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Dedicated to Full Member of the Russian Academy of Sciences B.A. Trofimov on the 65th Anniversary of His Birth

New Approach to the Synthesis of Strained Cyclic Systems: I. Iminocyclobutenes and Iminothietanes from 1,3-Dilithio-3-phenylpropyne and Methyl Isothiocyanate

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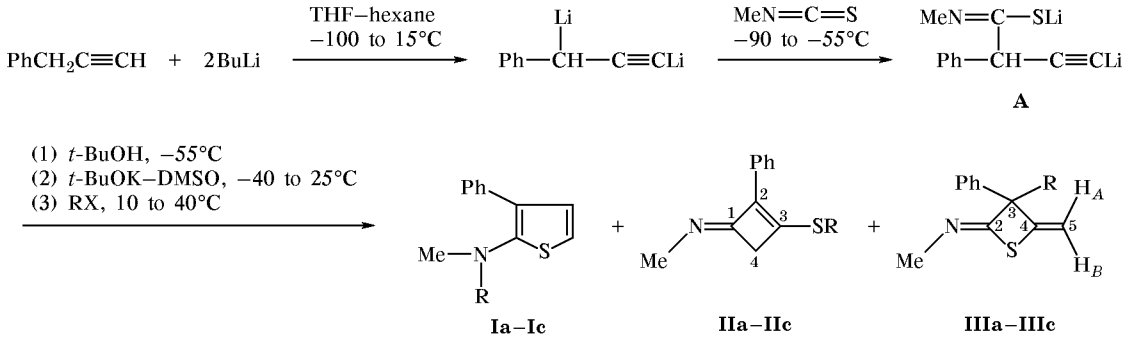
Abstract—The reaction of 1,3-dilithio-3-phenylpropyne with methyl isothiocyanate in THF–hexane at –90 to –55°C, followed by successive treatment of intermediate product with a donor of protons, superbase, and alkyl halide, yields isomeric iminocyclobutenes and iminothietanes in addition to the expected aminothiophene. The ratio of the products depends on the amount and nature of proton donor (MeOH, *t*-BuOH), base (MeONa, *t*-BuOM, M = Li, Na, K; *t*-AmOK), co-solvent (DMSO, HMPA), and alkyl halide (MeI, EtI, BuBr). The system *t*-BuOH(MeOH)–*t*-BuOK–DMSO is the most favorable for the formation of the corresponding iminocyclobutene.

We previously showed [1–6] that a number of adducts derived from alkyl or aryl isothiocyanates and lithiated allenes ($H_2C{=}C{=}CHR$; R = Alk, OMe, SMe) or alkynes ($CH_3C{\equiv}CAlk$, $HC{\equiv}CCH_2R$; R = H, Alk, OAlk, $NAlk_2$) undergo cyclization to give exclusively the corresponding 2-aminothiophenes by successive treatment with a strong base and water or MeI. Only in the reactions with 3-dialkylaminopropynes, the rearrangement resulted in formation of pyrrole derivatives, when the final alkylation was carried out at 40°C and above [2]. Lithiated 3-phenylpropyne has not been involved so far in this reaction.

It is known that reactions of 1,3-dilithioalkynes $RCH(Li)C{\equiv}CLi$ with electrophiles, e.g., alkyl halides, chlorotrialkylsilanes, oxirane, and carbon dioxide [7, 8], primarily involve substitution of Li^+ at the

Scheme 1.



I–**III**, R = Me (**a**, X = I), Et (**b**, X = I), Bu (**c**, X = Br).

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more basic 3-position of the alkyne chain. Taking the above stated into account, we expected to obtain previously unknown 2-dimethylamino-3-phenylthiophene (**Ia**) by reaction of 1,3-dilithio-3-phenylpropyne [9] with an equimolar amount of methyl isothiocyanate, followed by standard [1–6] treatment of the reaction mixture with *t*-BuOH (1 equiv), *t*-BuOK 1 equiv)–DMSO, and MeI under the conditions indicated in Scheme 1.

