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Reactions of Heterocumulenes with Organometallic Reagents: VIII.* Reactions of Carbanions Derived from Alkoxy- and Alkylsulfanylethenes with Isothiocyanates–A Convenient Route to 2-Propenethioamides, 1-Methylsulfanyl-2-propen-1-imines, and Benzothiazoles

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Abstract—Metalated alkoxy- and alkylsulfanylethenes readily add to isothiocyanates; the subsequent hydrolysis or alkylation of the adducts leads to formation of 2-propenethioamides or 1-methylsulfanyl-2- propen-1-imines (as mixtures of *syn* and *anti* isomers) in 74–100% yield. The reaction of metalated alkoxyethenes with 2-fluorophenyl isothiocyanate opens the way to new benzothiazole derivatives. Hydrolysis of the latter provides a simple method for the preparation of 2-benzothiazolyl ketones.

In 1970s, Schüllkopf [2] and Baldwin [3] initiated extensive application of metalated vinyl ethers in organic synthesis. However, α-metalation of ethyl vinyl ether with pentylsodium was accomplished for the first time by Paul [4–6] as early as 1951. Metalated vinyl ethers and vinyl sulfides (mostly, methyl and ethyl derivatives) have attracted researchers' attention primarily as synthetic equivalents of acyl anions [2–13]. As a rule, their use in the synthesis of carbonyl-containing compounds is more advantageous than classical procedures [7, 9, 11, 12]. On the other hand, the synthetic potential of these reagents with respect to electrophiles, in particular heterocumulenes, still remains poorly studied [7–12]. Expected products of reactions of metalated alkoxy- and alkylsulfanylethenes, e.g., with isocyanates and isothiocyanates, enamides, enethioamides, and enimines, are valuable and promising monomers and intermediate products. Some known representatives of such products have found wide and diverse application in organic synthesis [14–22]. Therefore, development of simple, convenient, and nontrivial methods for the preparation of these compounds is an important problem.

Prior to our studies [1, 23–27], only a few published data were available on reactions of isocyanates and isothiocyanates with metalated alkoxy- and alkylsulfanylethenes. The reaction of methylsulfanylethene potassium salt with methyl isothiocyanate was briefly reported [8]. Mild hydrolysis of the primary adduct afforded *N*-methyl-2-methylsulfanyl-2-propenethioamide. We were the first to examine reactions of methyl, allyl, 2-vinyloxyethyl, cyclohexyl, and phenyl isothiocyanates with carbanions derived from ethoxyethene, ethylsulfanylethene, 3,4-dihydro-2*H*-pyran, thiophene, norbornene, and norborna-2,5-diene, which were generated *in situ* by the action of superbases (BuLi–*t*-BuOK, BuLi–*t*-BuOK–LiBr, BuLi–*t*-BuOK–$MgBr_2$). These reactions can be regarded as a simple and convenient synthetic route to novel azadiene systems [23–25] which are promising monomers, synthons, and heterodienes [21, 22]. We have found that metalated alkoxy- and alkylsulfanylethenes add to nonactivated isothiocyanates at a high rate at low temperature. The subsequent alkylation of intermediate $R^1C(=NR^2)SM$ compounds (M = MgBr, Li, K) leads to the corresponding 1-alkylsulfanyl-2-propen-1-imines as mixtures of *syn* and *anti* isomers in 81–97% yield. In reactions with activated isothiocyanates, such as allyl and benzyl isothiocyanates, carbanions derived from ethoxyethene (with potassium or lithium cation as counterion) behave as deprotonating bases. As a result, thiazole derivatives were isolated, contrary to the expectations [24, 25]. Metalated 3,4-dihydro-2*H*-pyrane, thiophene, norbornene, and norborna-2,5-diene reacted with isothiocyanates to give in high yields previously inaccessible α,β-unsaturated carbothioimidates [25].

* For communication VII, see [1].

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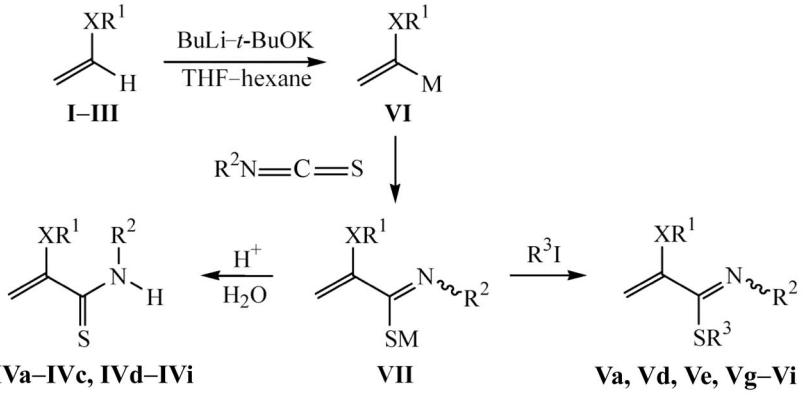
While continuing our systematic studies on reactions of heterocumulenes with organometallic compounds [1, 23–43], in the present work we examined the reactions of methyl, ethyl, methoxymethyl, cyclopropyl, allyl, 2-fluorophenyl, and 2-trifluoromethylphenyl isothiocyanates with carbanions generated *in situ* from ethoxyethene (**I**), butoxyethene (**II**), and ethylsulfanylethene (**III**) by the action of superbases. These reactions provide a simple synthetic route to previously unknown and inaccessible 2-alkoxy- and 2-alkylsulfanyl derivatives of N-substituted 2-propenethioamides and 1-alkylsulfanyl-2-propen-1-imines (compounds **IV** and **V**, respectively; Scheme 1) as promising monomers, intermediate products, and potential models for biological and physicochemical studies. Products **IV** and **V** combine properties of vinyl ethers (sulfides) and thioamides or Schiff bases.

Scheme 1.



M = K, MgBr; **I**, XR^1 = OEt; **II**, XR^1 = OBu; **III**, XR^1 = SEt; **IV**, XR^1 = OEt, R^2 = Me (**a**), $MeOCH_2$ (**b**), *cyclo*-C_3H_5 (**c**), 2-FC_6H_4 (**e**) 2-$CF_3C_6H_4$ (**f**); XR^1 = OBu, R^2 = Me (**g**); XR^1 = SEt, R^2 = Me (**h**), Et (**i**); **V**, R^3 = Me, XR^1 = OEt; R^2 = Me (**a**), allyl (**d**), 2-FC_6H_4 (**e**); XR^1 = OBu, R^2 = Me (**g**); XR^1 = SEt, R^2 = Me (**h**), Et (**i**).

