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DEVELOPMENT OF A NOVEL APPROACH TO FORMATION OF A PYRROLE RING: SYNTHESIS OF 2,3,5-SUBSTITUTED 1-[2-(VINYLOXY)ETHYL]PYRROLES*

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Reaction of 2-(vinyloxy)ethylisothiocyanate with unsaturated carbanions generated in situ from propargyl ethers and amines when treated with superbases, after S-alkylation and cyclization of the adducts in the presence of CuBr, leads to the previously unknown 2,3,5-substituted 1-[2-(vinyloxy)ethyl]pyrroles.

Keywords: 2-alkynes, 2,3-butadiene imidothioates, 2-(vinyloxy)ethylisothiocyanate, 1-[2-(vinyloxy)-ethyl]pyrroles, superbases, deprotonation, catalysis, cyclization.

Before our investigations, the only representative of vinyl ethers with pyrrole substituents described was 1-[2-(vinyloxy)ethyl]pyrrole, obtained in 57% yield by reaction of 1,4-bis(N,N-dimethylamino)-1,3-butadiene with 2-(vinyloxy)ethylamine in acetic acid [1, 2]. Recently, using a fundamentally new general strategy we developed for formation of the pyrrole ring [3, 4] based on the reaction of isothiocyanates with carbanions of 1,2-dienes and 2-alkynes, we synthesized two more representatives of vinyl ethers of the pyrrole series: 3-alkoxy-2-(methylthio)- [3, 5] and 5-*tert*-butyl-2-(methylthio)-1-[2-(vinyloxy)ethyl]pyrroles [3], starting from the accessible 2-(vinyloxy)ethylisothiocyanate (**1**) [6] and lithiated methoxyallene and 4,4-dimethyl-1,2-pentadiene [7] respectively.

The use of lithiated propargyl ethers and amines in the reaction with isothiocyanates made it possible fundamentally to extend the synthetic options for the developed approach and successfully to construct a 1,2,3,5-tetrasubstituted pyrrole ring in one preparative step [3, 4, 8]. 2-(Vinyloxy)ethylisothiocyanate, which as we showed in [3-5], in reactions of pyrrole synthesis plays the role of not only a structural unit but also a supplier of the active vinyloxy group (as an anchor vinyl ether [6,9]), so far has not been used in reaction with propargyl ethers and amines.

In this paper, with the aim of expanding the synthetic potential of both the reaction itself and the products formed, we have studied the reaction of isothiocyanate **1** with lithiated 1-methoxy-2-heptyne (**2a**), 3-methoxy-1-(methylthio)-1-propyne (**2b**), N,N-dimethyl-3-(methylthio)-2-propyne-1-amine (**2c**), N,N-dimethyl-3-phenyl-2-propyne-1-amine (**2d**), and N,N-diethyl-3-phenyl-2-propyne-1-amine (**2e**). This is a simple, original,

* Dedicated to Academician M. G. Voronkov on his 80th birthday.

