 18.58. $C_8H_{13}NOS$. Calculated, %: C 56.10; H 7.65; N 8.18; S 18.72.

From the "acidic" layer 11.56 g (65%) of 2,3-dihydropyridine **IVb** was isolated, content of the main substance 98% (by GLC data), light fluid. After distillation in a vacuum 9 g (53%) of compound **IVb** was obtained, content of the main substance 99% (by GLC data), bp 91–92°C (1 mm Hg), n_D^{20} 1.5376. IR spectrum (thin layer), ν, cm^{-1}: 550, 640, 690, 710, 780, 890, 920, 960, 995, 1010, 1030, 1040, 1060, 1100, 1140, 1170, 1185, 1200, 1240, 1265, 1290, 1300, 1340, 1370, 1400, 1420,

1445, 1450, 1570, 1640, 2830, 2870, 2920, 2960, 3000, 3060, 3130. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.29 d (3H, 2-Me, ^3J 6.8 Hz), 1.96, 2.00, 2.03 d.d.d (2H, 3-CH_2, ^3J 17.6, 3.8, ^2J 12.01 Hz), 2.29 s (3H, SMe), 3.58 m (1H, NCH), 3.58 s (3H, OMe), 5.02 d.d (1H, 4-CH=, ^3J 5.4, 3.8 Hz). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 11.43 (SMe), 21.98 (3-CH_2), 28.58 (Me), 53.68 (NCH), 54.68 (OMe), 98.09 (4-CH=), 147.98 (5-C=), 160.01 (6-C=). Found, %: C 55.57; H 7.74; N 7.81; S 18.79. $C_8H_{13}NOS$. Calculated, %: C 56.10; H 7.65; N 8.18; S 18.72.

Methyl-*N*-isopropyl-2-methoxybuta-2,3-dienimidothioate (VIc), 1-(methylsulfanyl)-*N*-(1-methylethylidene)-2-methoxybuta-1,3-dien-1-amine (VIIc), 1-isopropyl-2-(methylsulfanyl)-3-methoxypyrrole (IIIc), and 2,2-dimethyl-6-(methylsulfanyl)-5-methoxy-2,3-dihydropyridine (IVc). *a*. To a solution of 64 mmol of BuLi in 40 ml of hexane and 70 ml of THF at –100°C was added 6 g (85.7 mmol) of allene **Ia**, the mixture was stirred for 10 min at –70...–60°C, cooled again to –100°C, and 5.05 g (50 mmol) of isopropyl isothiocyanate was added (the temperature rose to –30°C). The reaction mixture was stirred for 15 min at –35...–30°C, cooled to –80°C, and 16 g (112.7 mmol) of MeI was added (the temperature rose to 20°C within 25 min). The mixture was cooled to –80°C, and 100 ml of saturated water solution of NH_4Cl was added at vigorous stirring. The reaction products were extracted into ether (3 × 50 ml), the extracts were washed with water (3 × 30 ml), and dried with $MgSO_4$. The solvents were removed on the rotary evaporator at room temperature to obtain 1-aza-1,3,4-triene **VIc** (mixture of *E*- and *Z*-isomers). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm, major isomer: 1.18 d [6H, CH(C$\underline{H}_3$)$_2$, ^3J 6.3 Hz], 2.41 s (3H, SMe), 3.50 s (3H, OMe), 3.92 septet (1H, NCH, ^3J 6.3 Hz), 5.71 s (2H, CH_2=); minor isomer: 1.11 d [6H, CH(C$\underline{H}_3$)$_2$, ^3J 6.1 Hz], 2.27 s (3H, SMe), 3.42 s (3H, OMe), 3.97 septet (1H, NCH, ^3J 6.1 Hz), 5.65 s (2H, CH_2=); isomers ratio ~1.3 : 1.

On removing the main part of solvents on the rotary evaporator at room temperature the reaction product was evacuated for 5 min at the bath temperature ~60°C, and then for 15 min in a vacuum of an oil pump (7 mm Hg). We obtained 9.06 g (98%) of light-brown fluid liquid containing according to ^{1}H NMR data, 89% of 2-aza-1,3,5-triene **VIIc** and 11% of pyrrolea **IIIc**. 1-Aza-1,3,4-triene **VIc** and 2,3-dihydropyridine **IVc** were not identified in the reaction products. ^{1}H NMR spectrum of compound **VIIc** (300 MHz, $CDCl_3$), δ, ppm: 1.78 s, 1.96 s [6H, $(CH_3)_2$C=], 2.06 C (3H, SMe), 3.52 s (3H, OMe), 4.78 d.d (1H, CH_2=, ^3J 10.8, ^2J 2.0 Hz), 5.06 d.d (1H, CH_2=, ^3J 17.1, ^2J 2.0 Hz), 5.80 d.d (1H, CH=, ^3J 17.1, 10.8 Hz).

After 3 min of evacuation at 60°C the reaction product contained 70% of 2-aza-1,3,5-triene **VIIc**, 30% of nonisomerized 1-aza-1,3,4-triene **VIc**, and traces of pyrrole **IIIc**. Short heating of the reaction products by the burner flame resulted in a mixture of pyrrole **IIIc** and 2,3-dihydropyridine **IVc** in the ratio ~1 : 9.

b. To a solution of 104 mmol of BuLi in 65 ml of hexane and 80 ml of THF at –100°C was added 9.69 g (138.4 mmol) of allene **Ia**, the temperature was allowed to rise to −50°C (within 5–7 min), the mixture was cooled again to –100°C, and 10.3 g (102 mmol) of isopropyl isothiocyanate was added (the temperature rose to –10°C). The mixture was cooled to –50°C, 22.8 g (160.6 mmol) of MeI was added (the temperature rose to 5°C within 10 min), the reaction mixture was again cooled to–30°C and it was treated with cold water at vigorous stirring. The reaction products were extracted with pentane (2 × 50 ml) and ether (2 × 50 ml), the extracts were dried with K_2CO_3. The solvents were removed on a rotary evaporator to obtain 17.64 g (94%) of 2-aza-1,3,5-triene **VIIc** with an impurity of pyrrole **IIIc** (by the data of ^{1}H NMR). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.89 s, 2.07 s [6H, $(CH_3)_2$C=], 2.17 s (3H, SMe), 3.63 s (3H, OMe), 4.90 d.d (1H, CH_2=, ^3J 10.8, ^2J 2.0 Hz), 5.18 d.d (1H, CH_2=, ^3J 17.1, ^2J 2.0 Hz), 5.91 d.d (1H, CH=, ^3J 17.1, 10.8 Hz). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 12.50 (SMe), 20.92, 27.53 [($\underline{C}H_3$)$_2$C=], 58.15 (OMe), 109.42 (CH_2=), 126.24 (CH=), 134.00 (S−C=), 137.82 (O−C=), 173.68 (C=N).