Surprisingly, the above reaction sequence afforded three isomeric products, the major of which (~68%) was 1-methylimino-3-methylsulfanyl-2-phenyl-2-cyclobutene (**IIa**) while the expected thiophene **Ia** (~16%) and 3-methyl-4-methylene-2-methylimino-3-phenylthietane (**IIIa**) (~16%) were the minor ones. This result was briefly (without experimental detailes) reported by us in [10]. A probable mechanism of formation of compounds **Ia**–**IIIa** was also given therein. Cyclobutene **IIa** was isolated as a light yellow crystalline substance, and thiophene **Ia** and thietane **IIIa** were liquids which were separated by preparative gas–liquid chromatography. The structure of **IIa** and **IIIa** was proved by the data of elemental analyses, mass spectra, IR spectra, and ^{1}H, ^{13}C, and ^{15}N NMR spectra, including those obtained by two-dimensional NMR techniques (NOESY, HMQC, HMBC). Also, direct ^{13}C–^{13}C coupling constants were meaured. The results of 2M HMQC experiment with compound **IIa** allowed us to assign signals from the aromatic carbon atoms, C^{o}, C^{m}, and C^{p}. Correlations observed in the HMBC spectrum between the *m*-H proton and carbon nucleus with δ_C 131.75 ppm (through 3 bonds) and between *o*-H and carbon nucleus with δ_C 137.55 ppm gave us grounds to assign the carbon signals to C^{i} and C^{2}, respectively. This assignment was confirmed by the corresponding direct ^{13}C–^{13}C coupling constants. Also, the HMBC spectrum showed correlations through 3 bonds between the NCH_3 proton signal and carbon signal at δ_C 158.96 ppm (C^{1}), as well as for the SCH_3 protons and carbon with δ_C 148.91 ppm (C^{3}). The presence of $C^{1}-C^{2}$, $C^{1}-C^{4}$, $C^{2}-C^{3}$, and $C^{3}-C^{4}$ bonds was proved by the existence of the corresponding direct ^{13}C–^{13}C couplings. The nitrogen signal at δ_N –118.34 ppm (relative to $MeNO_2$) is typical of an imino group, which provides an additional proof for the iminocyclobutene structure of **IIa**.

Likewise, we assigned the ^{1}H and ^{13}C signals of thietane **IIIa** and thiophene **Ia**. The presence of only one set of signals in the ^{1}H and ^{13}C NMR spectra of cyclobutene **IIa** and thietane **IIIa** indicates that these compounds are formed as a single stereoisomer. Their structure follows from the cross peaks corresponding to the NCH_3 and CH_2 protons of cyclobutene **IIa** in the NOESY spectrum, as well as from downfield shift of the *o*-H proton (phenyl group) by ~0.2 ppm due to effect of lone electron pair on the nitrogen atom; by contrast, the NOESY spectrum of **IIIa** lacks cross peak between the NCH_3 and *o*-H protons. These data unambiguously show that compounds **IIa** and **IIIa** are *anti* isomers with *trans* arrangement of the NCH_3 and phenyl groups with respect to the C=N bond.

In the IR spectrum of **IIa**, stretching vibrations of the C=N bond give rise to a band at 1696 cm^{-1} which has the highest intensity. The corresponding absorption band of thietane **IIIa** appears as a doublet at higher frequencies, 1712 and 1731 cm^{-1}.

Unlike thietane **IIIa**, the electron impact mass spectra of compounds **Ia** and **IIa** are characterized by abundant molecular ion peaks with *m*/*z* 203 (I_{rel} 100 and 87%, respectively). Thietane **IIIa** shows in the mass spectrum pseudomolecular 1-methyl-1-phenylallene ion, *m*/*z* 130 (I_{rel} 100%), which is formed by elimination of methyl isothiocyanate molecule from the molecular ion $[M]^{+}$.

Apart from compounds **Ia**–**IIIa**, we isolated from the reaction mixture by preparative gas–liquid chromatography and identified small amounts of volatile products, 1-phenylpropyne (**IV**) (arising from prototropic rearrangement of unreacted 3-phenylpropyne by the action of *t*-BuOK–DMSO) and methyl *N*-methylpentanimidothioate (**V**) (formed by reaction of methyl isothiocyanatate with BuLi and MeI). The overall yield of by-products **IV** and **V** varied from 6 to 10%, depending on the conditions.