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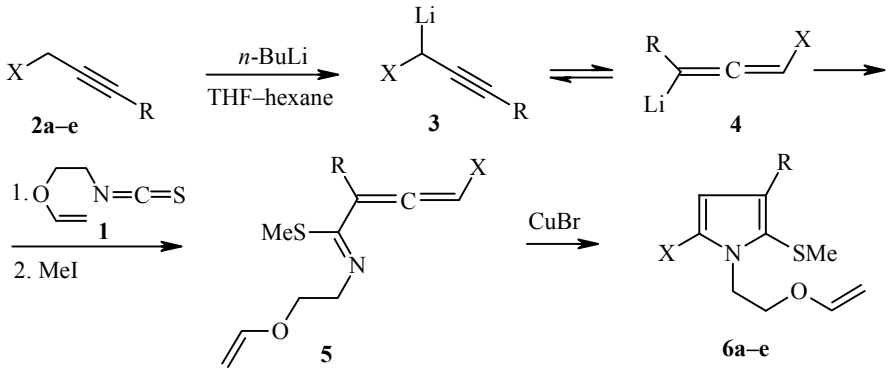
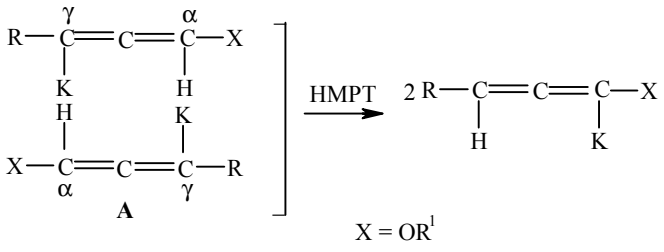
and convenient route to previously unknown and inaccessible 2,3,5-substituted 1-[2-(vinyloxy)ethyl]pyrroles (**6a-c**) [10], which are promising monomers and intermediates for diverse organic syntheses. The reaction was conducted in a single preparative step (without isolating intermediates from the reaction mixture).



6a X = MeO, R = Bu; **b** X = MeO, R = SMe; **c** X = Me_2N, R = SMe;
d X = Me_2N, R = Ph; **e** X = Et_2N, R = Ph

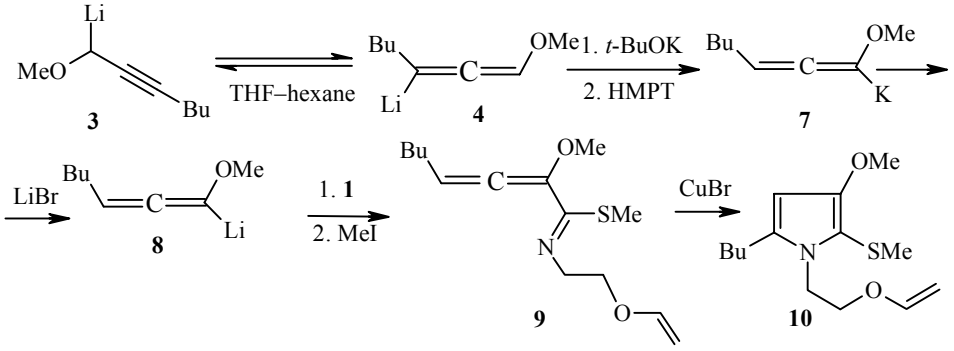
Alkynes **2a-e** is easily deprotonated by butyllithium in a tetrahydrofuran–hexane mixture at a temperature from -100°C to -20°C over the course of ~15-30 min with formation of an equilibrium mixture of acetylene and allene lithium derivatives **3** and **4** [11], which as we established in [8, 12], react with isothiocyanate **1** (-100°C to -25°C, 10-30 min) exclusively in allene form **4**. Alkylation of the adducts (lithium thiolates) by methyl iodide quantitatively leads to 2,3-butadiene imidothioate **5**, which in the presence of catalytic amounts of monovalent copper salts (CuBr or CuI [3, 13]) added to the reaction mixture at a temperature no higher than 10-15°C (with the goal of preventing 1,5-sigmatropic rearrangement of intermediate 2,3-butadiene imidothioates **5** [3], which is undesirable in this case) are smoothly transformed to pyrroles **6a-e**, isolated in preparative yield up to 74% (the yields are not optimized) by distillation of the products under vacuum.

The conditions for deprotonation of alkynes when treated with superbases have a fundamental effect not only on the product yield, but also on the result of the reaction as a whole. This especially pertains to the effect of the nature of the superbase and the solvent. It has been shown [14] that in strongly polar media, for example as created by replacing lithium in an intermediate of type **4** (X = O) with potassium and adding hexametapol (HMPT) as the cosolvent, γ-metalated allene ethers are rearranged to α-metalated derivatives. The mechanism of this unusual isomerization of carbanions has not yet been conclusively clarified. It possibly occurs via "head to tail" rearrangement of two metalated molecules in some aggregate structure **A**, as a result of which the α proton from one molecule moves to the γ position of the other molecule as the polarization of the =C–K bond increases on treatment with hexametapol [15].



