Reactions of Heterocumulenes with Organometallic Reagents: XI.* Quantum-Chemical Study on the Mechanism of Noncatalytic Cyclization of Methyl 2-Methoxy-*N*-methylbuta-2,3-dienimidothioate (1-Aza-1,3,4-triene) into Substituted Pyrrole

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Abstract—Rotational isomerism of methyl 2-methoxy-*N*-methylbuta-2,3-dienimidothioate (1-aza-1,3,4-triene), which is readily available from 1-lithio-1-methoxyallene, methyl isothiocyanate, and methyl iodide, was studied by quantum-chemical methods. Four most stable rotamers with the energies of activation of their mutual transformations exceeding 35 kJ/mol were identified. The potential energy surfaces for the formation of pyrrole structure from 1-aza-1,3,4-triene via different ring closure channels were analyzed. According to the results of calculations, the most probable is direct [1,5]-cyclization of 1-aza-1,3,4-triene through a cyclic carbene species.

Methyl 2-methoxy-*N*-methylbuta-2,3-dienimido-thioate (**I**) is the first representative of 1-aza-1,3,4-trienes, which are readily available (in almost quantitative yield) from α-lithiated methoxyallene, aliphatic isothiocyanates, and alkyl halides in one-pot reaction [2–4]. On heating in the absence of any catalyst and solvent, compound **I** is smoothly converted into previously unknown and inaccessible through other routes 3-methoxy-1-methyl-2-methylsulfanylpyrrole (**II**) and 5-methoxy-6-methylsulfanyl-2,3-dihydropyridine (**III**)

[2, 4] (Scheme 1). Although intermediate **IV** was not detected among products of thermally induced rearrangements of 1-aza-1,3,4-triene **I** (obviously, this intermediate is thermodynamically unstable), it was unambiguously shown that the formation of dihydropyridine ring is preceded by [1,5]-sigmatropic rearrangement of 2-methoxy-*N*-methylbuta-2,3-dienimido-thioate (**I**) into *N*-methylidene-2-methoxy-1-alkylsulfanylbuta-1,3-dien-1-amine (2-aza-1,3,5-triene) [2–5]. Some 2-aza-1,3,5-trienes were isolated in reactions of

Scheme 1.
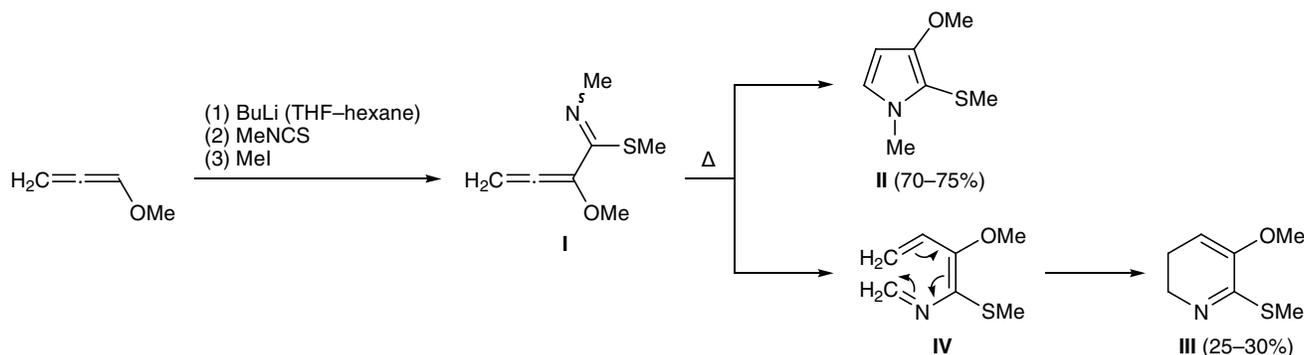
* For communication X, see [1].

lithiated allenes and alkynes, including 1-lithio-1-methoxyallene, with other isothiocyanates [alkyl (Alk ≠ Me), heteroalkyl, and cycloalkyl], and their structure was reliably proved by the IR and NMR data. Their ability to undergo 6π-electrocyclization to the corresponding 2-mono- or 2,2-disubstituted 6-alkylsulfanyl-2,3-dihydropyridines was confirmed experimentally [2–5]. Our quantum-chemical calculations also showed that the formation of dihydropyridine ring involves tandem isomerization of 1-aza-1,3,4-triene and subsequent electrocyclization of 2-aza-1,3,5-triene [1]. Interestingly, cyclic products **II** and **III** were also formed when 1-aza-1,3,4-triene **I** was stored in a refrigerator (compounds **II** and **III** were identified by NMR spectroscopy).