IV **V**

The reaction of 1,3-dilithio-3-phenylpropyne with methyl isothiocyanate is the first example illustrating a simple synthetic route to previously unknown functionally substituted cyclobutenes and thietanes. Therefore, our further efforts were directed at elucidating optimal parameters of the process for selective formation of these products. We examined the effects of the proton-donor compound (MeOH, *t*-BuOH), base (MeONa; *t*-BuOM, where M = Li, Na, K; *t*-AmOK), solvent (THF, DMSO, HMPA), alkylating agent (MeI, EtI, BuBr), temperature at the stage of addition of 3-phenylpropyne dianion to methyl isothiocyanate, and reactant ratio on the direction and selectivity of the reaction. The experimental results are collected in

Reaction of 1,3-dilithio-3-phenylpropyne with methyl isothiocyanate; PhCHLiC≡CLi, 50 mmol; MeNCS, 50 mmol; THF, 110 ml; temperature conditions: addition, –70 to –65°C (5 min); cyclization, –40 to 25°C (5 min); alkylation, 25–45°C (1.5 h)

Run no.	*t*-BuOH, mmol	Base (mmol)–DMSO (40 g)	RX	Product composition, %			Overall yield, %
				Ia	**IIa**	**IIIa**	
1	95	*t*-AmOK, 54	MeI	32	60	8	66
2	95	*t*-BuOK, 54	MeI	43	43	14	90
3	95	*t*-BuONa, 54	MeI	44	42	14	83
4	100	*t*-BuOLi,[a] 100	MeI	50	50	–	30[b]
5	54	*t*-BuOLi,[a] 54	MeI	30	70	–	58[b]
6	54	*t*-BuOK, 54	MeI	15	75	10	77
7[c]	54	*t*-BuOK, 54	MeI	15	71	14	68
8	54	*t*-BuOK (54)–HMPA	MeI	21	44	35	54
9	54	*t*-BuOK (54)–THF	MeI	29	71	–	49
10	MeOH, 54	*t*-BuOK, 54	MeI	8	80	12	74
11	MeOH, 54	MeONa, 54	MeI	100	–	–	6
12	27	*t*-BuOK, 54	MeI	Traces	–	–	<1
13	149	*t*-BuOK, 54	MeI	42	53	5	67
14	54	*t*-BuOK, 100	MeI	14	75	11	71
15	54	*t*-BuOK, 54	EtI	12 (**Ib**)	67 (**IIb**)	21 (**IIIb**)	79
16[d]				11 (**Ib**)	67 (**IIb**)	22 (**IIIb**)	78
17[e]				11 (**Ib**)	67 (**IIb**)	22 (**IIIb**)	77
18[f]				11 (**Ib**)	67 (**IIb**)	22 (**IIIb**)	80
19	54	*t*-BuOK, 54	BuBr	12 (**Ic**)	72 (**IIc**)	16 (**IIIc**)	70

[a] Lithium *tert*-butoxide is formed on addition of *t*-BuOH; it was not added specially to the mixture.
[b] Temperature at the cyclization stage –40 to 36°C (5 min).
[c] A 1.5-fold volume of THF was used (165 ml).
[d] Temperature at the addition stage –80 to –75°C (5 min).
[e] Temperature at the addition stage –60 to –55°C (5 min).
[f] Temperature at the alkylation stage 25°C (10 h).

table. In all experiments, the procedures for lithiation of 3-phenylpropyne and addition of reactants (methyl isothiocyanate, proton donor, and base) and temperature conditions were similar.

The results showed that the presence of proton donor (*t*-BuOH or MeOH) is necessary and that its amount should be no less than equimolar with respect to adduct **A**. When the ratio **A**:*t*-BuOH was 1:0.5 (base *t*-BuOK; see table, run no. 12), no compounds **Ia**–**IIIa** were formed. In this case, the product was a dark brown tarry material containing only traces of thiophene **Ia** (according to the ^{1}H NMR data). In the reaction with 1 equiv of *t*-BuOH (run no. 6), the mixture contained cyclobutene **IIa** as the major product (75%), while the fractions of thiophene **Ia** and thietane **IIIa** were 15 and 10%, respectively (overall yield 77%). Addition of 2 equiv of *t*-BuOH (run no. 2) leads to sharp increase in the fraction of thiophene **Ia** (up to 43%), the ratio of **Ia** to **IIa** becomes equal to 1:1, and the overall yield of compounds **Ia**–**IIIa** reaches the maximal value (90%). Further increase of the amount of *t*-BuOH (to 3 equiv, run no. 13) only slightly affects the isomer ratio, but their yield sharply decreases (down to 67%). The yield of cyclobutene **IIa** (59 and 58%; run nos. 6, 10) almost does not depend on the nature of the alcohol used as proton donor.