c. To a solution of 104 mmol of BuLi in 65 ml of hexane and 80 ml of THF at –100°C was added 9.4 g (134.3 mmol) of allene **Ia**, the temperature was allowed to rise to −60°C, the mixture was cooled again to –100°C, and 10.4 g (103 mmol) of isopropyl isothiocyanate was added (the temperature rose to –50°C). The reaction mixture was stirred for 15 min at –65 × –60°C (light-brown dispersion), the cooling was removed, and at –30°C 20.6 g (145.1 mmol) of MeI was added. The temperature rose to 5°C. The reaction mixture was stirred at this temperature for 15 min and treated with cold water. The reaction products were extracted with pentane (2 × 50 ml) and ether (2 × 50 ml), the extracts were dried with K_2CO_3. On removing the solvents on the rotary evaporator 17 g

(89%) of brown fluid was obtained containing according to the ^{1}H NMR data predominantly 2-aza-1,3,5-triene **VIIc** with an impurity of pyrrole **IIIc**. The vacuum distillation furnished 14 g (73%) of products of the same composition with the admixture of 2,3-dihydropyridine **IVc** (according to the ^{1}H NMR data), bp 80–83°C (0.5 mm Hg). The distillate was heated for several seconds in the flame of a burner to ~100°C, then the exothermic heterocyclization started. A mixture was obtained of practically pure 2,3-dihydropyridine **IVc** (main component) and pyrrole **IIIc** (according to the ^{1}H NMR data); overall content 96% (by GLC data). The products were separated with the help of hydrochloric acid as described above. From the organic fraction 2 g (11%) of pyrrolea **IIIc** was isolated, content of the main substance 98% (by GLC data), bp ~80°C (0.5 mm Hg), mp 34°C (EtOH). IR spectrum (KBr), ν, cm^{-1}: 590, 620, 650, 735, 870, 955, 960, 1035, 1065, 1100, 1130, 1170, 1230, 1260, 1330, 1360, 1400, 1410, 1460, 1540, 2830, 2870, 2930, 2965, 3110, 3120. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 1.33 d [6H, $CH(C\underline{H}_3)_2$, ^3J 6.8 Hz], 2.12 s (3H, SMe), 3.75 s (3H, OMe), 4.70 septet (1H, NCH, ^3J 6.8 Hz), 5.85 d (1H, 4-CH=, ^3J 3.3 Hz), 6.60 d (1H, 5-CH=, ^3J 3.3 Hz). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ, ppm: 20.36 (SMe), 23.21 [$CH(\underline{C}H_3)_2$], 46.32 (NCH), 57.60 (OMe), 94.30 (4-CH=), 105.00 (2-C=), 115.68 (5-CH=), 150.84 (3-C=). Found, %: C 58.31; H 8.52; N 7.45; S 17.30. $C_9H_{15}NOS$. Calculated, %: C 58.34; H 8.16; N 7.56; S 17.31.

From the "acidic" fraction 2,3-dihydropyridine **IVc** was obtained, after distillation 7.7 g (40%), content of the main substance 96% (by GLC data), bp ~115°C (15 mm Hg), n_D^{20} 1.5260. IR spectrum (thin layer), ν, cm^{-1}: 480, 555, 600, 690, 720, 750, 790, 870, 890, 950, 960, 1000, 1030, 1070, 1125, 1170, 1190, 1220, 1240, 1250, 1300, 1340, 1350, 1370, 1400, 1420, 1450, 1460, 1580, 1650, 2830, 2860, 2930, 2970, 3000, 3060, 3140. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.17 s [6H, 2-$C(CH_3)_2$], 2.20 s (3H, SMe), 2.20 d (2H, 3-CH_2, ^3J 4.8 Hz), 3.55 s (3H, OMe), 4.88 t (1H, 4-CH=, ^3J 4.8 Hz). ^{13}C NMR spectrum (J mod, 100 MHz, $CDCl_3$), δ, ppm: 10.94 (SMe), 28.13 [2-$C(\underline{C}H_3)_2$], 33.44 (3-CH_2), 54.11 (OMe), 54.95 [2-$\underline{C}(CH_3)_2$], 96.16 (4-CH=), 146.57 (5-C=), 157.27 (6-C=). Found, %: C 58.53; H 8.19; N 7.50; S 17.12. $C_9H_{15}NOS$. Calculated, %: C 58.34; H 8.16; N 7.56; S 17.31.

Methyl-*N*-(*sec*-butyl)-2-methoxybuta-2,3-dienimidothioate (VId), N-(1-methylpropylidene)-1-(methylsulfanyl)-2-methoxybuta-1,3-dien-1-amine (VIId), 1-(*sec*-butyl)-2-(methylsulfanyl)-3-methoxypyrrole (IIId) and 2-methyl-6-(methylsulfanyl)-5-methoxy-2-ethyl-2,3-dihydropyridine (IVd). *a*. To a solution of 64 mmol of BuLi in 40 ml of hexane and 70 ml of THF at –100°C was added 6.1 g (87.1 mmol) of allene **Ia**, the mixture was stirred for 10 min at –70... –60°C, cooled again to –100°C, and 5.75 g (50 mmol) of *sec*-butyl isothiocyanate was added (the temperature rose to –30°C). The reaction mixture was stirred for 15 min at –35 × –30°C, cooled to –80°C, and 16 g (112.7 mmol) of MeI was added. The temperature rose to 20°C within 25 min. On cooling to –80°C 100 ml of saturated water solution of NH_4Cl was added at vigorous stirring. The reaction products were extracted into ether (3 × 50 ml), extracts were washed with water (3 × 30 ml), and dried with $MgSO_4$. On removing the main amount of solvent on the rotary evaporator at room temperature the reaction product was subjected to a vacuum for 12 min more at the bath temperature ~60°C, then for 15 min to a vacuum of an oil pump (8 mm Hg) to get 9.76 g (98%) of broun mobile liquid containing according to ^{1}H NMR data 89% of 2-aza-1,3,5-triene **VIId** and 11% of pyrrole **IIId**. ^{1}H NMR spectrum of compound **VIId** (400 MHz, $CDCl_3$), δ, ppm: 1.17 t (3H, $CH_2C\underline{H}_3$, ^3J 7.4 Hz), 1.86 s (3H, Me), 2.06 s (3H, SMe), 2.42 q (2H, $C\underline{H}_2CH_3$, ^3J 7.4 Hz), 3.63 s (3H, OMe), 4.86 d.d (1H, CH_2=, ^3J 10.8, ^2J 1.8 Hz), 5.16 d.d (1H, CH_2=, ^3J 17.2, ^2J 1.8 Hz), 5.89 d.d (1H, CH=, ^3J 17.2, 10.8 Hz). ^{13}C NMR spectrum (J mod, 100 MHz, $CDCl_3$), δ, ppm: 10.46 ($CH_2\underline{C}H_3$), 12.61 (SMe), 19.91 (Me), 34.12 ($\underline{C}H_2CH_3$), 58.31 (OMe), 109.37 (CH_2=), 126.33 (CH=), 134.25 (S–C=), 137.52 (O–C=), 177.74 (C=N). The correct assignment of the signals in the ^{13}C NMR spectrum was done with the help of 2D HMBC NMR experiment.