We tested the possibility of transformation of carbanions if the polarity of the medium is changed [14] in the reaction under study, for the example of 1-methoxy-2-heptyne (**2a**). As has already been noted, treatment with *n*-BuLi results in formation of 3-lithio-1-methoxy-1,2-heptadiene (**4a**), the reaction of which with isothiocyanate **1** (after alkylation and cyclization of adduct **5a**) leads to 3-butyl-5-methoxy-2-(methylthio)-1-[2-(vinyloxy)ethyl]pyrrole (**6a**).

However, use of *n*-BuLi–*t*-BuOK as the deprotonating base and addition of hexametapol to the reaction mixture, followed by substitution of the potassium in intermediate **7** by lithium using LiBr (functionalization of lithium derivatives by electrophiles often occurs more easily and more selectively than for their potassium analogs [11]), as to be expected based on data from [14], leads to another intermediate: 1-lithio-1-methoxy-1,2-heptadiene (**8**). Evidence for its formation is synthesis of 5-butyl-3-methoxy-2-(methylthio)-1-[2-(vinyloxy)ethyl]pyrrole (**10**). Analysis of the ^{1}H and ^{13}C NMR spectra of pyrroles **6a** and **10** showed that these two structures differ from each other in the position of identical substituents on the ring, i.e., a change in the conditions for generation of unsaturated carbanions allowed us in fact to interchange the substituent sites in the 3 and 5 positions of the pyrrole ring. In the ^{1}H NMR spectra, this is very clearly apparent in the strong downfield shift of the singlet signal from the proton in the 4 position of the pyrrole ring (at 5.22 ppm for **6a**) to 5.67 ppm for **10**. We observed shifts of the remaining signals, but they were not so significant. In the ^{13}C NMR spectra, the signals that were the most sensitive to structural changes proved to be signals from all the C atoms of the pyrrole ring, the $\Delta\delta$ for which was 5-10 ppm.



Thus the results obtained clearly suggest that the nature and position of substituents on the pyrrole ring can be easily controlled not only by choosing appropriate isothiocyanates and alkynes or 1,2-dienes [3, 4], but also by choosing the reaction conditions. Knowledge and understanding of the processes occurring in the step of generation of unsaturated carbanions allow us to carry out controllable step-by-step assembly of various pyrrole structures from the same starting compounds, i.e., to guide the C-substituents, the supplier of which in the reaction under study is the alkyne, to prespecified positions on the pyrrole ring. The composition and structure of the synthesized compounds have been confirmed by elemental analysis, ^{1}H NMR, ^{13}C NMR, and IR spectroscopy.

EXPERIMENTAL

The IR spectra were taken on a Specord IR-75 spectrophotometer in a thin layer. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DPX-400 spectrometer (respectively at 400 MHz and 100 MHz) in $CDCl^3$ and acetone-d_6 solutions at room temperature (internal standard: HMDS). The reactions and purity of the compounds were monitored by GLC on a Varian 3400 gas chromatograph equipped with a flame ionization detector and a capillary column (15 m × 0.53 mm) with a coating of DB-5 (1.5 μm), with nitrogen as the carrier gas. The THF was purified mechanically with dispersed KOH (~50 g/l) and distilled over $LiAlH_4$ in the

presence of benzophenone under a nitrogen atmosphere. 2-(Vinyloxy)ethylisothiocyanate (**1**) was obtained by the method we developed in [3]. The synthesis of alkynes **2a-e** has been described in monographs [7, 16]. Butyllithium (1.6 M solution in hexane) and the rest of the reagents used in this work were obtained from Chemetall, Acros, and Merck. All operations were conducted under a nitrogen atmosphere. We used liquid nitrogen for cooling.