The effect of the base (*t*-BuOM, M = Na, K; *t*-AmOK) was studied at an adduct **A**-to-*t*-BuOH ratio of 1:2 (run nos. 1–3). It was found that *t*-AmOK favors formation of cyclobutene **IIa** to a greater extent than does *t*-BuOK (fraction in the mixture 60 and 43%, respectively), thouth the yield of **IIa** in both cases is the same (~39%). Replacement of potassium cation in *t*-BuOM by Na^+ had no effect on the ratio of isomeric products **Ia**–**IIIa**, but their yield decreased

by 7%. Even lesser yields were obtained with the use of *t*-BuOLi (30 and 58%; run nos. 4, 5). Sodium methoxide turned out to be inactive in these reactions (run no. 11): only 6% of thiophene **Ia** and no other products were obtained. Thus, potassium *tert*-butoxide is the most accessible and efficient catalyst for the rearrangement of adduct **A** into cyclobutene **IIa**. This follows from the results of experiments with 1 equiv of proton donor and 1 equiv of *t*-BuOK (run nos. 6, 7, 10, 15–19). Twofold increase of the amount of *t*-BuOK (run no. 14) almost does not affect the yield and ratio of products **Ia**–**IIIa**.

As co-solvents favoring the cyclization, we tested dimethyl sulfoxide (DMSO) and hexamethylphosphoramide (HMPA). Dimethyl sulfoxide was found to be the most appropriate for formation of cyclobutene derivatives. Addition of HMPA increased the fractions of thietane **III** and tarry products (run no. 8). In the absence of DMSO or HMPA, the rearrangements were not complete (run no. 9). According to the IR data, the reaction mixture contained acyclic compounds with a triple or allene bond: a weak band at 2020 cm^{-1} ($\nu C{\equiv}C$) and a medium-intensity band at 1942 cm^{-1} ($\nu C{=}C{=}C$) were present in the IR spectrum. Dilution of the reaction mixture with THF is not advisable. With the use of a 1.5-fold amount of THF (relative to its usual amount; run nos. 6, 7), the overall yield of the products was lower by 9%.

Both alkyl iodides and unbranched alkyl bromides can be used as electrophiles to stabilize the rearranged anions (run nos. 6, 15, 19).

As expected [11], variation of the temperature at the stage of addition of methyl isothiocyanate to 1,3-dilithio-3-phenylpropyne within the range from –90 to –55°C did not affect the cyclobutene–thietane ratio (run nos. 15–17).

The optimal conditions ensuring formation of cyclobutenes **IIa**–**IIc** in 50–59% yield are as follows: molar ratio 3-phenylpropyne–BuLi–MeNCS–MeOH (or *t*-BuOH)–*t*-BuOK–AlkX 1:2.2:1:1:1:3; temperature at the stage of addition of methyl isothiocyanate to 1,3-dilithio-3-phenylpropyne –90 to –55°C, temperature of the reaction with *t*-BuOH (MeOH) –55 to –40°C, temperature at the cyclization stage –40 to 25°C (5 min), and temperature at the alkylation stage 25 to 45°C (1.5 h).

Cyclobutenes **IIb** and **IIc** were isolated as individual substances. Their structure was confirmed by the NMR, IR, and mass spectra and elemental analyses. Thiophenes **Ib** and **Ic** and thietanes **IIIb** and **IIIc** were identified on the basis of the ^{1}H and ^{13}C NMR spectra and GC–MS data of the product mixtures.

EXPERIMENTAL

The ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.13 MHz for ^{1}H, 100.69 MHz for ^{13}C, and 40.55 MHz for ^{15}N. Samples were examined as ~5–30% solutions in $CDCl_3$ using HMDS as internal reference. NOESY, HMQC, and HMBC experiments were performed with the use of standard pulse sequences; the direct ^{13}C–^{13}C coupling constants were measured by the 1D INADEQUATE technique. The IR spectra were obtained on a Bruker IFS 25 spectrometer from thin films (liquids) or KBr pellets (solid substances). The mass spectra (electron impact, 60 eV) were recorded on an LKB-2091 instrument with either direct (cyclobutenes **II**) or chromatographic (thiophenes **I** and thietanes **III**) sample admission into the ion source; SE-54 capillary column, 38 m; injector temperature 250°C; oven temperature programming from 70 to 200°C at 10 deg/min; ion source temperature 240°C. GLC analysis was performed on a Varian 3400 gas chromatograph equipped with a flame-ionization detector; DB-5 capillary column, 15 m × 0.53 mm × 1.5 μm; carrier gas nitrogen. Compounds **Ia**, **IIIa**, **IV**, and **V** were isolated with the aid of a PAKhV-07 preparative gas chromatograph equipped with a thermal conductivity detector; 5-m × 10-mm column packed with 5% of XE-60 on Chromaton N-AW-HMDS; carrier gas helium; isothermal conditions, 160 or 100°C; detector temperature 200°C; injector temperature 230°C.