b. To a solution of 67.5 mmol of BuLi in 27 ml hexane (2.5 M solution) and 70 ml of THF at –100°C was added 6 g (85.6 mmol) of allene **Ia**, the mixture was stirred for 10 min at –70...–60°C, cooled again to –90°C, and 5.76 g (50 mmol) of *sec*-butyl isothiocyanate in 5 ml of THF was added (the temperature rose to –30°C). The reaction mixture was stirred for 30 min at –35...–30°C, cooled to –80°C, and 15 g (105.7 mmol) of MeI was added. The temperature rose to 18°C in 30 min. On cooling to –80°C 100 ml of saturated water solution of NH_4Cl was added at vigorous stirring. The reaction products were extracted into ether (3 × 50 ml), extracts were washed with water (2 × 30 ml), and dried with $MgSO_4$. The solvents were removed first on a rotary evaporator, and then in a vacuum

of an oil pump (1 mm Hg) at the bath temperature not exceeding 25°C to obtain 9.46 g (95%) of light-brown mobile liquid containing according to ^{1}H NMR data 65% of 1-aza-1,3,4-triene **VId** (mixture of *E*- and *Z*-isomers), 33% of 2-aza-1,3,5-triene **VIId**, 2% of pyrrole **IIId**, and traces of *s*-BuN=C=S (identified by the multiplet band at 2103 cm^{-1} in the IR spectrum). ^{1}H NMR spectrum of 1-aza-1,3,4-triene **VId** (400 MHz, $CDCl_3$), δ, ppm: 0.78 t, 0.83 t (3H, NCHCH$_2$C$\underline{H}_3$, ^3J 7.4 Hz), 1.08 d, 1.13 d (3H, NCHC$\underline{H}_3$, ^3J 6.2 Hz), 1.48 m, 1.57 m (2H, NCHC$\underline{H}_2$CH$_3$), 2.27 s, 2.41 C (3H, SMe), 3.44 s, 3.50 s (3H, OMe), 3.66 m (1H, NC$\underline{H}$CH$_3$), 5.64 s, 5.71 s (2H, CH$_2$=); isomers ratio 1.2 : 1.

To 9.16 g of reaction products 10 ml of toluene was added, the mixture was slowly heated at stirring till boiling (at virtually absent exothermic effect) and refluxed for 30 min. Toluene was removed in a vacuum (1 mm Hg) to obtain 8.36 g (87%) of dark-brown liquid containing 15% of pyrrole **IIId** and 85% of 2,3-dihydropyridine **IVd**. The reaction products (8.16 g) were separated with the use of dilute hydrochloric acid as described above. From the organic fraction 1.49 g (16%) of pyrrole **IIId** was isolated (dark viscous fluid). By chromatography on Al_2O_3 [eluents petroleum ether (bp 40–70°C), then a mixture petroleum ether–Et_2O, 10 : 1] 0.44 g of a fraction was isolated containing according to ^{1}H NMR data 85% of pyrrole **IIId,** and 0.47 g of pure pyrrole **IIId**, n_D^{25} 1.5257. Yield 9%. IR spectrum (thin layer), ν, cm^{-1}: 470, 488, 596, 623, 649, 667, 710, 803, 846, 899, 922, 950, 967, 994, 1014, 1036, 1079, 1098, 1180, 1198, 1225, 1284, 1308, 1330, 1379, 1397, 1410, 1462, 1486, 1547, 1599, 1659, 2829, 2876, 2932, 2968, 3112. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 0.79 t (3H, CH$_2$C$\underline{H}_3$, ^3J 7.4 Hz), 1.35 d (3H, NCHC$\underline{H}_3$, ^3J 6.8 Hz), 1.71 q (2H, C$\underline{H}_2$CH$_3$, ^3J 7.4 Hz), 2.15 s (3H, SMe), 3.80 s (3H, OMe), 4.49 sextet (1H, NC$\underline{H}$CH$_3$, ^3J 6.8 Hz), 5.89 d (1H, 4-CH=, ^3J 3.3 Hz), 6.59 d (1H, 5-CH=, ^3J 3.3 Hz). ^{13}C NMR spectrum (J mod, 100 MHz, $CDCl_3$), δ, ppm: 10.74 (CH$_2$$\underline{C}H_3$), 20.83 (SMe), 21.82 (NCH$\underline{C}$H$_3$), 30.64 ($\underline{C}$H$_2$CH$_3$), 52.42 (NCH), 58.01 (OMe), 94.66 (4-CH=), 105.81 (2-C=), 116.33 (5-CH=), 150.91 (3-C=). The correct assignment of the signals in the ^{13}C NMR spectrum was done with the help of 2D HMBC NMR experiment. Found, %: C 60.45; H 8.39; N 7.15; S 15.90. $C_{10}H_{17}NOS$. Calculated, %: C 60.26; H 8.60; N 7.03; S 16.09.