Unlike 2,3-dihydropyridines, the mechanism of formation of pyrrole ring from 1-aza-1,3,4-trienes has not been understood completely. In the early publications [2, 4] we postulated two possible cyclization paths: (1) through protonated 3-alkoxy-1-aza-1,3,4-triene and (2) through cyclic carbene-like species. The formation of pyrrole structures via protonation of

3-alkoxy-1-aza-1,3,4-triene has recently been confirmed by quantum-chemical calculations [1]. The most favorable for cyclization is attack by a proton on the π orbital localized on C_β and C_γ in the allene fragment. As a result, the p orbital on C_γ is activated so that it becomes capable of interacting with the π orbital on the nitrogen atom. According to the HF/6-31G** calculations [1], the energies of activation of the [1,5]-hydrogen shift and the subsequent electrocyclic rearrangement of 2-aza-1,3,5-triene **IV** into dihydropyridine **III** are 114.3 and 90.1 kJ/mol, respectively, whereas concurrent formation of substituted pyrrole **II** through intermediate protonated structure is characterized by an activation energy of 44.9 kJ/mol. The formation of pyrrole **II** as the major product (Scheme 1) is consistent with the calculation data. Nevertheless, no reliable experimental proofs were given so far for that mechanism.

The second hypothetical cyclization channel, which implies direct intramolecular nucleophilic attack by the nitrogen atom on the terminal allene carbon atom in 3-alkoxy-1-aza-1,3,4-triene with formation of new

Scheme 2.

$$(1)$$

$$(2)$$

$$(3)$$
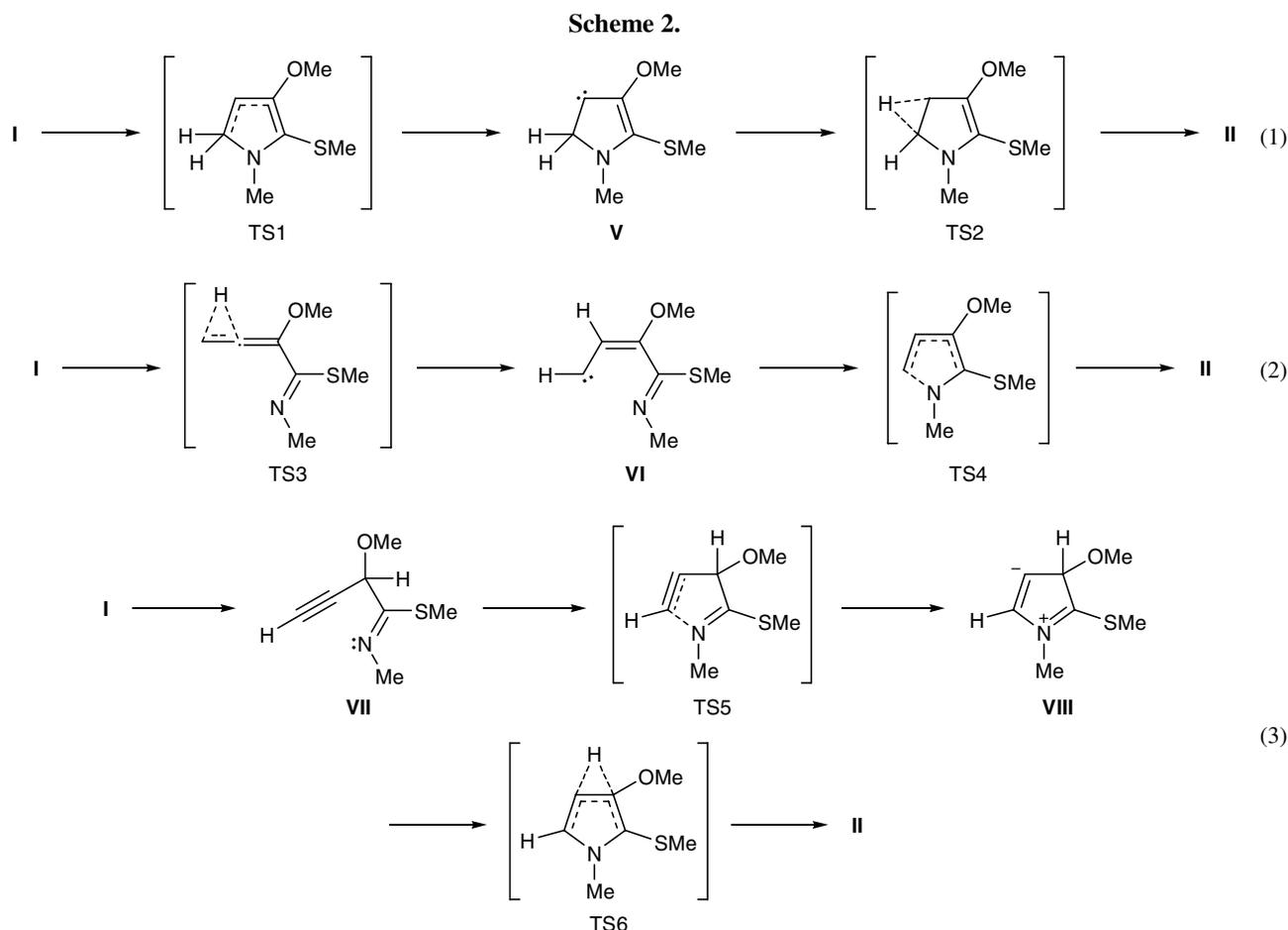
σ-C–N bond and gives a cyclic carbene species, needs to be validated at a quantitative level.