3-Butyl-5-methoxy-2-(methylthio)-1-[2-(vinyloxy)ethyl]pyrrole (6a). Compound **2a** (6.3 g, 0.05 mol) was added to a solution of *n*-BuLi (0.05 mol) in hexane (35 ml) and THF (50 ml) that had been cooled down to -80°C. After 30 min of stirring at -55°C, the reaction mixture was again cooled down to -90°C and a solution of isothiocyanate **1** (6.45 g, 0.05 mol) in THF (15 ml) was rapidly added to it. After raising the temperature up to -30°C, 15 g (0.05 mol) MeI was added to the reaction mixture and then (at 15°C) finely ground CuBr (1 g) was added. After the temperature had spontaneously risen to 30°C (over the course of ~5 min), a saturated solution of NH_4Cl with 10% NaCN (130 ml) was added; the mixture was stirred for 10 min and the organic layer was separated. The aqueous layer was extracted with ether (3 × 50 ml). The combined organic fraction was dried over $MgSO_4$; the solution was passed through a column with neutral Al_2O_3, the solvent was driven off under reduced pressure, and the residue was distilled. Yield 9.89 g (73.5%) pyrrole **6a**; bp 135-140°C (0.7 mm Hg), content of the major compound ~100% (GLC). IR spectrum, ν, cm^{-1}: 620, 730, 820, 960, 1000, 1010, 1060, 1080, 1170, 1190, 1280, 1310, 1350, 1360, 1420, 1450-1480, 1500, 1560, 1610, 1630, 2820, 2850, 2870, 2920, 2950. ^{1}H NMR spectrum ($CDCl_3$-d_6), δ, ppm, *J* (Hz): 6.40 (1H, q, $^3J_{trans}$ = 14.32, $^3J_{cis}$ = 6.79, OCH=); 5.22 (1H, s, CH=); 4.17 (1H, dd, $^3J_{trans}$ = 14.32, ^2J = 2.10, CH_2=); 4.16 (2H, t, *J* = 6.60, OCH_2); 3.96 (1H, dd, $^3J_{cis}$ = 6.79, ^2J = 2.10, CH_2=); 3.85 (2H, t, *J* = 6.60, NCH_2); 3.74 (3H, s, OMe); 2.50 (2H, m, α-CH_2); 2.07 (3H, s, SMe); 1.49 (2H, m, β-CH_2); 1.33 (2H, m, γ-CH_2); 0.89 (3H, t, Me). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 151.51 (OCH=); 149.48 (5-C); 129.75 (2-C); 110.50 (3-C); 86.36 (CH_2=); 84.77 (4-CH=); 66.62 (OCH_2); 56.87 (OMe); 40.80 (NCH_2); 33.43 (CH_2); 26.69 (CH_2); 22.37 (CH_2); 21.07 (SMe); 13.58 (Me). Found, %: C 63.26; H 8.35; N 5.18; S 12.64. $C_{14}H_{23}NO_2S$. Calculated, %: C 62.42; H 8.61; N 5.24; S 11.90.