From the "acidic" fraction 5.89 g (63%) of 2,3-dihydropyridine **IVd** was isolated, dark brown mobile fluid. The distillation in a vacuum provided two fractions. I fraction, 0.35 g, bp 84–86°C (<1 mm Hg), contained according to ^{1}H NMR data 60% of 2,3-dihydropyridine **IVd**. II fraction (main), 4.03 g (43%), light-yellow mobile fluid, bp 86–88°C (<1 mm Hg), n_D^{24} 1.5220, contained according to ^{1}H NMR data pure 2,3-dihydropyridine **IVd**. IR spectrum (thin layer), ν, cm^{-1}: 457, 475, 505, 536, 568, 580, 607, 619, 696, 719, 753, 795, 853, 877, 903, 916, 964, 998, 1011, 1025, 1035, 1053, 1081, 1105, 1133, 1151, 1184, 1204, 1230, 1246, 1284, 1300, 1311, 1341, 1367, 1410, 1430, 1452, 1461, 1586, 1649, 2834, 2877, 2924, 2965, 3063, 3153. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 0.90 t (3H, CH$_2$C$\underline{H}_3$, ^3J 7.4 Hz), 1.08 C (3H, 2-Me), 1.55 q (2H, C$\underline{H}_2$CH$_3$, ^3J 7.4 Hz), 2.08, 2.27 d.d (2H, 3-CH$_2$, ^3J 5.5, 4.0, ^2J 17.2 Hz), 2.24 s (3H, SMe), 3.58 s (3H, OMe), 4.88 d.d (1H, 4-CH=, ^3J 5.5, 4.0 Hz). ^{13}C NMR spectrum (J mod, 100 MHz, $CDCl_3$), δ, ppm: 8.66 (2-CH$_2$$\underline{C}H_3$), 11.41 (SMe), 24.70 (2-Me), 31.41 (3-CH$_2$), 34.74 (2-$\underline{C}$H$_2$CH$_3$), 54.57 (OMe), 57.84 (2-C), 96.52 (4-CH=), 146.91 (5-C=), 157.30 (6-C=). The correct assignment of the signals in the ^{13}C NMR spectrum was done with the help of 2D HMBC and HSQC NMR experiments. Found, %: C 60.59; H 8.44; N 6.88; S 15.79. $C_{10}H_{17}NOS$. Calculated, %: C 60.26; H 8.60; N 7.03; S 16.09.

2-(Methylsulfanyl)-3-methoxy-1-cyclopropylpyrrole (IIIe). To a solution of 64 mmol of BuLi in 40 ml of hexane and 60 ml of THF at –100°C was added 5.5 g (78.5 mmol) of allene **Ia**, the reaction mixture was stirred for 10 min at –65 × –60°C, cooled to –100°C, and 4.95 g (50 mmol) of cyclopropyl isothiocyanate was added. The reaction mixture was stirred for 20 min at –35...–30°C, cooled to –70°C, and 12 g (84.5 mmol) of MeI was added, the cooling bath was removed, and the reaction mixture was stirred for 30 min, cooled to –80°C, and treated with a saturated water solution of NH_4Cl. The reaction products were extracted into ether, extracts were washed with water, and dried with $MgSO_4$. On removing the solvents at a reduced pressure and heating we obtained 7.31 g (80%) of pyrrole **IIIe**, content of the main substance 95% (by GLC data). ^{1}H NMR spectrum (90 MHz, CCl_4), δ, ppm: 0.88 m [4H, $(CH_2)_2$], 2.18 s (3H, SMe), 3.20 m (1H, NCH), 3.67 s (3H, OMe), 5.65 d (1H, 4-CH=, ^3J 3.3 Hz), 6.40 d (1H, 5-CH=, ^3J 3.3 Hz). Found, %: C 58.70; H 7.03; N 7.88; S 17.21. $C_9H_{13}NOS$. Calculated, %: C 58.98; H 7.15; N 7.64; S 17.50.

1-(Methylsulfanyl)-2-methoxy-*N*-(cyclopentylidene)buta-1,3-dien-1-amine (VIIf), 2-(methylsulfanyl)-3-methoxy-1-cyclopentylpyrrole (IIIf),

7-(methylsulfanyl)-8-methoxy-6-azaspiro-[4.5]deca-6,8-diene (IVf). To a solution of 67.5 mmol of BuLi in 27 ml of hexane (2.5 M solution) and 70 ml of THF at –100°C was added 6 g (85.6 mmol) of allene **Ia**, the reaction mixture was stirred for 10 min at –70...–60°C, cooled to –90°C, and 6.36 g (50 mmol) of cyclopentyl isothiocyanate in 5 ml of THF was added (the temperature rose to –30°C). The reaction mixture was stirred for 30 min at –35 × –30°C, cooled to –80°C, and 16.6 g (117 mmol) of MeI was added. The temperature rose to 18°C within 30 min. The mixture was cooled to –80°C, and 100 ml of saturated aqueous NH_4Cl was added at vigorous stirring. The reaction products were extracted into ether (2 × 50 ml), extracts were washed with water 2 times, and dried with $MgSO_4$. The solvents were removed at the bath temperature not exceeding 25°C first on the rotary evaporator at 10–20 mm Hg, then in a vacuum of an oil pump (1 mm Hg) to get 10.57 g (100%) of brown mobile liquid that after 18 h storage at –15°C contained according to ^{1}H NMR data 2-aza-1,3,5-triene **VIIf** (99%) with traces (<1%) of pyrrole **IIIf**. IR spectrum (thin layer), ν, cm^{-1}: 552, 581, 609, 645, 692, 723, 754, 848, 892, 958, 976, 988, 1050, 1123, 1166, 1187, 1236, 1256, 1287, 1311, 1344, 1419, 1437, 1452, 1546, 1565, 1606, 1667, 2826, 2871, 2928, 2959, 3095. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.83 m (4H, 3',4'-CH_2), 2.09 s (3H, SMe), 2.22 m, 2.51 m (4H, 2',5'-CH_2), 3.63 s (3H, OMe), 4.91 d.d (1H, CH_2=, ^3J 10.9, ^2J 1.8 Hz), 5.19 d.d (1H, CH_2=, ^3J 17.2, ^2J 1.8 Hz), 6.02 d.d (1H, CH=, ^3J 17.2, 10.9 Hz). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 13.12 (SMe), 24.68, 24.85 (3',4'-CH_2), 31.69, 35.84 (2',5'-CH_2), 58.54 (OMe), 109.97 (CH_2=), 126.56 (CH=), 135.42 (S–C=), 138.47 (O–C=), 187.36 (C=N).