The reactions were carried out as described in [1, 25], i.e., in a THF–hexane mixture at low temperature (–100 to –80°C) using the superbasic system BuLi–*t*-BuOK (Lochmann–Schlosser base) as deprotonating agent. We previously found [1–13, 23–27] that heteroalkenes **I**–**III** react with superbases to give α-metalated intermediates **VI** and that effective lithiation of alkoxyethenes is usually achieved with the use of *t*-BuLi [2, 3, 10], while alkylsulfanylethenes are effectively lithiated with *s*-BuLi [10, 13]. For example, the lithiation of ethoxyethene **I** is carried out with *t*-BuLi in pentane in the presence of a stoichiometric amount of *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMEDA) at –30°C [2]. The reaction is complete in 1 h at 25°C. On the other hand, both vinyl ethers and vinyl sulfides can be metalated with excellent efficiency (quickly, quantitatively, and at low temperature) using more accessible and less expensive Lochmann–Schlosser base [8], so that just the latter was selected by us as deprotonating agent.

As might be expected on the basis of our previous data [24, 25], carbanions **VI** generated *in situ* readily add to isothiocyanates at the C=S bond to give intermediates **VII**, whose mild hydrolysis with dilute hydrochloric acid or aqueous ammonium chloride leads to N-substituted 2-alkoxy- and 2-alkylsulfanyl)-2-propenethioamides **IVa**–**IVc** and **IVe**–**IVi** (Scheme 1). These products constitute a new family of α,β-unsaturated carbothioamides..

No protolytic cleavage of the vinyloxy or vinylsulfanyl group was observed during isolation of thioamides **IV** from the reaction mixture. As a rule, the yields of crude products were almost quantitative. According to the GLC and NMR data, they contained ~100% of the main substance. However, vacuum distillation of thioamides **IV** was usually accompanied by their decomposition and tarring; therefore, the yield of the target product decreased by a factor of 2 and more. Thioamides **IVe**, **IVf**, **IVh**, and **IVi** decomposed almost completely, so that their purification by vacuum distillation is impossible and unreasonable.

Unlike oxygen-containing analogs, i.e., adducts of carbanions **VI** with isocyanates [1, 26, 27], alkylation of intermediates **VII** occurs exclusively at the sulfur rather than nitrogen atom, affording 91–100% of new α,β-unsaturated compounds, 2-alkoxy- and 2-alkylsulfanyl-2-propen-1-imines **Va**, **Vd**, **Ve**, and **Vg**–**Vi** as mixtures of *syn* and *anti* isomers. Although unsaturated lithium and

potassium imidothioates (compounds **VII** among these) usually react with methyl iodide under very mild conditions and at a high rate [25, 28], in order to avoid contamination of the target imines **V** with thioamides **IV** (assuming incomplete S-alkylation) it is advisable to perform this reaction at 30–40°C over a period of 15–30 min. Otherwise, i.e., when the reaction mixture was treated with an aqueous solution of ammonium chloride immediately after addition of the alkylating agent (at –50 to –30°C) and fairly fast spontaneous heating of the reaction mixture to room temperature, the product (Schiff base **V**) sometimes contained a small impurity (~10–15%) of the corresponding thioamide **IV**.

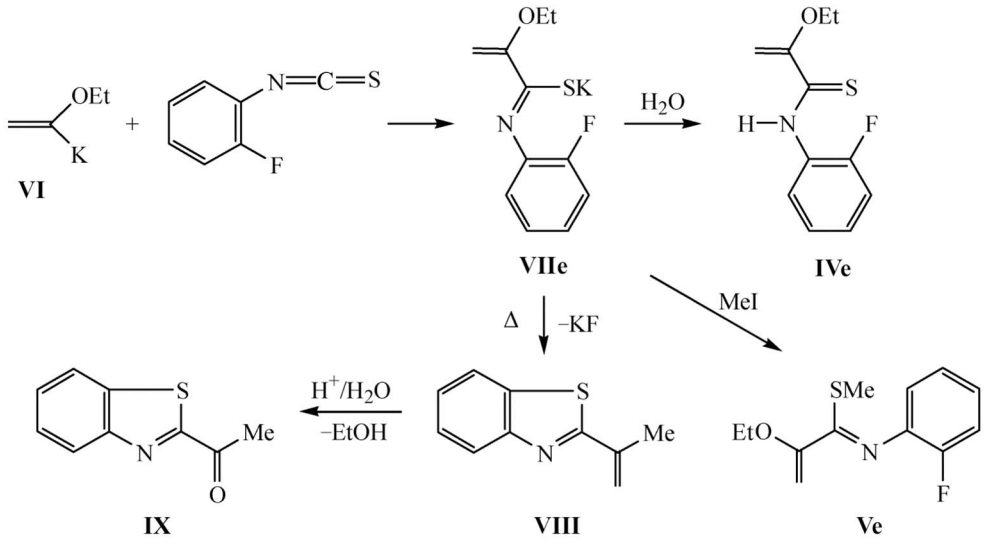
Thioamides **IV** are readily alkylated under mild conditions at the sulfur atom to give Schiff bases **V** via successive treatment with a strong base and alkyl halide. For example, *N*-ethyl-2-ethylsulfanyl-2-propenethioamide **IVi** was treated first with potassium *tert*-butoxide in THF at –30°C and then with methyl iodide (–30 to –10°C, 10–15 min) to obtain Schiff base **Vi** in a yield of about 80% (unoptimized). Intermediates **VII** are not prone to polyaddition reactions. Therefore, replacement of the potassium counterion by lithium or $MgBr^+$ (in some cases, such a replacement made it possible to avoid or minimize the contribution of polyaddition process in reactions of salts **VI** with isocyanates [1]) is unnecessary, except for the reaction with allyl isothiocyanate. However, the reasons for performing counterion replacement, e.g., in ethoxyethene salt **VI** (XR^1 = OEt, M = K), in its reactions with isocyanates and allyl isothiocyanate are quite different. In the first case, such replacement suppresses concurrent reaction of highly nucliophilic N-centered 2-ethoxyacrylamide anion with isocyanate (polyaddition reactions) [1, 26, 27], while in the second case it prevents deprotonation of isothiocyanate by the action of strongly basic carbanion **VI** [24, 25].

As we found previously [24, 25], both potassium and lithium salts derived from ethoxyethene react with allyl isothiocyanate exclusively as deprotonating agents to afford previously unknown and inaccessible *N*-allyl-*N*-methyl-5-amino-2-methylsulfanyl-4-vinyl-1,3-thiazole. This result opens an unexpectedly simple synthetic route to new polyunsaturated thiazole derivatives (which are promising building blocks); it also deserves attention at least taking into account that selective metalation of compounds containing functional groups with multiple carbon–heteroelement bonds (including isothiocyanates) is usually difficult to effect because of their high sensitivity to nucleophilic attack. For this purpose, strongly basic but weakly nucleophilic reagents are required, e.g., triphenylmethyllithium or sterically hindered lithium amides, such as lithium diisopropylamide or lithium 2,2,6,6-tetramethylpiperidide [35].