In the present work we performed quantum-chemical simulation of the potential energy surfaces for the formation of pyrrole structure **II** by intramolecular cyclization of 1-aza-1,3,4-triene **I**. Apart from the [1,5]-cyclization channel [path (1) in Scheme 2], we analyzed two other possible paths of pyrrole ring closure. Thus channel (1) is direct nucleophilic attack by the nitrogen atom on the terminal carbon atom of the allene fragment; channel (2) is intramolecular [1,2]-hydride shift (through TS3) to give carbenoid structure **VI**, followed by reaction of the carbene center with the nitrogen atom; and channel (3) is cyclization of the acetylenic isomer of 1-aza-1,3,4-triene **I**, methyl 2-methoxy-*N*-methylbut-3-ynimidothioate (**VII**).

The parts of potential energy surfaces corresponding to carbene intermediates were also analyzed for the lowest triplet states. Furthermore, the cyclization to pyrrole **II** and sigmatropic rearrangement to 2-aza-1,3,5-triene **IV** are concurrent processes, and their probability in the initial step should or at least may be determined by the most favorable (in each case) configuration of the 1-aza-1,3,4-triene **I** molecule. The latter exists as a mixture of geometric isomers, *syn*-(*Z*) and *anti*-(*E*), with respect to the double carbon–nitrogen bond (^{1}H NMR data), and several conformers are possible due to restricted rotation about single bonds; these conformers are characterized by different mutual orientations of molecular fragments, e.g., N=C and C=C=C, MeO and C=C=C, etc. Therefore, we believed it to be necessary to estimate the relative stability of possible rotational isomers of compound **I**.

Nonempirical calculations were performed at the B3LYP/6-311G** level using GAUSSIAN-98 soft-

ware package [6]. The geometric parameters were optimized to a value of 10^{-5} a.u./bohr. Flat areas on the total potential energy surface were analyzed using a gradient value of 10^{-6} a.u./bohr. The force constant matrix was calculated in the analytical mode using a program built in GAUSSIAN. Structures corresponding to energy minima on the potential energy surface were identified by moving along the gradient line from a saddle point to the nearest critical point through a small initial shear along the transition vector [7].