To 0.48 g of reaction products 10 ml of toluene was added, the mixture was slowly heated at stirring till boiling (at virtually absent exothermic effect) and refluxed for 30 min. Toluene was removed in a vacuum (1 mm Hg) to obtain 9.37 g (90%) of dark brown very viscous fluid. The reaction products (9.23 g) were separated with the use of dilute hydrochloric acid as described above. From the organic fraction 1.6 g was isolated of relatively mobile brown liquid which was subjected to column chromatography on Al_2O_3 [eluents petroleum ether (bp 40–70°C), then a mixture petroleum ether–Et_2O, 10 : 1] to separate 1.07 g of fraction containing according to ^{1}H NMR data 10% of pyrrole **IIIf** (yield 1%) and two unidentified compounds. ^{1}H NMR spectrum of pyrrole **IIIf** (400 MHz, $CDCl_3$), δ, ppm: 1.75 m [8H, $(CH_2)_4$], 2.12 s (3H, SMe), 3.68 s (3H, OMe), 4.80 m (1H, NCH), 5.89 d (1H, 4-CH=, ^3J 3.3 Hz), 6.66 d (1H, 5-CH=, ^3J 3.3 Hz).

From the "acidic" water 4 g of insoluble solid dark-brown polymer was isolated and 3.58 g of brown viscous fluid which was subjected to column chromatography on Al_2O_3 (eluent a mixture of petroleum ether –Et_2O, 3 : 1) to isolate 0.99 g of fraction containing 60% of 2,3-dihydropyridine **IVf** (red-orange mobile fluid) and 0.09 g of 2,3-dihydropyridine **IVf** (light-yellow fluid, n_D^{25} 1.5434), content of the main substance 90% (according to ^{1}H NMR data). Yield 6%. IR spectrum (thin layer), cm^{-1}: 417, 559, 583, 646, 697, 722, 795, 920, 962, 984, 1037, 1062, 1087, 1104, 1123, 1150, 1180, 1222, 1243, 1295, 1314, 1341, 1410, 1449, 1462, 1582, 1632, 1646, 1659, 2883, 2868, 2992, 2954, 3061, 3143. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.59 m (4H, 3',4'-CH_2), 1.74 m, 1.80 m (4H, 2',5'-CH_2), 2.23 s (3H, SMe), 2.27 d (2H, 3-CH_2, ^3J 4.6 Hz), 3.57 s (3H, OMe), 4.94 t (1H, 4-CH=, ^3J 4.6 Hz). ^{13}C (J mod, 100 MHz, $CDCl_3$), δ, ppm: 11.31 (SMe), 23.67 (3',4'-CH_2), 31.84 (3-CH_2), 39.37 (2',5'-CH_2), 54.50 (OMe), 66.59 (2-C), 97.35 (4-CH=), 147.59 (5-C=), 157.40 (6-C=). The correct assignment of signals in the ^{1}H NMR spectrum was performed with the help of 2D COSY NMR experiment.

2-Methoxy-N-cyclohexylidene-1-(ethyl-sulfanyl) buta-1,3-dien-1-amine (VIIg), 3-methoxy-1-cyclohexyl-2-(ethylsulfanyl)pyrrole (IIIg) and 3-methoxy-2-(ethylsulfanyl)-1-azaspiro[5.5]-undeca-1,3-diene (IVg). To a solution of 52.8 mmol BuLi in 33 ml of hexane and 60 ml of THF at –90°C was added 5.4 g (77.1 mmol) of allene **Ia**. After warming to –40°C the reaction mixture was cooled to –100°C, and 7.2 g (51.1 mmol) of cyclohexyl isothiocyanate was added. The temperature was allowed to rise to −35°C (bright yellow dispersion), then the reaction mixture was cooled to −50°C, and 11 g (70.5 mmol) of EtI was added. After the temperature rose to 5°C the reaction mixture was treated with 50 ml of cold water at vigorous stirring. The reaction products were extracted into pentane (3 × 50 ml), extracts were dried with K_2CO_3, the solvent was removed on a rotary evaporator to obtain the residue of 9.2 g (75%) of mobile light yellow liquid (n_D^{20} 1.5575) containing according to ^{1}H NMR data 2-aza-1,3,5-triene **VIIg** with impurity of pyrrole **IIIg** and 1-aza-1,3,4-triene **VIg**. ^{1}H NMR spectrum of 2-aza-1,3,5-triene **VIIg** (400 MHz, $CDCl_3$), δ, ppm: 1.24 t (3H, $SCH_2C\underline{H}_3$, ^3J 7.4 Hz), 1.61, 1.87 m (6H, 3',4',5'-CH_2), 2.26, 2.44 m (4H, 2',6'-CH_2), 2.59 q (2H, $SC\underline{H}_2CH_3$, ^3J 7.4 Hz), 3.62 s (3H, OMe),

4.89 d.d (1H, CH_2=, ^3J 10.9, ^2J 2.0 Hz), 5.18 d.d (1H, CH_2=, ^3J 17.2, ^2J 2.0 Hz), 5.95 d.d (1H, CH=, ^3J 17.2, 10.9 Hz). ^{13}C NMR spectrum (J mod, 100 MHz, $CDCl_3$), δ, ppm: 15.39 ($SCH\underline{C}H_3$), 24.09 (SCH_2), 25.55 (4'-CH_2), 26.85, 27.85 (3',5'-CH_2), 31.87, 38.86 (2',6'-CH_2), 58.58 (OMe), 109.88 (CH_2=), 126.62 (CH=), 133.45 (S–C=), 138.71 (O–C=), 179.19 (C=N). The correct assignment of the signals in the ^{13}C NMR spectrum was done with the help of 2D HMBC NMR experiment.