We succeeded in synthesizing *N*-allyl-2-ethoxy-1-methylsulfanyl-2-propen-1-imine (**Vd,** a mixture of *syn* and *anti* isomers) from allyl isothiocyanate and ether **I** via replacement of potassium cation in intermediate **VI** by $MgBr^+$ (a solution $MgBr_2$ in diethyl ether was added to the reaction mixture). However, organomagnesium reagents are much less active than potassium derivatives in reactions with heterocumulenes. In order to accelerate the formation (from RM and CS_2) and alkylation (with alkyl halides) of carbodithioates RC(=S)SM (M = MgCl, MgBr, Li), the reaction is carried out in the presence of copper(I) salts (5–30 mol %) [44, 45] or using hexamethylphosphoramide (HMPA) as co-solvent [46]. We used CuBr to activate the formation and alkylation of adduct **VII** (M = MgBr). A catalytic amount of CuBr (~7 mol %) was added to the reaction mixture immediately after addition of isothiocyanate (before alkylation) [25]. Addition of HMPA (together with CuBr) also favored the alkylation process [25]. On the other hand, further study of the above reaction showed that the use of CuBr and HMPA simultaneously in the final stage is not necessary. The yields of the isolated product **Vd** prepared in the presence of HMPA [25] and in the absence of it are almost of the same order, 81 and 76%, respectively. The only experimental difference is that quantitative alkylation of intermediate **VII** in the presence of HMPA is complete in 3–5 min at ~35°C [25]; otherwise, the reaction mixture should be heated at 40–45°C for ~0.5 h. An analogous conclusion was drawn by Meijer *et al*. [46]. Addition of 10–20 vol. % of HMPA to THF allowed us to reduced the temperature of both reaction stages: in the reaction of EtMgBr with carbon disulfide, from –15 to –70°C, and in the alkylation of the resulting EtCSSMgBr with methyl iodide, from 20–40 to –35°C, but the product yield remained unaffected. Nevertheless, the use of HMPA in the alkylation with less reactive alkyl bromides is believed to be quite reasonable and justified [46]. No appreciable effect on the reaction course and product yield was observed on variation of the order of mixing of the reactants at the stage of deprotonation of ether **I** or on treatment of the reaction mixture with water [25] or aqueous ammonium chloride.

We also showed (as yet, qualitatively) that reactions of metalated heteroelement-containing ethenes with aryl isothiocyanates having a halogen atom in the *ortho* position make it possible to obtain new benzothiazole derivatives (in addition to enethioamides and enimidothioates). The reaction of ethoxyethene potassium salt

Scheme 2.



VI with 2-fluorophenyl isothiocyanate gave *N*-(2-fluorophenyl)-2-ethoxy-2-propenethioamide **(IVe)**, *N*-(2-fluorophenyl)-2-ethoxy-1-methylsulfanyl-2-propen-1-imine **(Ve)**, or 2-(1-ethoxyvinyl)-1,3-benzothiazole **(VIII)**, depending on the conditions (Scheme 2). Compound **VIII** was formed via intramolecular nucleophilic substitution in intermediate **VIIe** when the reaction was carried out in the presence of $Pd(Ph_3P)_4$ in 1-methylpyrrolidin-2-one at 100–110°C (8 h; the conditions were not optimized). An attempt to synthesize benzothiazole **VIII** by heating intermediate **VIIe** in the presence of HMPA (45–62°C, 30 min) or *t*-BuOH (60–65°C, 75 min) was unsuccessful. After treatment of the reaction mixture with water, we isolated 86% of thioamide **IVe**. The presence of a highly reactive vinyloxy group in molecule **VIII** gives rise to further transformations typical of vinyl ethers. Acid hydrolysis of benzothiazole **VIII** (HCl, aqueous dioxane, room temperature, 2–3 min) afforded previously unknown 1-(1,3-benzothiazol-2-yl)-1-ethanone **(IX)** (Scheme 2). Here, metalated ethoxyethene acts as synthetic equivalent of acyl anion.

The structure of the prepared compounds was confirmed by elemental analysis and IR [47] and ^1H and ^{13}C NMR spectroscopy. The ^{13}C signals were assigned by analysis of the unidimensional *J* spectra optimized for a direct ^{13}C–^1H coupling constant of 145 Hz. As with N-monosubstituted acrylamides [1], in going from alkoxy to ethylsulfanyl derivatives we observed a sharp downfield shift of the vinyl proton signals in the ^1H NMR spectra of N-substituted thioamides **IV**: by ~1.09 ($\Delta\delta_{cis}$) and ~0.55 ppm ($\Delta\delta_{trans}$), though the *trans*-protons in **IV** turned out to be less sensitive to structural variations than the corresponding protons in acrylamides ($\Delta\delta_{trans}$ 1.06 ppm) [1]. On the other hand, the value $\Delta\delta_{cis-trans}$ for thioamides **IV** considerably exceeds that found for the oxygen analogs ($\Delta\delta$ 1.35–1.40 ppm in compounds **IV** and 0.95 ppm in acrylamides [1]).

EXPERIMENTAL

The IR spectra of samples prepared as thin films and KBr pellets were recorded on a Specord 75IR spectrophotometer. The ^1H and ^{13}C NMR spectra were measured on a Bruker DPX-400 instrument at 400 MHz for ^1H and 100 MHz for ^{13}C from ~5–10% solutions in $CDCl_3$ relative to HMDS as internal reference and on a Varian EM-390 spectrometer (90 MHz) from ~20% solutions in carbon tetrachloride using TMS as internal reference. GLC analysis was performed on a Varian 3400 gas chromatograph equipped with a flame-ionization detector and a DB-5 capillary column, 15 m×0.53 mm× 1.5 mm; carrier gas nitrogen.

All operations were performed under nitrogen or argon. Tetrahydrofuran was purified over mechanically dispersed potassium hydroxide (~50 g/l) and was distilled over $LiAlH_4$ in the presence of benzophenone under nitrogen. Butyllithium (a 1.6 M solution in hexane) was synthesized from metallic lithium and butyl chloride or a commercial product was used (Chemetall, Germany). Cyclopropyl, 2-fluorophenyl, and 2-trifluoromethylphenyl isothiocyanates were prepared by the procedures developed by us previously [28]. Methoxymethyl isothiocyanate was prepared from methyl chloromethyl ether and KSCN on heating in boiling pentane [48]. The

other reagents and solvents were commercial products. Liquid nitrogen was used as cooling agent.