According to the calculations, azatriene **I** is characterized by high rotational lability, and it gives rise to several stable conformers, some of which are shown in Fig. 1 and below (structures **Ia–Ii**). The principal structural parameters describing the rotational state of azatriene **I** are the dihedral angle between the planes of the methoxyallene and carbimidothioate fragments and torsion angles for the methyl groups. The structure of one or another rotamer determines the probability for cyclization of azatriene **I** into pyrrole and thermodynamic and kinetic parameters of this process.

We analyzed the total potential energy surface for rotational transformations of azatriene **I** with a view to identify the most stable conformers and estimate the probability for their participation in the cyclization to pyrrole **II**. The structures and principal geometric parameters of the most stable rotamers are shown in Fig. 1. Their relative stabilities estimated as the difference in the total energies with account taken of zero-point vibration energy (ZPE) range from 0 to 36 kJ/mol (Table 1). All rotamers **Ia–Ii** are characterized by noncoplanar arrangement of the imidothioate and methoxyallene fragments (Ψ_1, Table 1) as a result of steric repulsion between the methyl groups. The most flattened structures are **Id**, **Ig**, and **Ih** where the

trans Conformers (*trans* orientation of the N=C and C=C=C fragments)

Ia　　　**Ib**　　　**Ic**　　　**Id**

cis Conformers (*cis* orientation of the N=C and C=C=C fragments)