All operations were carried out under nitrogen or argon. Tetrahydrofuran was purified by treatment with powdered potassium hydroxide (~50 g/l) and subsequent distillation over metallic sodium in the presence of benzophenone. 3-Phenylpropyne was prepared by reaction of phenylmagnesium bromide with methoxyallene, following the procedure described in [7]. Butyllithium (a 1.6 M solution in hexane) and the other reagents and solvents used in this work were commercial products. Liquid nitrogen was used as cooling agent.

Reaction of 1,3-dilithio-3-phenylpropyne with methyl isothiocyanate and methyl iodide (see table, run no. 6). A solution of 5.8 g (50 mmol) of 3-phenylpropyne in 110 ml of THF was cooled to –100°C, and 110 mmol of butyllithium (68 ml of a 1.6 M solution of BuLi in hexane) was added over a period of ~1 min under argon. The mixture was stirred for 10 min at 10–14°C (it turned yellow–brown) and cooled to –90°C (a yellow suspension was thus obtained), a solution of 3.65 g (50 mmol) of methyl isothiocyanate in 5 ml of THF was added in one portion, and

the mixture was stirred for 5 min at –70 to –65°C. The cooling bath was removed, a mixture of 4 g (54 mmol) of *t*-BuOH and ~2 ml of diethyl ether was added at –55°C (crimson solution), and a solution of 6 g (54 mmol) of *t*-BuOK in 40 g of DMSO was added at –40°C (the temperature sharply rose to –20°C). The mixture was quickly (over a period of 2–3 min) warmed from –20°C to 25°C (dark brown suspension) and immediately cooled to 10°C, and 22 g (150 mmol) of methyl iodide was added. The mixture was stirred for 1.5 h at 25–40°C (yellow–orange suspension), 100 ml of a saturated aqueous solution of ammonium chloride was added, and the organic phase was separated. The aqueous phase was extracted with diethyl ether (2 × 50 ml), and the extracts were combined with the organic phase, washed with four portions of water, dried over $MgSO_4$, and evaporated on a rotary evaporator. The residue was distilled under reduced pressure (0.2–0.4 mm) to isolate 0.52 g of a fraction boiling in the temperature range from 60 to 100°C. According to the GLC data, this fraction contained 44% of 1-phenylpropyne (**IV**) (yield 4%) and 56% of methyl *N*-methylpentanimidothioate (**V**) (yield 4%); the subsequent distillation gave 7.82 g of a fraction boiling in the temperature range from 110 to 160°C, which quickly crystallized on storage. According to the ^{1}H NMR data, the high-boiling fraction contained 15% of tiophene (**Ia**), 75% of cyclobutene **IIa**, and 10% of thietane **IIIa**. Cyclobutene **IIa** was isolated by recrystallization from hexane or petroleum ether, yield 5.8 g (58%). Thiophene **Ia** and thietane **IIIa** were isolated from the mother liquor (after removal of the solvent) by preparative gas–liquid chromatography. Their yields (according to the ^{1}H NMR data) were 11 and 8%, respectively. Compounds **IV** and **V** were also separated by preparative GLC and were identified by the ^{1}H and ^{13}C NMR spectra.

The other experiments were carried out in a similar way (see table). High-boiling butyl bromide was added at 25°C (without cooling).