***N*-Methyl-2-ethoxy-2-propenethioamide (IVa).** A solution of 6 g (53.6 mmol) of potassium *tert*-butoxide in 50 ml of THF and 20 g (277.8 mmol) of ether **I** were added in succession to a solution of 59.2 mmol of BuLi in 37 ml of hexane, cooled to –100°C. The mixture was stirred for 5–10 min at –70 to –40°C and cooled to –100°C, and a solution of 4 g (54.8 mmol) of methyl isothiocyanate in 15 ml of THF was quickly added. The mixture was allowed to warm up to –40°C and was cooled to –100°C, and a solution of 20 g of 30% hydrochloric acid in 100 ml of water was added (the mixture sharply warmed up). The organic phase was separated, the aqueous phase was treated with pentane (3 × 50 ml), and the extracts were combined with the organic phase, washed with water, dried over $MgSO_4$, and evaporated under reduced pressure on a rotary evaporator. The residue, 6.9 g (95%), was a mobile liquid which, according to the ^{1}H NMR data (CCl_4) was almost pure thioamide **IVa**, δ, ppm: 1.40 t (3H, OCH_2**Me**), 3.18 d (3H, NMe), 3.85 q (2H, OCH_2), 4.42 d and 5.78 d (2H, CH_2=), 8.60 br.s (1H, NH). Vacuum distillation gave 4.27 g (~59%) of a quickly crystallizing bright yellow material, bp 60–65°C (0.3 mm), n_D^{20} = 1.5670; mp 44–45°C, which contained ~100% of the main substance (GLC). IR spectrum (KBr), ν, cm^{-1}: 670, 710, 730, 750, 840, 860, 870, 980, 1010, 1050 sh, 1070, 1130, 1170, 1300, 1350, 1380 sh, 1440, 1480, 1530, 1630, 2880, 2935, 2970, 3300. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.39 t (3H, OCH_2**Me**, *J* = 7.0 Hz), 3.24 d (3H, NMe, *J* = 5.1 Hz), 3.87 q (2H, OCH_2, *J* = 7.0 Hz), 4.51 d (1H, CH_2=, J_{cis} = 2.4 Hz), 5.92 d (1H, CH_2=, J_{trans} = 2.4 Hz), 8.52 br.s (1H, NH). ^{13}C NMR spectrum, d_C, ppm: 14.47 (OCH_2**Me**), 32.67 (NMe), 64.65 (OCH_2), 94.18 (CH_2=), 156.31 (OC=), 190.76 (C=S). Found, %: C 49.69; H 8.36; N 9.38; S 22.13. $C_6H_{11}NOS$. Calculated, %: C 49.62; H 7.63; N 9.64; S 22.08.

***N*-Methoxymethyl-2-ethoxy-2-propenethioamide (IVb).** A solution of 2.25 g (20.1 mmol) of *t*-BuOK in 40 ml of THF and 6 g (83.3 mmol) of ether **I** were added in succession to a solution of 25.6 mmol of BuLi in 16 ml of hexane, cooled to –100°C. After 5–10 min, the mixture warmed up to –40°C. It was cooled to –100°C, a solution of 2.6 g (25.2 mmol) of methoxymethyl isothiocyanate in 10 ml of THF was quickly added, the cooling bath was removed, and (when the mixture warmed up to –40°C) 100 ml of a saturated aqueous solution of ammonium chloride was added. The mixture was extracted with diethyl ether (3 × 50 ml), and the extracts were combined, dried over K_2CO_3, and evaporated under reduced pressure. The residue, 2.6 g (74%) was distilled in a vacuum. Yield 1.11 g (32%), bp 93–95°C (0.6–1 mm), n_D^{20} = 1.5360. IR spectrum (film), n, cm^{-1}: 550, 660, 720, 860, 910, 970, 1000, 1020, 1050, 1090, 1130, 1200, 1300 br, 1340, 1410, 1450, 1500 br, 1620, 2820, 2890, 2030, 2980, 3300. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.39 t (3H, OCH_2**Me**, *J* = 7.0 Hz), 3.43 s (3H, OMe), 3.88 q (2H, OCH_2, *J* = 7.0 Hz), 4.57 d (1H, CH_2=, J_{cis} = 2.3 Hz), 5.91 d (1H, CH_2=, J_{trans} = 2.3 Hz), 5.19 d (2H, NCH_2, *J* = 5.7 Hz), 8.70 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 14.23 (OCH_2**Me**), 57.18 (OMe), 64.59 (OCH_2), 76.68 (NCH_2O), 94.96 (CH_2=), 156.08 (OC=), 191.56 (C=S). Found, %: C 48.36; H 8.10; N 8.06; S 18.54. $C_7H_{13}NO_2S$. Calculated, %: C 47.97; H 7.48; N 7.99; S 18.30.

***N*-Cyclopropyl-2-ethoxy-2-propenethioamide (IVc).** A solution of 2.25 g (0.1 mmol) of *t*-BuOK in 40 ml of THF and 6 g (83.3 mmol) of ether **I** were added in succession to a solution of 25.6 mmol of BuLi in 16 ml of hexane, cooled to –100°C. The mixture was allowed to warm up to –40°C (within 5–10 min) and cooled to –100°C, a solution of 1.98 g (20 mmol) of cyclopropyl isothiocyanate in 10 ml of THF was quickly added, and the mixture was allowed to warm up again to –40°C and was treated as described above. The solvent was removed under reduced pressure, and the residue, 3.22 g (94%) was distilled in a vacuum. Yield 1.69 g (49%), bp 104–107°C (0.6–1 mm), n_D^{20} = 1.5680. IR spectrum (film), ν, cm^{-1}: 610 br, 720, 860, 870, 940, 980, 1020, 1080 br, 1120, 1190, 1210, 1290, 1350, 1390, 1430, 1450, 1500 br, 1620, 2890, 2930, 2990, 3350. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.72 m (2H, CH_2), 0.97 m (2H, CH_2), 1.37 t (3H, OCH_2**Me**, *J* = 7.0 Hz), 3.30 m (1H, NCH), 3.86 q (2H, OCH_2, *J* = 7.0 Hz), 4.49 d (1H, CH_2=, J_{cis} = 2.3 Hz), 5.88 d (1H, CH_2=, J_{trans} = 2.3 Hz), 8.33 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 7.37 [$(CH_2)_2$], 14.44 (OCH_2**Me**), 28.74 (NCH), 64.72 (OCH_2), 93.99 (CH_2=), 156.24 (OC=), 191.24 (C=S). Found, %: C 55.81; H 7.98; N 8.25; S 18.62. $C_8H_{13}NOS$. Calculated, %: C 56.10; H 7.65; N 8.18; S 18.72.

***N*-(2-Fluorophenyl)-2-ethoxy-2-propenethioamide (IVe).** *a*. Potassium *tert*-butoxide, 6.28 g (56.1 mmol), was added at –50°C to a solution of 10.2 g (141.7 mmol) of ether **I** in 80 ml of THF, the mixture was cooled to –95°C, and a solution of 59.2 mmol of butyllithium in 37 ml of hexane was added (the solution turned bright yellow). The mixture was allowed to warm up to –30°C (in 15 min) and was cooled to –100°C, a solution of 8 g (52.3 mmol) of 2-fluorophenyl isothio-cyanate in 15 ml of THF was added, the cooling bath was removed, the mixture was allowed to warm up to –15°C (in 15

min), and two samples of an arbitrary volume were withdrawn from the mixture. One of these was treated with a saturated aqueous solution of ammonium chloride, and the other, with dilute hydrochloric acid. After appropriate treatment, in both cases almost pure thioamide **IVe** was isolated. ^{1}H NMR spectrum (CCl_4), δ, ppm: 1.44 t (3H, OCH_2**Me**), 3.90 q (2H, OCH_2), 4.54 d and 5.87 d (2H, CH_2=), 7.14 m (4H, H_{arom}), 9.08 br.s (1H, NH). A small part of the reaction mixture was treated with excess methyl iodide and, a few minutes later, with water. The organic phase was separated and dried over K_2CO_3, and the solvent was removed under reduced pressure. The residue was *N*-(2-fluorophenyl)-2-ethoxy-1-methylsulfanyl-2-propen-1-imine (**Ve**). ^{1}H NMR spectrum (CCl_4), δ, ppm: 0.93 t (3H, OCH_2**Me**), 2.43 s (SMe), 3.46 q (2H, OCH_2), 4.20 d and 5.56 d (2H, CH_2=), 6.87 m (4H, H_{arom}).