Ie　　**If**　　**Ig**　　**Ih**　　**Ii**
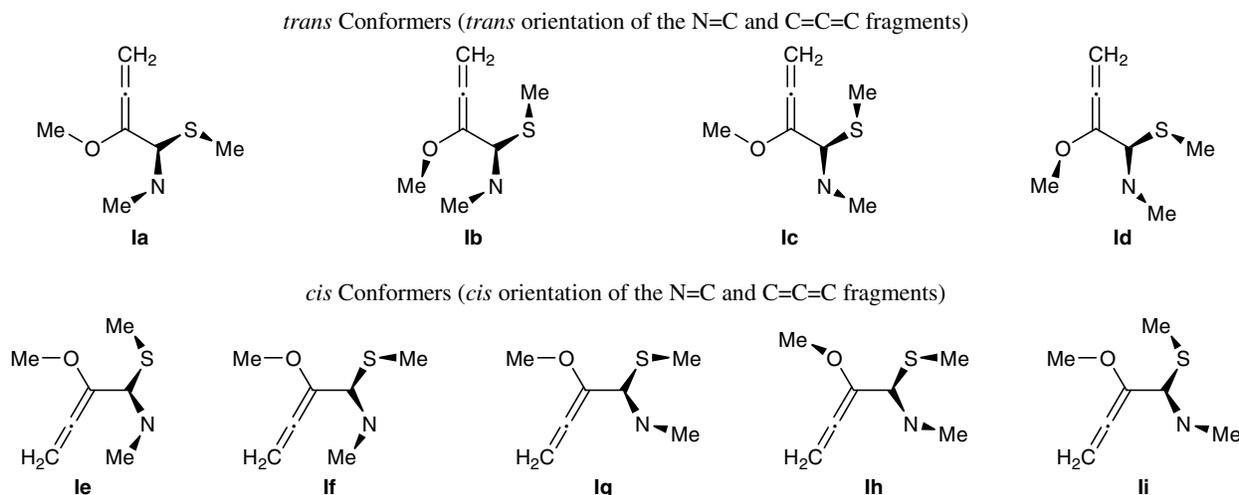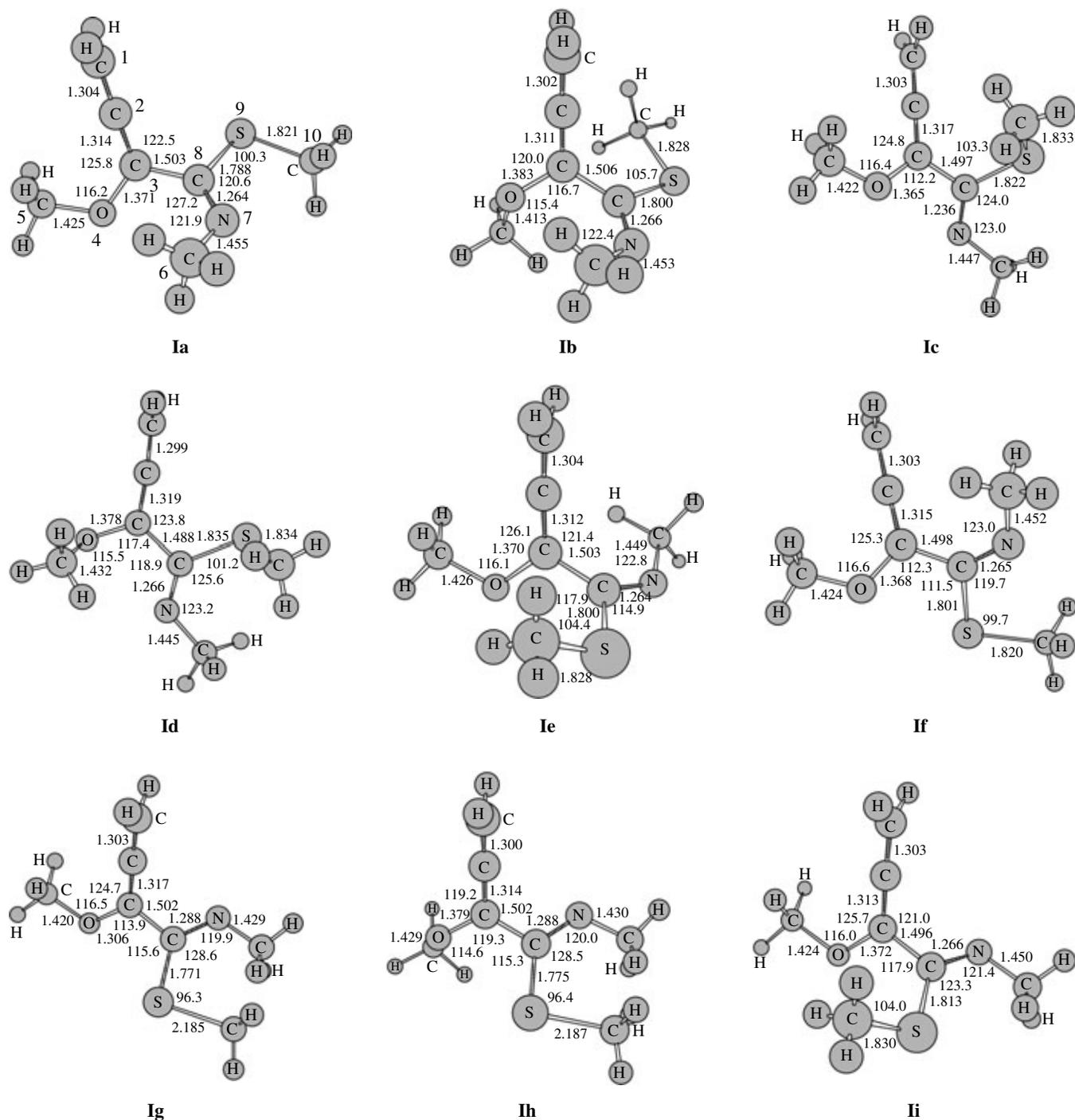
Fig. 1. Molecular structures and principal geometric parameters of most stable rotational isomers of compound **I** according to the B3LYP/6-311G** calculations (here and in Figs. 3, 5, and 7, bond lengths are given in Å, and angles, in deg).

dihedral angle between the above fragments does not exceed 30°, and structures **Ia**, **If**, and **Ii** are the most stable from the viewpoint of thermodynamics (in the gas phase). However, strong differences in the charge separation (judging by the calculated dipole moments; Table 1) could give rise to essential redistribution of rotamer populations in going to condensed phases with different polarities. Mutual orientation of the nitrogen atom and allene fragment in rotamers **Ia–Id** (Fig. 1) may be regarded as skewed *trans* (the deviation from planarity is 8.6 to 59°). Cyclization of these structures into pyrrole is the least probable. Structures **Ie–Ii**