5-Methoxy-2,3-bis(methylthio)-1-[2-(vinyloxy)ethyl]pyrrole (6b). Compound **2b** (5.8 g, 0.05 mol) was added to a solution of *n*-BuLi (0.05 mol) in hexane (35 ml) and THF (50 ml) that had been cooled down to -100°C. After raising the temperature up to -20°C, the reaction mass was again cooled down to -100°C and a solution of isothiocyanate **1** (6.45 g, 0.05 mol) in THF (15 ml) was rapidly added to it. The mixture was stirred for 10 min at -45°C, and at -25°C MeI (14 g, 0.01 mol) was added to it and then (at 15°C) CuBr (2 g) was added. After the temperature spontaneously rose up to 35°C (over the course of ~40 min) and additional stirring at 40°C for 30 min, the reaction mixture was treated as described above. Yield 9.57 g (73.9%) of pyrrole **6b**; bp 130°C (0.5 mm Hg), n_D^{20} 1.5659, content of major compound 97.2% (GLC). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 6.37 (1H, q, $^3J_{trans}$ = 14.27, $^3J_{cis}$ = 6.77, OCH=); 5.36 (1H, s, CH=); 4.16 (2H, t, *J* = 6.31, OCH_2); 4.15 (1H, dd, $^3J_{trans}$ = 14.27, ^2J = 2.37, CH_2=); 3.95 (1H, dd, $^3J_{cis}$ = 6.77, ^2J = 2.37, CH_2=); 3.83 (2H, t, *J* = 6.31, NCH_2); 3.77 (3H, s, OMe); 2.33 (3H, s, SMe); 2.07 (3H, s, SMe). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 151.02 (OCH=); 149.12 (5-C); 121.47 (2-C); 114.76 (3-C); 86.71 (CH_2=); 86.60 (4-CH=); 66.12 (OCH_2); 57.09 (OMe); 41.19 (NCH_2); 20.74 (SMe); 18.66 (SMe). Found, %: C 51.54; H 6.68; N 5.45; S 24.68. $C_{11}H_{17}NO_2S_2$. Calculated, %: C 50.93; H 6.61; N 5.40; S 24.72.

2-Dimethylamino-4,5-bis(methylthio)-1-[2-(vinyloxy)ethyl]pyrrole (6c). Compound **2c** (5.16 g, 0.04 mol) was added to a solution of *n*-BuLi (0.04 mol) in hexane (28 ml) and THF (40 ml) that had been cooled down to -100°C. After the temperature was raised to -70°C, the reaction mass was again cooled down to -95°C and a solution of isothiocyanate **1** (5.16 g, 0.04 mol) in THF (15 ml) was added rapidly to it. When the temperature of the mixture reached -25°C, MeI (8 g, 0.06 mol) was added to it and then (at 15°C) CuBr (0.8 g) was added. After the temperature rose spontaneously up to 37°C (over the course of ~2 min), the reaction mixture was treated as described above. Yield 6.46 g (59.4%) of pyrrole **6c**; bp 105-115°C (0.5 mm Hg). IR spectrum, ν, cm^{-1}: 500, 580, 630, 660, 690, 780, 810, 920, 960, 1000, 1030, 1080, 1110, 1150, 1200, 1260, 1280, 1310, 1320, 1360, 1400, 1410-1460, 1520, 1610, 1630, 2780, 2820, 2850, 2910, 2930, 2990, 3100.

^{1}H NMR spectrum (acetone-d_6), δ, ppm, J (Hz): 6.42 (1H, q, $^3J_{trans}$ = 14.27, $^3J_{cis}$ = 6.76, OCH=); 5.85 (1H, s, 3-H); 4.26 (2H, t, J = 6.40, OCH_2); 4.20 (1H, dd, $^3J_{trans}$ = 14.27, $^3J_{cis}$ = 1.83, CH_2=); 3.94 (1H, dd, $^3J_{cis}$ = 6.76, ^2J = 1.83, CH_2=); 3.93 (2H, t, J = 6.40, NCH_2); 2.60 (6H, s, NMe_2); 2.29 (3H, s, SMe); 2.18 (3H, s, SMe). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 152.37 (OCH=); 147.67 (5-C); 123.51 (2-C); 118.22 (3-C); 99.74 (4-CH=); 87.31 (CH_2=); 68.25 (OCH_2); 45.93 (NMe_2); 43.00 (NCH_2); 20.63 (SMe); 18.45 (SMe). Found, %: C 52.61; H 7.77; N 10.02; S 23.31. $C_{12}H_{20}N_2OS_2$. Calculated, %: C 52.90; H 7.40; N 10.28; S 23.54.