The remaining part of the reaction mixture was poured into 100 ml of a saturated solution of NH_4Cl, and (after appropriate treatment) we isolated almost pure thioamide **IVe** as a quickly crystallizing liquid.

b. Potassium *tert*-butoxide, 6.68 g (59.6 mmol), was added to a solution of 9.96 g (138.3 mmol) of ether **I** in 80 ml of THF, cooled to –70°C (the mixture warmed up to –50°C). The mixture was cooled to –90°C, a solution of 59.2 mmol of BuLi in 37 ml of hexane was added, the mixture was allowed to warm up to –30°C and cooled to –100°C, a solution of 7.77 g (50.8 mmol) of 2-fluorophenyl isothiocyanate in 15 ml of THF was added, and the cooling bath was removed. When the mixture warmed up to –10°C (in 20 min), 30 ml of HMPA was added, the mixture was heated for 30 min at 45–62°C, a solution of 7 g (94.6 mmol) of *tert*-butyl alcohol in 10 ml of THF was added, the mixture was heated for 75 min at 60–65°C and cooled, and 100 ml of water was added. The organic phase was separated, and the aqueous phase was extracted with diethyl ether (3×50 ml). The extracts were combined with the organic phase, washed with 5 portions of water to remove HMPA and *t*-BuOH, dried over K_2CO_3, and evaporated under reduced pressure. The residue was 9.7 g (86%) of thioamide **IVe**. ^{1}H NMR spectrum (CCl_4), δ, ppm: 1.47 t (3H, OCH_2**Me**), 3.90 q (2H, OCH_2), 4.52 d and 5.87 d (2H, CH_2=), 7.15 m (4H, H_{arom}), 9.08 br.s (1H, NH). The product decomposed on attempted vacuum distillation. A small amount of a liquid substance was isolated. According to the ^{1}H NMR data, it was a mixture of thioamide **IVe** and benzothiazole **VIII** at a ratio of ~3 : 1.

***N*-(2-Trifluoromethylphenyl)-2-ethoxy-2-propenethioamide (IVf).** A solution of 25.6 mmol of BuLi in 16 ml of hexane was cooled to –90°C, and a solution of 2.25 g (20.1 mmol) of *t*-BuOK in 40 ml of THF and 6 g (83.3 mmol) of ether **I** were added in succession. The mixture was allowed to warm up to –40°C and cooled again to –90°C, a solution of 4.04 g (19.9 mmol) of 2-trifluoromethylphenyl isothiocyanate in 10 ml of THF was quickly added, and the mixture was allowed to warm up to –40°C and was treated with a saturated aqueous solution of ammonium chloride. The organic phase was separated, and the aqueous phase was extracted with diethyl ether (3×50 ml). The extracts were combined with the organic phase, washed with water, dried over K_2CO_3, and evaporated on a rotary evaporator. The residue was 5.01 g (91%) of thioamide **IVf** containing a small amount of the initial isothiocyanate (according to the IR data). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.43 t (3H, OCH_2**Me**); 3.94 q (2H, OCH_2); 4.67 d and 5.99 d (2H, CH_2=); 7.61 d.d, 7.70 d, and 8.38 d (4H, H_{arom}); 10.23 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 14.34 (OCH_2**Me**), 65.27 (OCH_2), 95.65 (CH_2=), 156.84 (OC=), 189.79 (C=S). The product decomposed on attempted vacuum distillation.

***N*-Methyl-2-butoxy-2-propenethioamide (IVg).** A solution of 3 g (26.8 mmol) of *t*-BuOK in 40 ml of THF and 6 g (60 mmol) of ether **II** were added in succession to a solution of 32 mmol of BuLi in 20 ml of hexane, cooled to –100°C. The mixture warmed up to –40°C (in 5–10 min) and was cooled to –100°C, a solution of 2 g (27.4 mmol) of methyl isothiocyanate in 15 ml of THF was quickly added, and the mixture was allowed to warm up to –40°C and was treated as described above. Removal of the solvent under reduced pressure left 3.8 g (88%) of almost pure (according to the ^{1}H NMR data) thioamide **IVg**. By vacuum distillation we isolated 1.85 g (43%) of compound **IVg**, bp 108–111°C (0.6–1 mm), n_D^{20} = 1.5430. IR spectrum (film), ν, cm^{-1}: 600 br, 710, 830, 920, 1060 br, 1150, 1280, 1340 br, 1420, 1450, 1500, 1610, 2860, 2920, 2950, 3300. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.95 t [3H, $O(CH_2)_3$**Me**, *J* = 7.3 Hz], 1.44 m (2H, γ-CH_2), 1.73 m (2H, b-CH_2), 3.23 d (3H, NMe, *J* = 5.0 Hz), 3.80 q (2H, OCH_2, *J* = 7.3 Hz), 4.51 d (1H, CH_2=, J_{cis} = 2.2 Hz), 5.89 d (1H, CH_2=, J_{trans} = 2.2 Hz), 8.51 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 13.87 [$O(CH_2)_3$**Me**], 19.44 (γ-CH_2), 30.92 (β-CH_2), 32.78 (NMe), 68.91 (OCH_2), 94.13 (CH_2=), 156.47 (OC=), 190.81 (C=S). Found, %: C 54.97; H 9.09; N 8.17; S 18.63. $C_8H_{15}NOS$. Calculated, %: C 55.45; H 8.73; N 8.08; S 18.51.

***N*-Methyl-2-ethylsulfanyl-2-propenethioamide (IVh).** A solution of 6 g (53.6 mmol) of *t*-BuOK in 50 ml of THF and 5.13 g (58.3 mol) of sulfide **III** were added to a solution of 56 mmol of BuLi in 35 ml of hexane, cooled to –100°C. The mixture was allowed to warm up to –50 to –40°C, and a solution of 4 g (54.8 mmol) of

methyl isothiocyanate in 15 ml of THF was quickly added. After 5–10 min, the mixture was cooled to –100°C again, and a solution of 20 g of 30% hydrochloric acid in 150 ml of water was added. The organic phase was separated, and the aqueous phase was treated with pentane (3×50 ml). The extracts were combined with the organic phase, washed with water, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was 7.48 g (93%) of compound **IVg** containing ~100% of the main substance (GLC). ^{1}H NMR spectrum (CCl_4), δ, ppm: 1.30 m (3H, SCH_2**Me**), 2.65 q (2H, SCH_2), 3.22 d (3H, NMe), 5.60 d and 6.47 d (2H, CH_2=), 8.72 br.s (1H, NH). The product decomposed during vacuum distillation.