Table 1. Total energies E_{tot}[a] (a.u.), energies of zero-point harmonic vibrations ZPE (a.u.), relative energies ΔE (kJ/mol), least harmonic frequencies ω_1 (cm^{-1}), dipole moments μ (D), dihedral angles Ψ_1[b] (deg), and torsion angles Ψ_2, Ψ_3, and Ψ_4[c] (deg) of the most stable rotamers of azatriene **I**, calculated by the B3LYP/6-311G** method

Rotamer no.	$-E_{tot}$	ZPE	ΔE	ω_1	μ	Ψ_1	Ψ_2	Ψ_3	Ψ_4
Ia	801.57023	0.16688	0.0	32	2.07	128.5	0.6	3.8	178.0
Ib	801.55757	0.16649	32.2	33	2.87	121.0	130.3	165.9	173.9
Ic	801.56435	0.16659	14.7	25	2.26	144.4	3.1	138.7	4.2
Id	801.56083	0.16656	23.8	31	2.68	171.4	77.1	59.6	3.0
Ie	801.56406	0.16681	16.0	29	4.42	66.3	1.0	168.9	176.0
If	801.56971	0.16700	1.7	37	2.47	41.5	3.6	3.5	177.6
Ig	801.56253	0.16699	20.5	33	1.45	27.4	3.9	0.3	1.9
Ih	801.55731	0.16769	36.0	36	2.26	27.0	111.8	2.4	2.5
Ii	801.56731	0.16682	7.5	34	2.52	49.2	2.6	156.7	3.7

[a] 1 a.u. = 2622.9897 kJ/mol.
[b] Ψ_1 is the dihedral angle formed by the *2-3-4* and *7-8-9* planes (relative to the *cis* orientation of the *2* and *7* centers; for numbering, see Fig. 1).
[c] Ψ_2, Ψ_3, and Ψ_4 are the torsion angles *2-3-4-5*, *7-8-9-10*, and *9-8-7-6*, respectively.

(skewed *cis* conformation, Ψ_1 27.0–66.3°) are spatially more favorable for intramolecular ring closure.

The activation barriers to mutual transformations of rotamers **Ia–Ii** depend on the dihedral angles Ψ_i ($i = 1–4$), which contribute most to the reaction coordinate in these transformations. The latter can arbitrarily be divided into three groups. The first group includes transitions in which the main components of

Fig. 2. Path (1). Schematic profile of the direct intramolecular nucleophilic reaction (the low triplet state is shown with a hashed bar; here and in Figs. 4 and 6, the relative energies are given in kJ/mol).

Fig. 3. Path (1). Molecular structures and principal geometric parameters of carbenoid intermediate **V**, product **IIa**, and transition states TS1 and TS2 (the torsion angle *1-2-3-4* in TS2 is 127.2°).

the reaction coordinate are angles Ψ_2 and Ψ_3 (**Ib → Ia**, **Ie → If**, **Ih → Ig**); these transitions are low-barrier: the corresponding energies of activation do not exceed 20 kJ/mol.

The second type of transitions whose reaction coordinate is contributed mainly by the orthogonal inversion of the angle Ψ_1 (**If → Ia**, **Ic → Ii**, **Ih → Id**); the corresponding activation barrier is almost twice as high (E_{act} 35–50 kJ/mol). The main component of the reaction coordinate in the third type transitions is *cis–trans* rearrangement of the *N*-methyl group (**Ic → Ia**,

Id → Ia, **Ie → Ii**); these transitions are characterized by the highest activation barriers which exceed 100 kJ/mol (107.9, 117.8, and 109.2 kJ/mol for **Ic → Ia**, **Id → Ia**, and **Ie → Ii**, respectively). In this case, *syn–anti* isomerism typical of Schiff bases is concerned [8].

The results of thermodynamic and kinetic analysis of the potential energy surface for rotational transformations indicate that compound **I** can exist as four most stable isomers **Ia**, **Ic**, **If**, and **Ii** which are spectroscopically distinguishable. These isomers differ

insignificantly in their stability. The difference between the energies of the most (**Ia**) and least stable (**Ic**) conformers does not exceed 15 kJ/mol. The other stationary states with low activation barriers slide down to one of the above listed. According to the calculations, the most favorable structure for the formation of pyrrole ring following path (1) is **Ii**. The other rotamers are more likely to undergo intramolecular transformations via cyclization processes initiated by spatially favorable [1,5]-sigmatropic proton migration, leading to the formation of dihydropyridine structures (Scheme 1) [2–4].