2-Dimethylamino-3-phenylthiophene (Ia). Purity 98% (after preparative GLC), n_D^{21} = 1.5934. ^{1}H NMR spectrum, δ, ppm: 7.65 d (*o*-H), 7.33 t (*m*-H), 7.19 t (*p*-H), 6.99 d (4-H), 6.76 d (5-H, $^3J_{HH}$ = 5.6 Hz), 2.64 s (6H, NMe_2). ^{13}C NMR spectrum, δ_C, ppm: 155.55 (C^2), 136.54 (C^i), 128.46 (C^m), 127.87 (C^o), 126.35 (C^3), 126.19 (C^p), 126.19 (C^4), 114.87 (C^5), 45.75 (NMe_2). IR spectrum, ν, cm^{-1}: 503, 559 w, 631, 653 w, 698 s, 714, 767, 810, 869, 914, 1027, 1082 s, 1140, 1262, 1314, 1418 w, 1443, 1453, 1478, 1493, 1544, 1576 w, 1600, 1637 w, 2785, 2837, 2902, 2946, 2980 w, 3058 w, 3080 w, 3104 w. Found, %: C 70.67; H 6.50; N 6.93; S 15.90. $C_{12}H_{13}NS$. Calculated, %: C 70.89; H 6.45; N 6.89; S 15.77.

***N*-Methyl-3-methylsulfanyl-2-phenylcyclobutenimine (IIa).** Light yellow crystals, mp 100°C (from hexane). ^{1}H NMR spectrum, δ, ppm: 7.72 d (*o*-H), 7.32 t (*m*-H), 7.18 t (*p*-H), 3.42 s (2H, CH_2), 3.18 s (3H, NMe), 2.45 s (3H, SMe). ^{13}C NMR spectrum, δ_C, ppm ($^1J_{CC}$, Hz): 158.96 (C^1, $J_{1,2}$ = 52.2, $J_{1,4}$ = 27.7), 148.91 (C^3, $J_{3,4}$ = 34.2), 137.55 (C^2, $J_{2,3}$ = 60.5), 131.75 (C^i, $J_{i,o}$ = 56.1), 128.44 (C^m), 127.26 (C^p), 127.09 (C^o), 40.99 (C^4), 39.16 (NMe), 15.36 (SMe). IR spectrum, ν, cm^{-1}: 497, 630, 698 s, 771 s, 792, 965, 1010, 1072 w, 1164, 1275, 1290, 1315 w, 1419, 1450, 1487, 1571, 1597, 1696 s (C=N), 2264 w, 2884 w, 2909, 2997, 3041 w (KBr). Found, %: C 71.10; H 6.26; N 6.72; S 15.92. $C_{12}H_{13}NS$. Calculated, %: C 70.89; H 6.45; N 6.89; S 15.77.

3-Methyl-4-methylene-2-methylimino-3-phenylthietane (IIIa). Purity ~100% (after preparative GLC), n_D^{21} = 1.5710. ^{1}H NMR spectrum, δ, ppm: 7.55 d (*o*-H), 7.34 t (*m*-H), 7.26 t (*p*-H), 5.31 d (H_A), 5.21 d (H_B, $^2J_{AB}$ = 2.8 Hz), 3.09 s (3H, NMe), 1.82 s (3H, CMe). ^{13}C NMR spectrum, δ_C, ppm: 162.57 (C^2), 144.79 (C^4), 140.43 (C^i), 128.56 (C^m), 127.47 (C^p), 125.74 (C^o), 104.93 (C^5), 74.96 (C^3), 41.64 (NMe), 25.19 (Me). IR spectrum, ν, cm^{-1}: 503, 554, 627, 644 w, 698, 756, 810, 858, 941, 1009, 1028, 1080, 1151 w, 1181 w, 1262, 1369 w, 1401, 1444, 1549, 1637 s, 1731 and 1712 (C=N), 2858 w, 2886 w, 2927, 2970, 3025 w, 3060 w, 3087 w. Found, %: C 70.95; H 6.40; N 6.79; S 15.86. $C_{12}H_{13}NS$. Calculated, %: C 70.89; H 6.45; N 6.89; S 15.77.

1-Phenylpropyne (IV). Purity 87% (after preparative GLC). ^{1}H NMR spectrum, δ, ppm: 7.37 m (*o*-H), 7.25 m (*m*-H, *p*-H), 2.02 s (Me). ^{13}C NMR spectrum, δ_C, ppm: 131.58 (C^o), 128.68 (C^m), 127.60 (C^p), 124.17 (C^i), 85.83 (C^1), 79.83 (C^2), 4.34 (Me).