***N*-Ethyl-2-ethylsulfanyl-2-propenethioamide (IVi).** *a.* To a solution of 6 g (53.6 mmol) of *t*-BuOK in 50 ml of THF we added at –95 to –90°C in succession a solution of 56 mmol of BuLi in 35 ml of hexane, ~15 ml of diethyl ether (over a period of ~5 min), and 5.3 g (60.2 mmol) of freshly distilled sulfide **III** (at –80°C, over a period of ~5 min). The mixture was allowed to warm up to –50°C, and 5 g (57.5 mmol) of ethyl isothiocyanate was quickly added. When the mixture warmed up to –20°C, it was treated with a solution of NH_4Cl (the mixture turned first brown and then orange). The organic phase was separated, and the aqueous phase was extracted with diethyl ether (3×50 ml). The extracts were combined with the organic phase, washed with water, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was 7.8 g (89%) of thioamide **IVi** containing ~100% of the main substance (GLC). ^{1}H NMR spectrum (CCl_4), δ, ppm: 1.30 m (6H, SCH_2**Me**, NCH_2**Me**), 2.55 q (2H, SCH_2), 3.65 m (2H, NCH_2), 5.67 d and 6.57 d (2H, CH_2=), 8.55 br.s (1H, NH). The product decomposed during vacuum distillation.

b. A solution of 6 g (53.6 mmol) of *t*-BuOK in 50 ml of THF was added to a solution of 56 mmol of BuLi in 35 ml of hexane and ~15 ml of diethyl ether, cooled to –100°C. After 2–3 min, 5 g (56.8 mmol) of freshly distilled sulfide **III** was added. The mixture was stirred for 15 min at –55 to –40°C and cooled again to –100°C, 5 g (57.5 mmol) of ethyl isothiocyanate was added, the mixture was allowed to warm up to –30°C, and 15 ml of an aqueous solution of ammonium chloride was added (the mixture turned bright yellow). The mixture was then treated with ~100 ml of cold water at 0°C and was extracted with pentane (3×50 ml). The combined extracts were washed with water, dried over $MgSO_4$, and evaporated under reduced pressure (first, on a rotary evaporator and then in a high vacuum). The residue was 8.08 g (>92%) of compound **IVi** containing ~100% of the main substance (GLC, NMR).

***N*-Methyl-2-ethoxy-1-methylsulfanyl-2-propen-1-imine (Va).** *a.* A solution of 6 g (53.6 mmol) of *t*-BuOK in 50 ml of THF was added to a solution of 59.2 mmol of BuLi in 37 ml of hexane, cooled to –85°C. The mixture was cooled to –100°C, 20 g (277.8 mmol) of ether **I** was added, the mixture was allowed to spontaneously warm up to –30°C (the cooling bath was removed) and was cooled again to –100°C, and a solution of 4 g (54.8 mmol) of methyl isothiocyanate in 15 ml of THF was quickly added (the mixture became a light yellow suspension). Methyl iodide, 12 g (83.3 mmol), was added to the mixture at –40°C, and the mixture was allowed to warm up to 20°C, treated with a saturated aqueous solution of ammonium chloride, and extracted with pentane (3×50 ml). The combined extracts were dried over $MgSO_4$, and the solvent was removed on a rotary evaporator. According to the GLC and ^{1}H NMR (CCl_4) data, the residue was compound **Va** [δ, ppm: 1.35 d.t (3H, OCH_2**Me**), 2.20 s and 2.35 s (3H, SMe), 3.15 s and 3.20 s (3H, NMe), 3.72 d.q (2H, OCH_2), 4.13 d and 4.25 d (2H, CH_2=)] containing ~16% of thioamide **IVa** [δ, ppm: 4.35 d and 5.70 d (2H, CH_2=)]. Vacuum distillation gave 4.46 g (56%) of compound **Va** containing ~97% of the main substance (GLC), bp 80–82°C (7.2–8 mm), n_D^{20} = 1.5040. ^{1}H NMR spectrum (CCl_4), δ, ppm: 1.37 d.t (3H, OCH_2**Me**), 2.27 s and 2.40 s (3H, SMe), 3.20 s and 3.27 s (3H, NMe), 3.77 d.q (2H, OCH_2), 4.15 d and 4.30 d (2H, CH_2=); also, weak signals from the vinyl protons of thioamide **IVa** were observed at δ 4.43 (d) and 5.80 ppm (d). The high-boiling fraction, 1.58 g, bp ~135°C (7.2–8 mm), n_D^{20} = 1.5630, contained 63.2% of compound **IVa**, 23.3% of **Va**, and heavier products (GLC) which were absent in the crude product. ^{1}H NMR spectrum (CCl_4), δ, ppm: 1.40 t (3H, OCH_2**Me**), 3.10 s and 3.15 s (3H, NMe), 3.85 q (2H, OCH_2), 4.40 d and 5.70 d (2H, CH_2=), 8.70 br.s (1H, NH).

b. A solution of 6 g (53.6 mmol) of *t*-BuOK in 50 ml of THF and 22 g (305.6 mmol) of ether **I** were added in succession to a solution of 59.2 mmol of BuLi in 37 ml of hexane, cooled to –100°C. The mixture was allowed to warm up to –30°C and cooled to –100°C, and a solution of 4 g (54.8 mmol) of methyl isothiocyanate in 15 ml of THF was quickly added. The cooling bath was removed, the mixture was allowed to warm up to –40°C, 16 g (111.1 mmol) of methyl iodide was added, and the mixture was stirred for 30 min at –30 to –40°C, treated with an aqueous solution of NH_4Cl, and extracted with pentane (3×50 ml). The combined extracts were dried over $MgSO_4$, and the solvent was distilled off on a rotary evaporator to obtain almost pure compound **Va** as a mixture of *syn* and *anti* isomers (NMR). ^{1}H NMR spectrum (CCl_4),

δ, ppm: 1.35 d.t (3H, OCH_2**Me**), 2.20 s and 2.35 s (3H, SMe), 3.15 s and 3.20 s (3H, NMe), 3.70 d.q (2H, OCH_2), 4.15 d and 4.25 d (2H, CH_2=). Vacuum distillation gave 5.47 g (69%) of a light yellow liquid containing 99% of compound **Va** (GLC), bp 80–82°C (7.2–8 mm), n_D^{20} = 1.5030. IR spectrum (film), ν, cm^{-1}: 700, 740, 750, 820 s, 840 sh, 860, 960 sh, 970, 1000, 1030, 1060 v.s, 1090 sh, 1110, 1140, 1150 sh, 1290 v.s, 1360, 1380, 1400, 1440, 1480, 1600 v.s, 1620, 2860 sh, 2920, 2970, 3110. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.33 t and 1.36 t (3H, OCH_2**Me**, J = 7.0 Hz), 2.28 s and 2.41 s (3H, SMe), 3.25 s and 3.27 s (3H, NMe), 3.79 q and 3.83 q (2H, OCH_2, J = 7.0 Hz), 4.26 d and 4.40 d (1H, CH_2=, J = 2.6 Hz), 4.32 d and 4.35 d (1H, CH_2=, J = 2.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.01 and 14.34 (SMe), 14.46 and 14.67 (OCH_2**Me**), 40.33 and 41.13 (NMe), 63.34 and 63.55 (OCH_2), 87.05 and 87.70 (CH_2=), 155.49 and 157.78 (OC=), 162.86 and 163.87 (N=C). Found, %: C 51.99; H 8.43; N 8.74; S 19.92. $C_7H_{13}NOS$. Calculated, %: C 52.79; H 8.23; N 8.80; S 20.14.