2-Dimethylamino-5-methylthio-4-phenyl-1-[2-(vinyloxy)ethyl]pyrrole (6d). Compound **2d** (7.95 g, 0.05 mol) was added to a solution of *n*-BuLi (0.05 mol) in hexane (35 ml) and THF (50 ml) that had been cooled down to -70°C. After 20 min of stirring at -40°C, the reaction mixture was again cooled down to -100°C and a solution of isothiocyanate **1** (6.45 g, 0.05 mol) in THF (15 ml) was added to it. When the temperature of the mixture reached -30°C, MeI (10 g, 0.07 mol) was added to it and then (at 11°C) CuBr (1.5 g) was added. After the temperature rose spontaneously up to 27°C (over the course of 20 min) and additional mixing at 40°C for 30 min, the reaction mixture was treated. Yield 7.84 g (51.9%) of pyrrole **6d**; bp 135-150°C (0.5 mm Hg). IR spectrum, ν, cm^{-1}: 530, 620, 630, 700, 760, 790, 820, 920, 960, 1000, 1030, 1070, 1090, 1150, 1180, 1200, 1290, 1320, 1340, 1380, 1400, 1430, 1450, 1500, 1550, 1570, 1600, 1620, 1630, 2790, 2820, 2850, 2910, 2930, 2980, 3030, 3060, 3110. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, J (Hz): 7.70 (2H, m, *o*-HPh); 7.30 (2H, m, *m*-HPh); 7.15 (1H, m, *p*-HPh); 6.40 (1H, q, $^3J_{trans}$ = 14.45, $^3J_{cis}$ = 6.95, OCH=); 5.98 (1H, s, 3-H); 4.31 (2H, t, J = 6.76, OCH_2); 4.20 (1H, dd, $^3J_{trans}$ = 14.45, ^2J = 2.10, CH_2=); 3.96 (1H, dd, $^3J_{cis}$ = 6.95, ^2J =2.10, CH_2=); 3.94 (2H, t, J = 6.76, NCH_2); 2.62 (6H, s, NMe_2); 2.07 (3H, s, SMe). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 151.36 (OCH=); 146.74 (5-C); 136.21 (2-C); 129.10 (3-C); 128.02 (*o*-CPh); 127.95 (*m*-CPh); 125.79 (*p*-CPh); 97.70 (4-CH=); 86.89 (CH_2=); 67.11 (OCH_2); 45.70 (NMe_2); 42.77 (NCH_2); 20.81 (SMe). Found, %: C 67.54; H 7.69; N 9.22; S 10.54. $C_{17}H_{22}N_2OS$. Calculated, %: C 67.51; H 7.33; N 9.26; S 10.60.

2-Diethylamino-5-methylthio-4-phenyl-1-[2-(vinyloxy)ethyl]pyrrole (6e). Compound **2e** (9.35 g, 0.05 mol) was added to a solution of *n*-BuLi (0.05 mol) in hexane (35 ml) and THF (50 ml) that had been cooled down to -100°C. After 30 min of stirring at -30°C, the reaction mass was again cooled down to -60°C, a solution of isothiocyanate **1** (6.45 g, 0.05 mol) in THF (15 ml) was added to it, and it was stirred for 30 min at -30°C to -10°C. Then MeI (10 g, 0.07 mol) was added to the mixture (at -30°C) and then (at 13°C) CuBr (1.5 g) was added. After the temperature rose spontaneously up to 27°C (over the course of ~20 min) and additional stirring at 40°C for 30 min, the reaction mixture was treated. Yield 2.87 g (17.4%) of pyrrole **6e**; bp 160°C (0.5 mm Hg). IR spectrum, ν, cm^{-1}: 610-650, 690, 760, 780, 810, 870, 900, 960, 1000, 1020, 1060, 1070, 1100, 1130-1200, 1280, 1310, 1330, 1360, 1380, 1400, 1420-1470, 1500, 1540, 1560, 1600, 1620, 2810, 2860, 2920, 2970, 3020, 3050, 3100. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, J (Hz): 7.83 (2H, m, *o*-HPh); 7.44 (2H, m, *m*-HPh); 7.26 (1H, m, *p*-HPh); 6.52 (1H, q, $^3J_{trans}$= 14.27, $^3J_{cis}$ = 6.77, OCH=); 6.14 (1H, s, 3-H); 4.40 (2H, t, J = 6.67, OCH_2); 4.33 (1H, dd, $^3J_{trans}$ = 14.27, ^2J = 2.01, CH_2=); 4.08 (1H, dd, $^3J_{cis}$ = 6.77, ^2J = 2.01, CH_2=); 4.04 (2H, t, J = 6.67, NCH_2); 3.01 (4H, m, $N(CH_2)_2$); 2.22 (3H, s, SMe); 1.11 (6H, t, 2Me). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 151.39 (OCH=); 143.30 (5-C); 136.31 (2-C); 129.64 (3-C); 128.97 (*o*-CPh); 127.94 (*m*-CPh); 125.71 (*p*-CPh); 100.50 (4-CH=); 86.82 (CH_2=); 67.12 (OCH_2); 49.19 ($N(CH_2)_2$); 41.41 (NCH_2); 20.82 (SMe); 12.71 (2Me). Found, %: C 69.49; H 7.98; N 8.45; S 9.80. $C_{19}H_{26}N_2OS$. Calculated, %: C 69.05; H 7.93; N 8.48; S 9.70.