The heating of the reaction product at ~190°C quantitatively provided a mixture of pyrrole **IIIg** (12%) and 2,3-dihydropyridine **IVg** (88%) (according to ^{1}H NMR and GLC), bp ~180°C (15 mm Hg). Compounds **IIIg** and **IVg** were separated using hydrochloric acid as described above. From the organic fraction 1.3 g (11%) of pyrrole **IIIg** was isolated, bright yellow fluid, bp 110–118°C (1 mm Hg), n_D^{20} 1.5332. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.16 t (3H, $SCH_2C\underline{H}_3$, ^3J 7.2 Hz), 1.21, 1.41 m (2H, 4'-CH_2), 1.52, 1.91 m (4H, 2',6'-CH_2), 1.71, 1.84 m (4H, 3',5'-CH_2), 2.54 q (2H, SCH_2, ^3J 7.2 Hz), 3.79 s (3H, OMe), 4.32 t.t (1H, NCH, ^3J 11.5, 3.5 Hz), 5.90 d (1H, 4-CH=, ^3J 2.9 Hz), 6.65 d (1H, 5-CH=, ^3J 2.9 Hz). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 14.40 ($SCH\underline{C}H_3$), 25.41 (4'-CH_2), 25.79 (3',5'-CH_2), 31.04 (SCH_2), 34.38 (2',6'-CH_2), 54.26 (NCH), 57.82 (OMe), 94.15 (4-CH=), 109.03 (2-C=), 116.77 (5-CH=), 151.66 (3-C=). Found, %: C 64.92; H 8.51; N 6.27; S 13.69. $C_{13}H_{21}NOS$. Calculated, %: C 65.23; H 8.84; N 5.85; S 13.40.

After workup of the "acidic" layer we obtained 7.5 g (61%) of 2,3-dihydropyridine **IVg**, content of the main substance 90% (by GLC data), colorless crystals, mp 32–34°C. IR spectrum (KBr), ν, cm^{-1}: 470, 490, 520, 570, 610, 680, 710, 760, 800, 850, 910, 935, 950, 960, 1020, 1040, 1050, 1060, 1110, 1140, 1150, 1180, 1210, 1240, 1260, 1340, 1360, 1440, 1570, 1640, 2850, 2920, 2980, 3050. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.27 t (3H, $SCH_2C\underline{H}_3$, ^3J 7.5 Hz), 1.37 m (6H, 3',4',5'-CH_2), 1.73 m (4H, 2',6'-CH_2), 2.16 d (2H, 3-CH_2, ^3J 4.6 Hz), 2.90 q (2H, SCH_2, ^3J 7.5 Hz), 3.56 s (3H, OMe), 4.85 t (1H, 4-CH=, ^3J 4.6 Hz). ^{13}C NMR spectrum (J mod, 100 MHz, $CDCl_3$), δ, ppm: 14.14 ($SCH_2\underline{C}H_3$), 22.08 (3',5'-CH_2), 22.53 (4'-CH_2), 26.42 (SCH_2), 32.86 (3-CH_2), 37.61 (2',6'-CH_2), 54.59 (OMe), 56.94 (2-C), 96.19 (4-CH=), 146.84 (5-C=), 156.16 (6-C=). Found, %: C 64.92; H 8.51; N 6.27; S 13.69. $C_{13}H_{21}NOS$. Calculated, %: C 65.23; H 8.84; N 5.85; S 13.39.

Methyl[1-(methylsulfanyl)-2-methoxybuta-1,3-dien-1-yl]imidoformiate (VIIh), 2,5-dimethoxy-6-(methylsulfanyl)-2,3-dihydropyridine (IVh). To a solution of 57.6 mmol of BuLi in 36 ml of hexane and 70 ml of THF at –90°C was added 5 g (71.4 mmol) of allene **Ia**. The reaction mixture was stirred for 5–7 min at –65... –60°C, cooled to –100°C, and 5.15 g (50 mmol) of methoxymethyl isothiocyanate was added. After warming to –70°C 20 g (138.9 mmol) of MeI was added, the reaction mixture was stirred for 15 min at room temperature and poured into 100 ml of water. The reaction products were extracted into pentane, the extracts were dried with K_2CO_3, the solvent was removed on a rotary evaporator to obtain the residue of 9.4 g (100%) of light yellow liquid that was according to ^{1}H NMR data 2-aza-1,3,5-triene **VIIh**, content of the main substance 100% (by GLC data). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 2.19 s (3H, SMe), 3.68 s (3H, OMe), 3.82 s (3H, OMe), 5.08 d.d (1H, CH_2=, ^3J 10.9, ^2J 1.8 Hz), 5.39 d.d (1H, CH_2=, ^3J 17.4, ^2J 1.8 Hz), 6.74 d.d (1H, CH=, ^3J 17.4, 10.9 Hz), 7.97 C (1H, N=CH).

2-Aza-1,3,5-triene **VIIh** was heated to ~40°C, and on the completion of exothermic electrocyclization (self-heating up to 150°C) the reaction product was distilled in a vacuum. Yield of 2,3-dihydropyridine **IVh** 6.8 g (73%), content of the main substance 99% (by GLC data), bp 85–90°C (1 mm Hg), n_D^{20} 1.5365. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 2.21–2.40 m (2H, 3-CH_2), 2.31 s (3H, SMe), 3.55 s (3H, 5-OMe), 3.58 s (3H, 2-OMe), 4.61 d.d (1H, 2-CH, ^3J 13.6, 6.3 Hz), 5.02 d.d (1H, 4-CH=, ^3J 6.3, 2.8 Hz). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 11.56 (SMe), 26.71 (3-CH_2), 54.75 (2-OMe), 54.84 (5-OMe), 90.59 (2-CH), 97.22 (4-CH=), 148.00 (5-C=), 160.64 (6-C=). The correct assignment of the signals in the ^{13}C NMR spectrum was done with the help of 2D HMBC NMR experiment. Mass spectrum, *m/z* (I_{rel}, %): 187 (72) $[M]^{+\cdot}$, 172 (100), 156, 155, 140. Found, %: C 51.62; H 7.21; N 6.91; S 16.80. $C_8H_{13}NO_2S$. Calculated, %: C 51.31; H 7.00; N 7.48; S 17.12. *M* 187.26.