***N*-Allyl-2-ethoxy-1-methylsulfanyl-2-propen-1-imine (Vd).** A solution of 6 g (53.6 mmol) of *t*-BuOK in 50 ml of THF and 20 g (277.8 mmol) of ether **I** were added in succession to a solution of 60.8 mmol of BuLi in 38 ml of hexane, cooled to –100°C. The mixture was allowed to warm up to –40°C, and a solution of 50 mmol of $MgBr_2$ in 50 ml of diethyl ether (a milk white suspension was formed), 5 g (50.5 mmol) of allyl isothiocyanate (at 0°C; the mixture warmed up to 5°C), and 0.5 g of CuBr were added (the temperature rose to 27°C). Methyl iodide, 20 g (138.9 mmol), was then added, and the mixture was heated for 0.5 h at 40–45°C and treated with an aqueous solution of NH_4Cl. The organic phase was separated, and the aqueous phase was treated with pentane. The extracts were combined with the organic phase, washed with water, and dried over $MgSO_4$, the solvent was removed on a rotary evaporator, and the residue was distilled in a vacuum. Yield of **Vd** 7.06 g (76%), purity 97% (GLC), bp 68–70°C (0.5 mm), n_D^{20} = 1.5080. IR spectrum (film), ν, cm^{-1}: 830, 860, 920, 970, 990, 1040, 1060 v.s, 1090, 1110, 1140, 1150, 1240 sh, 1280 v.s, 1320, 1360 sh, 1380, 1410, 1440, 1480, 1600 v.s, 1630, 2870, 2930, 2980, 3010, 3080. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.34 d.t (3H, OCH_2**Me**); 2.32 s and 2.41 s (3H, SMe); 3.80 d.q (2H, OCH_2); 4.03 t, 4.04 t, 4.10 t, and 4.12 t (2H, NCH_2); 4.25 d, 4.32 d, 4.34 d, and 4.44 d (2H, CH_2=, vinyl); 5.06 q, 5.08 q, 5.11 q, 5.13 q, 5.18 q, 5.20 q, 5.22 q, and 5.25 q (2H, CH_2=, allyl); 6.05 br.m (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: 13.11 and 14.35 (SMe), 14.48 and 14.86 (OCH_2**Me**), 55.94 and 56.15 (NCH_2), 63.44 and 63.59 (OCH_2), 87.32 and 87.72 (CH_2=, vinyl), 114.82 and 116.03 (CH_2=, allyl), 135.37 and 136.88 (CH=), 155.69 and 157.78 (OC=), 162.30 and 162.93 (N=C). Found, %: C 58.02; H 8.38; N 7.81; S 17.09. $C_9H_{15}NOS$. Calculated, %: C 58.34; H 8.16; N 7.56; S 17.31.

***N*-(2-Fluorophenyl)-2-ethoxy-methylsulfanyl-2-propen-1-imine (Ve)** was isolated in the synthesis of thioamide **IVe**.

***N*-Methyl-2-butoxy-1-methylsulfanyl-2-propen-1-imine (Vg).** Methyl iodide, 8.5 g (59 mmol), was added at –35°C to a solution of intermediate **VII,** prepared as described above in the synthesis of thioamide **IVg** from a solution of 32 mmol of BuLi in 20 ml of hexane, a solution of 3 g (26.8 mmol) of *t*-BuOK in 40 ml of THF, and 6 g (60 mmol) of ether **II**. The mixture was allowed to warm up to room temperature, stirred for 40 min, and treated as described above. Removal of the solvent under reduced pressure left 4.23 g (91%) of compound **Vg**. Vacuum distillation gave 2.7 g (58%) of the product with bp 60–65°C (0.6–1 mm), n_D^{20} = 1.4940. IR spectrum (film), ν, cm^{-1}: 550, 630, 700, 730, 760, 820 br, 900, 950, 970, 1010, 1040, 1060 br, 1150, 1210, 1300 br, 1390, 1410, 1440, 1460, 1610, 1640 br, 2790, 2880, 2930, 2960. ^{1}H NMR ($CDCl_3$), δ, ppm: 0.93 t and 0.95 t [3H, $O(CH_2)_3$**Me**, J = 4 Hz], 1.44 m (2H, γ-CH_2), 1.71 m (2H, β-CH_2), 2.29 s and 2.40 s (3H, SMe), 3.25 s and 3.27 s (3H, NMe), 3.74 m (2H, OCH_2), 4.24 d and 4.39 d (1H, CH_2=, J = 2.4 Hz), 4.32 d and 4.35 d (1H, CH_2=, J = 2.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.00 and 13.81 (SMe), 13.86 and 14.54 [$O(CH_2)_3Me$], 19.42 and 19.44 (γ-CH_2), 30.90 and 31.04 (β-CH_2), 40.30 and 41.20 (NMe), 67.48 and 63.73 (OCH_2), 86.85 and 87.57 (CH_2=), 155.75 and 158.07 (OC=), 162.88 and 163.93 (C=N). Found, %: C 57.53; H 9.29; N 7.61; S 17.63. $C_9H_{17}NOS$. Calculated, %: C 57.71; H 9.15; N 7.48; S 17.12.

***N*-Methyl-2-ethylsulfanyl-1-methylsulfanyl-2-propen-1-imine (Vh).** A solution of 6 g (53.6 mmol) of *t*-BuOK in 50 ml of THF and 5.3 g (60.2 mmol) of sulfide **III** were added in succession to a solution of 56 mmol of BuLi in 35 ml of hexane, cooled to –100°C. The mixture was allowed to warm up to –40°C and cooled to –100°C, a solution of 3.8 g (52 mmol) of methyl isothiocyanate in 10 ml of THF was quickly added, the mixture was allowed to warm up to –50°C, 12 g (83.3 mmol) of methyl iodide was added, and the mixture was heated to 20°C and, after 2–3 min, was treated with an aqueous solution of ammonium chloride. After appropriate treatment, removal of the solvent gave 8.25 g (94%) of compound **Vh** [δ 5.17 (d) and 5.30 ppm (d) (CH_2=)] containing less than 10% of thioamide **IVh** [δ 5.60 (d) and 6.60 ppm (d)