5-Butyl-3-methoxy-2-methylthio-1-[2-(vinyloxy)ethyl]pyrrole (10). Compound **2a** (6.3 g, 0.05 mol) was added to a solution of *n*-BuLi (0.05 mol) in hexane (35 ml) and THF (50 ml) that had been cooled down to -70°C, holding it at -70°C to -65°C. Then a solution of *t*-BuOK (6 g, 0.05 mol) in THF (20 ml) and hexametapol (25 ml) was added to the mixture, holding the temperature at no higher than -65°C. This was stirred for 30 min at -65°C, and LiBr (6 g, 0.07 mol) was added. The reaction mass was cooled down to -100°C and a solution of isothiocyanate **1** (6.45 g, 0.05 mol) in THF (15 ml) was added to it dropwise over the course of 5 min. When the temperature of the reaction mixture reached -20°C, MeI (14 g, 0.05 mol) was added to it and then (at 15°C) CuBr (2 g) was added. After the temperature spontaneously rose up to 25°C (over the course of ~10 min) and

additional stirring at 40°C for 30 min, the reaction mixture was treated. Yield 4.45 g (33.1%) of pyrrole **10**; bp 80-90°C (0.5 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 6.38 (1H, q, $^3J_{trans}$ = 14.27, $^3J_{cis}$ = 6.77, OCH=); 5.67 (1H, s, 4-H); 4.19 (2H, t, *J* = 6.31, OCH_2); 4.16 (1H, dd, $^3J_{trans}$ = 14.27, ^2J = 2.37, CH_2=); 3.98 (1H, dd, $^3J_{cis}$ = 6.77, ^2J = 2.37, CH_2=); 3.83 (2H, t, *J* = 6.31, NCH_2); 3.77 (3H, s, OMe); 2.55 (2H, m, α-CH_2); 2.17 (3H, s, SMe); 1.60 (2H, m, β-CH_2); 1.38 (2H, m, γ-CH_2); 0.89 (3H, t, Me). ^{13}C NMR ($CDCl_3$), δ, ppm: 151.03 (OCH=); 144.20 (5-C); 134.09 (2-C); 120.16 (3-C); 93.02 (4-CH=); 86.70 (CH_2=); 67.35 (OCH_2); 57.66 (OMe); 41.99 (NCH_2); 30.42 (CH_2); 26.45 (CH_2); 22.22 (CH_2); 20.79 (SMe); 13.58 (Me). Found, %: C 61.42; H 7.94; N 5.47; S 11.11. $C_{14}H_{23}NO_2S$. Calculated, %: C 62.42; H 8.61; N 5.24; S 11.90.

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