Methyl *N*-methylpentanimidothioate (V). Purity 95% (after preparative GLC). ^{1}H NMR spectrum, δ, ppm: *anti* isomer (*trans* arrangement of the NMe and Bu groups with respect to the C=N bond): 3.22 s (3H, NMe), 2.47 t (2H, α-CH_2), 2.43 s (3H, SMe), 1.56 m (2H, β-CH_2), 1.37 m (2H, γ-CH_2), 0.92 t (3H, Me); *syn* isomer: 3.15 t (3H, NMe, $^4J_{HH}$ = 1.1 Hz), 2.36 t (2H, α-CH_2), 2.24 s (3H, SMe), 1.56 m (2H, β-CH_2), 1.37 m (2H, γ-CH_2), 0.92 t (3H, Me). Ratio of the *syn* and *anti* isomers 53 : 47. ^{13}C NMR spectrum, δ_C, ppm: 169.01, 166.33 (C=N); 39.53, 38.74 (NMe); 37.40, 33.48 (α-CH_2); 29.53, 29.09 (β-CH_2);

22.69, 22.41 (γ-CH_2); 14.06, 13.94, 13.81, 12.45 (SMe, Me).

2-Ethyl(methyl)amino-3-phenylthiophene (Ib). ^{1}H NMR spectrum, δ, ppm: 7.66 m (*o*-H), 7.31 m (*m*-H), 7.22 m (*p*-H), 6.99 d (4-H), 6.82 d (5-H, $^3J_{4,5}$ = 5.8 Hz), 2.87 q (2H, NCH_2, $^3J_{HH}$ = 7.0 Hz), 2.65 s (3H, NMe), 0.98 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 154.56 (C^2), 136.52 (C^i), 128.25 ($2C^m$), 128.09 (C^3), 127.89 (C^o), 127.89 (C^4), 126.17 (C^p), 116.12 (C^5), 53.38 (NCH_2), 43.05 (NCH_3), 12.29 ($CH_2\mathbf{C}H_3$). Mass spectrum: *m*/*z* 217 $[M]^+$ (I_{rel} 63%).

***N*-Methyl-3-ethylsulfanyl-2-phenyl-2-cyclobutenimine (IIb).** Yellow crystals, mp 90°C (from petroleum ether, bp 40–70°C). ^{1}H NMR spectrum, δ, ppm: 7.75 m (*o*-H), 7.33 m (*m*-H), 7.19 m (*p*-H), 3.44 s (CH_2), 3.19 s (3H, NMe), 2.93 q (2H, SCH_2, $^3J_{HH}$ = 7.5 Hz), 1.38 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 159.40 (C^1), 148.51 (C^3), 137.75 (C^2), 131.67 (C^i), 128.35 (C^m), 127.16 (C^p), 127.02 (C^o), 40.99 (C^4), 39.14 (NMe), 27.24 (SCH_2), 16.23 ($CH_2\mathbf{C}H_3$). IR spectrum, ν, cm^{-1}: 485, 497, 630 s, 699 s, 772 s, 788, 854 w, 899 w, 919, 964 s, 1007, 1031 w, 1055 w, 1069 w, 1126, 1164 w, 1183 w, 1257 s, 1275, 1292, 1304 sh, 1323, 1338 w, 1376, 1397, 1409, 1438 sh, 1453, 1485, 1560 and 1571, 1597, 1696 v.s (C=N), 2766 w, 2798 w, 2856, 2885, 2908, 2931, 2946, 2968, 2987 w, 3039. Mass spectrum: *m*/*z* 217 $[M]^+$ (I_{rel} 81%). Found, %: C 71.89; H 6.99; N 6.74; S 14.76. $C_{13}H_{15}NS$. Calculated, %: C 71.84; H 6.96; N 6.44; S 14.75.

3-Ethyl-4-methylene-2-methylimino-3-phenylthietane (IIIb). ^{1}H NMR spectrum, δ, ppm: 7.58 m (*o*-H), 7.31 m (*m*-H), 7.25 m (*p*-H), 5.35 d (H_A), 5.24 d (H_B, $^2J_{AB}$ = 2.7 Hz), 3.09 s (3H, NMe), 2.20 m and 1.99 m (2H, $C\mathbf{H}_2CH_3$), 1.04 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 161.22 (C^2), 142.26 (C^4), 139.86 (C^i), 128.39 (C^m), 125.89 (C^o), 127.30 (C^p), 105.63 (=CH_2), 79.38 (C^3), 41.51 (NMe), 32.12 ($\mathbf{C}H_2CH_3$), 9.23 ($CH_2\mathbf{C}H_3$). Mass spectrum: *m*/*z* 144 $[M]^+$ (I_{rel} 100%).