2-(Methylsulfanyl)-3-methoxypyridine (VIII). The solution of 1.75 g (9.36 mmol) of 2,3-dihydropyridine **IVh** and 2.5 g of ~30% HCl in 25 ml of Et_2O was stirred for 1.5 h at boiling of ether, the reaction mixture was treated with KOH solution (till neutral reaction), the organic phase was dried with K_2CO_3, the ether was removed under a reduced pressure. Yield 1.04 g (72%), bp 82–84°C (1.5 mm Hg), n_D^{20} 1.5742. ^{1}H NMR spectrum (250 MHz, $CDCl_3$), δ, ppm: 2.53 s (3H, SMe), 3.88 s (3H, OMe),

6.95 m (1H, 5-CH=), 6.96 m (1H, 4-CH=), 8.07 d.d (1H, 6-CH=, ^3J 3.8, 2.3 Hz). ^{13}C NMR spectrum (62.9 MHz, $CDCl_3$), δ, ppm: 12.03 (SMe), 55.58 (OMe), 114.65 (4-CH=), 119.10 (5-CH=), 140.89 (6-CH=), 149.58 (2-C=), 152.37 (3-C=). Mass spectrum, *m/z* (I_{rel}, %): 155 (100) $[M]^+$, 140, 124, 122, 108. Found, %: C 54.31; H 5.42; N 8.77; S 20.32. C_7H_9NOS. Calculated, %: C 54.17; H 5.84; N 9.02; S 20.66. *M* 155.21.

1-[2-(Vinyloxy)ethyl]-2-(methylsulfanyl)-3-methoxypyrrole (IIIi) and 2-[(vinyloxy)methyl]-6-(methylsulfanyl)-5-methoxy-2,3-dihydropyridine (IVi). To a solution of 104 mmol of BuLi in 65 ml of hexane and 65 ml of THF at –100°C was added 9.1 g (130 mmol) of allene **Ia**. The reaction mixture was stirred for 10 min at –60°C, cooled again to –100°C, and within several seconds 12.9 g 100 mmol) of 2-(vinyloxy)ethyl isothiocyanate was added. The reaction mixture was stirred for 10 min at –60°C, 27 g (190.1 mmol) of MeI was added, and after warming to 5°C the mixture was treated with 100 ml of ice water at vigorous stirring. The reaction products were extracted into pentane 4 × 50 ml), the extracts were dried with K_2CO_3, the solvent was removed on a rotary evaporator to obtain the residue of 20 g (94%) of reaction product, whose distillation in a vacuum gave 15 g (70%) of light yellow fluid, bp 110–120°C (0.5 mm Hg), that was according to ^{1}H NMR data a mixture of pyrrole **IIIi** and 2,3-dihydropyridine **IVi** in the ratio ~1 : 1; overall content of the reaction products 96% (by GLC data).

The solution of the mixture of pyrrole **IIIi** and 2,3-dihydropyridine **IVi** in 30 ml of pentane was treated with cold (1–3°C) 1 M solution of HCl, taken in the exact amount necessary for the neutralization of 2,3-dihydropyridine. Further workup was carried out as described above. From the organic fraction 7 g (33%) of pyrrole **IIIi** was isolated, bp 131–132°C (3 mm Hg), n_D^{20} 1.5414. IR spectrum (thin layer), ν, cm^{-1}: 700, 820, 940, 960, 1090, 1190, 1330, 1350, 1400, 1460, 1550, 1620, 1635, 2830, 2870, 2920–2940, 3000, 3100, 3120. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 2.14 s (3H, SMe), 3.76 s (3H, OMe), 3.84 t (2H, OCH_2, ^3J 5.6 Hz), 3.96 d.d (1H, CH_2=, ^3J 6.5, ^2J 2.1 Hz), 4.14 d.d (1H, CH_2=, ^3J 14.3, ^2J 2.1 Hz), 4.19 t (2H, NCH_2, ^3J 5.6 Hz), 5.85 d (1H, 4-CH=, ^3J 3.2 Hz), 6.34 q (1H, OCH=, ^3J 14.3, 6.5 Hz), 6.65 d (1H, 5-CH=, ^3J 3.2 Hz). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 20.58 (SMe), 45.68 (NCH_2), 57.90 (OMe), 67.45 (OCH_2), 86.94 (CH_2=), 94.88 (4-CH=), 105.31 (2-C=), 121.11 (5-CH=), 151.15 (OCH=), 151.83 (3-C=). Found, %: C 56.03; H 7.29; N 6.32; S 14.88. $C_{10}H_{15}NO_2S$. Calculated, %: C 56.31; H 7.09; N 6.57; S 15.03.

After workup of the "acidic" water layer we obtained 7.3 g (34%) of 2,3-dihydropyridine **IVi**, content of the main substance in the crude product 92% (by GLC data), bp 136–137°C (3 mm Hg), n_D^{20} 1.5392; crystallized on cooling. IR spectrum (thin layer), ν, cm^{-1}: 680, 700–710, 780, 800, 930, 950, 970, 1000, 1025, 1050, 1100, 1120, 1140, 1200, 1220, 1240, 1300, 1330, 1400, 1430, 1450, 1570, 1600, 1630, 2830, 2865, 2920, 2950, 3000, 3050, 3100. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 1.98–2.26 m (2H, 3-CH_2), 2.17 s (3H, SMe), 3.50 s (3H, OMe), 3.60 m (1H, 2-CH), 3.68 m, 3.88 m (2H, OCH_2), 3.90 d.d (1H, CH_2=, ^3J 6.5, ^2J 2.0 Hz), 4.15 d.d (1H, CH_2=, ^3J 14.2, ^2J 2.0 Hz), 4.98 d.d (1H, 4-CH=, ^3J 3.6 Hz), 6.41 q (1H, OCH=, ^3J 14.2, 6.5 Hz). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ, ppm: 11.17 (SMe), 23.51 (3-CH_2), 54.32 (OMe), 56.79 (2-CH), 70.96 (OCH_2), 86.15 (CH_2=), 97.50 (4-CH=), 147.65 (5-C=), 151.60 (OCH=), 161.61 (6-C=). Found, %: C 56.19; H 7.02; N 6.61; S 15.20. $C_{10}H_{15}NO_2S$. Calculated, %: C 56.31; H 7.09; N 6.57; S 15.03.