(CH_2=)]. By vacuum distillation of the residue we isolated 6.57 g (75%) of compound **Vh** as a mixture of *syn* and *anti* isomers, which contained >96% of the main substance (GLC); bp 60–65°C (0.4 mm), n_D^{20} = 1.5530. IR spectrum (film), ν, cm^{-1}: 760, 790, 860, 960 sh, 970, 1000, 1030, 1050 sh, 1140, 1160–1200, 1260, 1310, 1370, 1400, 1440 sh, 1450, 1580, 1610, 2860, 2920, 2960, 3080. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 d.t (3H, SCH_2**Me**); 2.30 s and 2.44 s (3H, SMe); 2.73 br.m (2H, SCH_2); 3.28 s and 3.30 s (3H, NMe); 5.20 d, 5.23 d, 5.25 d, and 5.43 d (2H, CH_2=). ^{13}C NMR spectrum, δ_C, ppm: 13.20 and 15.70 (SMe), 13.65 (SCH_2**Me**), 25.91 (SCH_2), 40.59 and 40.69 (NMe), 112.83 and 113.41 (CH_2=), 139.97 and 142.34 (SC=), 164.49 and 164.61 (N=C). Found, %: C 48.19; H 7.83; N 7.77; S 36.21. $C_7H_{13}NS_2$. Calculated, %: C 47.96; H 7.47; N 7.99; S 36.58.

***N*-Ethyl-2-ethylsulfanyl-1-methylsulfanyl-2-propen-1-imine (Vi).** *a.* A solution of 6 g (53.6 mmol) of *t*-BuOK in 25 ml of THF was added at –30°C to a solution of 7.9 g (45 mmol) of thioamide **IVi** in 30 ml of THF (the mixture warmed up to 0°C). The mixture was cooled to –30°C, 12 g (83.3 mmol) of methyl iodide was added, and the mixture was stirred for 10–15 min at –15 to –10°C and was treated first with an aqueous solution of NH_4Cl and then with water. The mixture was extracted with pentane (3×50 ml), the combined extracts were dried over $MgSO_4$, and the solvent was removed on a rotary evaporator. Yield 6.8 g (80%); the product contained more than 93% of the main substance (GLC). ^{1}H NMR spectrum (CCl_4), δ, ppm: 1.25 m (6H, SCH_2**Me**, NCH_2**Me**); 2.25 s and 2.40 s (3H, SMe); 2.65 d.q (2H, SCH_2); 3.45 m (2H, NCH_2); 5.17 d.d, 5.25 d, and 5.33 d (2H, CH_2=).

b. A solution of 6 g (53.6 mmol) of *t*-BuOK in 50 ml of THF was added to a solution of 56 mmol of BuLi in 35 ml of hexane, cooled to –100°C, and (after 2–3 min) 5.23 g (59.4 mmol) of freshly distilled sulfide **III** was added. After 5 min (at –60°C), a suspension was obtained. The mixture was cooled to –100°C, 5 g (57.5 mmol) of ethyl isothiocyanate was added, and the cooling bath was removed. When the mixture warmed up to –35°C, 10 g (69.4 mmol) of methyl iodide was added, the mixture was heated to 20°C, and (after ~10 min) the resulting yellow suspension was treated with ~100 ml of cold water. The organic phase was separated, the aqueous phase was treated with pentane (3×50 ml), the extracts were combined with the organic phase and dried over $MgSO_4$, the solvent was removed on a rotary evaporator, and the residue was distilled under reduced pressure. Yield 9.4 g (99.5%). Compound **Vi** was isolated as a mixture of *syn* and *anti* isomers (NMR), containing 92% of the main substance (GLC); bright yellow moderately viscous liquid, bp 105–107°C (7.2 mm), n_D^{20} = 1.5390. IR spectrum (film), ν, cm^{-1}: 760, 790, 830, 860, 890 pl, 910, 970, 1000, 1050, 1100, 1150 sh, 1190, 1270, 1350, 1380, 1450, 1580, 1620, 2860, 2940, 2960. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.18 t and 1.30 m (6H, SCH_2**Me**, NCH_2**Me**); 2.31 s and 2.44 s (3H, SMe); 2.73 m (2H, SCH_2); 3.48 d.m (2H, NCH_2); 5.18 d, 5.19 d, 5.24 d, and 5.39 d (2H, CH_2=). ^{13}C NMR spectrum, δ_C, ppm: 13.02 and 13.44 (SMe); 13.56, 15.35, 15.51, and 16.47 (SCH_2**Me**, NCH_2**Me**); 25.72 and 25.79 (SCH_2); 47.74 and 47.80 (NCH_2); 112.14 and 113.02 (CH_2=); 140.18 and 142.09 (SC=); 162.04 and 162.23 (N=C). Found, %: C 50.46; H 8.42; N 7.37; S 33.75. $C_8H_{15}NS_2$. Calculated, %: C 50.75; H 7.99; N 7.40; S 33.87.

2-(1-Ethoxyvinyl)-1,3-benzothiazole (VIII) and 1-(1,3-benzothiazol-2-yl)-1-ethanone (IX). Potassium *tert*-butoxide, 6.8 g (60.7 mmol), was added to a solution of 10.5 g (145.8 mmol) of ether **I** in 100 ml of THF, cooled to –80°C (the mixture warmed up to –50°C). The mixture was cooled to –100°C, and a solution of 59.2 mmol of BuLi in 37 ml of hexane was added over a period of 10 min. The mixture was allowed to warm up to –40°C and cooled to –100°C, and a solution of 7.4 g (48.4 mmol) of 2-fluorophenyl isothiocyanate in 15 ml of THF was added using a pipette at –100 to –85°C. The cooling bath was removed, the mixture was stirred for 15–20 min at –10°C and transferred into an Erlenmeier flask, 1 g of $Pd(Ph_3P)_4$ and 30 ml of 1-methylpyrrolidin-2-one were added, and the mixture was stirred for ~8 h at 100–110°C using a magnetic stirrer and reflux condenser. The mixture was cooled, treated with an aqueous solution of ammonium chloride and KCN, and extracted with diethyl ether. The combined extracts were dried over K_2CO_3, the solvent was distilled off on a rotary evaporator, and the residue was diluted with diethyl ether and was passed through a column charged with neutral Al_2O_3. The solvent was removed to obtain benzothiazole **VIII** as a ruby viscous liquid. ^{1}H NMR spectrum (CCl_4), δ, ppm: 1.45 t (3H, OCH_2**Me**), 4.00 q (2H, OCH_2), 4.44 d and 5.50 d (2H, CH_2=), 7.45 m and 8.10 m (4H, H_{arom}). The product was dissolved in ~20 ml of dioxane, a solution of 2.3 g of 30% hydrochloric acid in ~15 ml of water was added (the mixture turned green), and (after 2–3 min), the mixture was treated with water and extracted with diethyl ether. The combined extracts were washed with water (to remove dioxane) and dried over K_2CO_3. The solvent was removed to obtain benzothiazole **IX** as a cherry red liquid. ^{1}H NMR spectrum (CCl_4), δ, ppm: 2.70 s (3H, Me), 7.45 m (4H, H_{arom}).

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