2-Butyl(methyl)amino-3-phenylthiophene (Ic). ^{1}H NMR spectrum, δ, ppm: 7.63 m (*o*-H), 7.31 m (*m*-H), 7.18 m (*p*-H), 6.98 d (4-H), 6.80 d (5-H, $^3J_{4,5}$ = 5.8 Hz), 2.82 t (2H, α-CH_2 in Bu, $^3J_{HH}$ = 7.3 Hz), 2.63 s (3H, NMe), 1.42 m (2H, β-CH_2 in NBu), 1.18 m (2H, γ-CH_2 in NBu), 0.78 t (3H, CH_3 in NBu, $^3J_{HH}$ = 7.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 155.10 (C^2), 136.54 (C^i), 128.24 ($2C^m$), 128.09 (C^3), 128.00 (C^o), 128.00 (C^5), 126.18 (C^p), 116.06 (C^4), 57.98 (α-CH_2 in NBu), 43.83 (NMe), 29.48 (β-CH_2 in NBu), 20.24 (γ-CH_2 in NBu), 13.89 (CH_3 in NBu). Mass spectrum: *m*/*z* 245 $[M]^+$ (I_{rel} 84%).

***N*-Methyl-3-butylsulfanyl-2-phenyl-2-cyclobutenimine (IIc).** Light yellow crystals, mp 94°C (from petroleum ether, bp 40–70°C). ^{1}H NMR spectrum, δ, ppm: 7.80 m (*o*-H), 7.38 m (*m*-H), 7.24 m (*p*-H), 3.48 s (2H, CH_2), 3.24 s (3H, NMe), 2.96 t (2H, SCH_2, $^3J_{HH}$ = 7.3 Hz), 1.72 m (2H, β-CH_2 in SBu), 1.50 m (2H, γ-CH_2 in SBu), 0.98 t (3H, CH_3 in SBu, $^3J_{HH}$ = 7.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 159.38 (C^1), 148.82 (C^3), 137.64 (C^2), 131.72 (C^i), 128.37 (C^m), 127.15 (C^p), 127.02 (C^o), 41.16 (C^4), 39.16 (NMe), 32.99 (SCH_2), 32.82 (β-CH_2 in SBu), 21.72 (γ-CH_2 in SBu), 13.65 (CH_3 in SBu). IR spectrum, ν, cm^{-1}: 487 sh, 498, 632 s, 697 s, 729, 770 s, 792, 850 w, 898 w, 915, 965 s, 1003, 1014 sh, 1032 w, 1068 w, 1098 w, 1129, 1168 w, 1220 s, 1276 and 1291, 1321, 1339 w, 1376, 1400, 1410 sh, 1427, 1449, 1460, 1488, 1562 and 1572, 1598, 1695 v.s (C=N), 2770 w, 2809 sh, 2855, 2875, 2909, 2925, 2958, 3045. Mass spectrum: *m*/*z* 245 $[M]^+$ (I_{rel} 25%). Found, %: C 73.45; H 7.84; N 6.16; S 12.85. $C_{15}H_{19}NS$. Calculated, %: C 73.42; H 7.80; N 5.71; S 13.07.

3-Butyl-4-methylene-2-methylimino-3-phenylthietane (IIIc). ^{1}H NMR spectrum, δ, ppm: 7.59 m (*o*-H), 7.31 m (*m*-H), 7.21 t (*p*-H), 5.36 d (H_A), 5.23 d (H_B, $^2J_{AB}$ = 2.7 Hz), 3.09 s (3H, NMe), 2.16 m and 1.95 m (2H, α-CH_2 in Bu), 1.43 m (2H, β-CH_2 in Bu), 1.20 m (2H, γ-CH_2 in Bu), 0.86 t (3H, CH_3 in Bu, $^3J_{HH}$ = 7.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 161.45 (C^2), 142.69 (C^4), 140.05 (C^i), 128.42 (C^m), 125.87 (C^o), 127.30 (C^p), 105.61 (=CH_2), 78.91 (C^3), 41.53 (NMe), 39.12 (α-CH_2 in Bu), 26.78 (β-CH_2 in Bu), 23.03 (γ-CH_2 in Bu), 13.96 (CH_3 in Bu). Mass spectrum: *m*/*z* 172 $[M - MeNCS]^+$ 172 (I_{rel} 45%).

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