Methyl-2-*tert*-butoxy-N-methylbuta-2,3-dienimidothioate (VIj), 3-*tert*-butoxy-1-methyl-2-(methylsulfanyl)pyrrole (IIIj) and 5-*tert*-butoxy-6-(methylsulfanyl)-2,3-dihydropyridine (IVj). To a solution of 104 mmol of BuLi in 65 ml of hexane and 60 ml of THF at –100°C was added 11.75 g (104.9 mmol) of allene **Ib**. The reaction mixture slowly (within 15 min) warmed to –15°C, was cooled again to –95°C, and 7.3 g (100 mmol) of methyl isothiocyanate was added. After warming to –70°C the reaction mixture was again cooled to –75°C, and 18.2 g (128.2 mmol) of MeI was added. At –12°C the reaction mixture was treated with cold water, the organic fraction was dried with K_2CO_3, the solvents were removed on a rotary evaporator to obtain in the residue 17.2 g (86%) of 1-aza-1,3,4-triene **VIj**. ^{1}H NMR spectrum (90 MHz, CCl_4), δ, ppm: 1.30 s, 1.40 s [9H, $OC(CH_3)_3$], 2.20 s, 2.45 s (3H, SMe), 3.15 s, 3.32 s (3H, NMe), 5.50 s (2H, CH_2=).

The reaction product was heated and on the completion of exothermic electrocyclization (self-heating up to 192°C) we obtained pyrrole **IIIj** containing 17% of 2,3-dihydropyridine **IVj** (according to ^{1}H NMR and GLC data). Compounds **IIIj** and **IVj** were separated with the use of hydrochloric acid as described above. From the organic fraction 10.8 g (54%) of pyrrole **IIIj** was isolated,

content of the main substance 97% (by GLC data), bp 102–103°C (3 mm Hg), n_D^{20} 1.5180. IR spectrum (thin layer), ν, cm^{-1}: 690, 700, 750, 870, 960, 1000, 1050, 1170, 1220, 1240, 1250, 1300, 1340, 1360, 1390, 1530, 2870, 2930, 2970, 3100. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.32 s [9H, $OC(CH_3)_3$], 2.13 s (3H, SMe), 3.58 s (3H, NMe), 5.81 d (1H, 4-CH=, ^3J 3.2 Hz), 6.50 d (1H, 5-CH=, ^3J 3.2 Hz). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 19.87 (SMe), 28.78 [$OC(\underline{C}H_3)_3$], 34.38 (NMe), 78.05 [$O\underline{C}(CH_3)_3$], 103.33 (4-CH=), 114.04 (2-C=), 120.92 (5-CH=), 145.27 (3-C=). Found, %: C 60.09; H 8.69; N 6.87; S 15.99. $C_{10}H_{17}NOS$. Calculated, %: C 60.26; H 8.60; N 7.03; S 16.09.

After workup of the "acidic" water layer we obtained 1.2 g (6%) of 2,3-dihydropyridine **IVj**. IR spectrum (thin layer), ν, cm^{-1}: 860, 920, 950, 980, 1020, 1050, 1080, 1150, 1200, 1240, 1290, 1355, 1380, 1420, 1560, 1610, 2830–2920–2940. ^{1}H NMR spectrum (90 MHz, CCl_4), δ, ppm: 1.32 s [9H, $OC(CH_3)_3$], 2.15 s (3H, SMe), 2.25 m (2H, 3-CH_2), 3.47 t (2H, NCH_2, ^3J 7.5 Hz), 5.40 t (1H, 4-CH=, ^3J 4.5 Hz). Found, %: C 60.42; H 8.38; N 7.15; S 15.80. $C_{10}H_{17}NOS$. Calculated, %: C 60.26; H 8.60; N 7.03; S 16.09.

Ethyl-2-*tert*-butoxy-N-methylbuta-2,3-dieneimidothioate (VIk), 3-*tert*-butoxy-1-methyl-2-(ethylsulfanyl)pyrrole (IIIk) and 5-*tert*-butoxy-6-(ethylsulfanyl)-2,3-dihydropyridine (IVk). To a solution of 104 mmol of BuLi in 65 ml of hexane and 80 ml of THF at –100°C was added 11.85 g (105.8 mmol) of allene **Ib**. The temperature quickly rose to –50°C. The reaction mixture was stirred at this temperature for 10 min, cooled to –95°C, and 7.3 g (100 mmol) of methyl isothiocyanate was added. The temperature was allowed to rise to –50°C, the reaction mixture was stirred for 15 min at –60... –50°C, and 22.6 g (144.9 mmol) of EtI was added. After relatively slow warming to 5°C the reaction mixture was treated with 70 ml of cold water. After usual treatment and removal of the solvent on the rotary evaporator we obtained in residue 19 g (89%) of 1-aza-1,3,4-triene **VIk** with traces of pyrrole **IIIk** (according to ^{1}H NMR data). ^{1}H NMR spectrum (90 MHz, CCl_4), δ, ppm: 1.25 m (3H, $SCH_2C\underline{H}_3$), 1.35 s, 1.40 s [9H, $OC(CH_3)_3$], 2.80 q, 3.05 q (2H, $SC\underline{H}_2CH_3$, ^3J 7.3 Hz), 3.20 s, 3.30 s (3H, NMe), 5.40 s, 5.45 s (2H, CH_2=).

The reaction product was heated and on the completion of exothermic heterocyclization it was distilled in a vacuum. We collected a wide fraction with bp 85–120°C (0.7 mm Hg), containing a mixture of pyrrole **IIIk** and 2,3-dihydropyridine **IVk** (according to ^{1}H NMR data) of a 88 : 12 ratio (by GLC data); yield 15.5 g (73%). Compounds **IIIk** and **IVk** were separated with the use of hydrochloric acid as described above. ^{1}H NMR spectrum of pyrrole **IIIk** (90 MHz, CCl_4), δ, ppm: 1.15 t (3H, $SCH_2C\underline{H}_3$, ^3J 7.2 Hz), 1.35 s [9H, $OC(CH_3)_3$], 2.52 q (2H, $SC\underline{H}_2CH_3$, ^3J 7.2 Hz), 3.60 c (3H, NMe), 5.75 d (1H, 4-CH=, ^3J 3.2 Hz), 6.48 d (1H, 5-CH=, ^3J 3.2 Hz). ^{1}H NMR spectrum of 2,3-dihydropyridine **IVk** (90 MHz, CCl_4), δ, ppm: 1.10 t (3H, $SCH_2C\underline{H}_3$, ^3J 7.3 Hz), 1.20 s [9H, $OC(CH_3)_3$], 2.00 m (2H, 3-CH_2), 2.70 q (2H, $SC\underline{H}_2CH_3$, ^3J 7.3 Hz), 3.50 t (2H, NCH_2, ^3J 7.5 Hz), 5.40 t (1H, 4-CH=, ^3J 4.5 Hz).

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