It was interesting to compare the pyrrole ring closure of azatriene **I** with the well studied (both experimentally and theoretically) endothermic ring opening of unsubstituted 1*H*-pyrrole [9], as well to estimate the validity of the calculation scheme used in the present work. According to [9], the energy of activation for the thermolysis of 1*H*-pyrrole is 310 ± 12 kJ/mol. Bacskay et al. [10] performed CASSCF, CASPT2, and G2(MP2) studies on different mechanisms of pyrrole ring opening and found that the inverse direct nucleophilic attack is preferred. The energy of activation of the rate-determining stage (4,5-H shift) in this process is 314 (CASSCF), 316 (CASPT2), and 302 kJ/mol [G2(MP2)]. The heats of reaction (4) (Scheme 3) are 190, 185, and 178 kJ/mol, as calculated by the CASSCF, CASPT2, and G2(MP2) methods, respec-

tively. Our calculations performed in terms of the B3LYP/6-311G** procedure gave $E_a = 316$ and $\Delta H = 176$ kJ/mol for the same reaction. These data indicate that the employed basis set in the B3LYP version of the density functional theory (DFT) is quite appropriate for analysis of the cyclization of 1-aza-1,3,4-triene **I**.

Scheme 3.

(4)
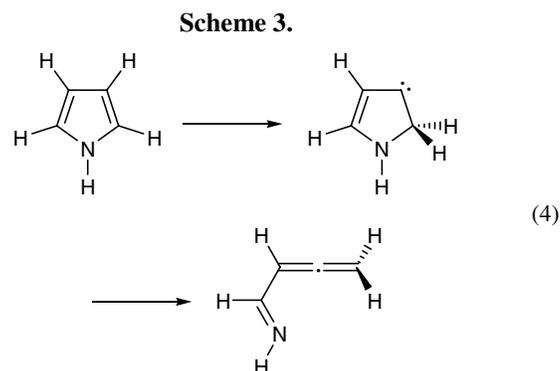
Examination of the gradient channel for the direct nucleophilic attack [path (1) in Scheme 2; Fig. 2] showed that closure of pyrrole ring and formation of carbene-like species **V** involve transition state TS1 (Fig. 3). The energy of activation at this stage is 96.2 kJ/mol; i.e., it is almost twice as high as the activation barrier (44.9 kJ/mol) to the formation of pyrrole **II** through protonated structures [1]. The main

Table 2. Total energies E_{tot} (a.u.), energies of zero-point harmonic vibrations ZPE (a.u.), relative energies ΔE (kJ/mol), imaginary or least harmonic frequencies $i\omega/\omega_1$ (cm^{-1}), and dipole moments μ (D) of structures **I**, **II**, and **V–VIII** and transition states TS1–TS6, calculated by the B3LYP/6-311G** method

Structure no.	$-E_{tot}$	ZPE	ΔE	$i\omega/\omega_1$	μ
Path (1)					
Ii	801.56731	0.16682	156.6	34	2.52
Ii→V (TS1)	801.53081	0.16698	252.8	*i*305	1.88
V	801.54490	0.16894	221.0	23	3.86
V→IIa (TS2)	801.51860	0.16609	282.5	*i*1076	3.11
Path (2)					
Ii→VI (TS3)	801.45586	0.16088	433.4	*i*640	2.80
VI	801.49033	0.16546	355.0	48	4.45
VI→IIb (TS4)	801.47757	0.16514	387.6	*i*273	4.32
Path (3)					
VII	801.55391	0.16713	192.6	44	2.13
VII→VIII (TS5)	801.52022	0.16653	279.4	*i*462	1.21
VIII	801.51545	0.16835	296.7	38	5.15
VIII→IIa (TS6)	801.50074	0.16593	328.9	*i*842	3.51
IIa	801.63118	0.17098	0.0	43	2.33
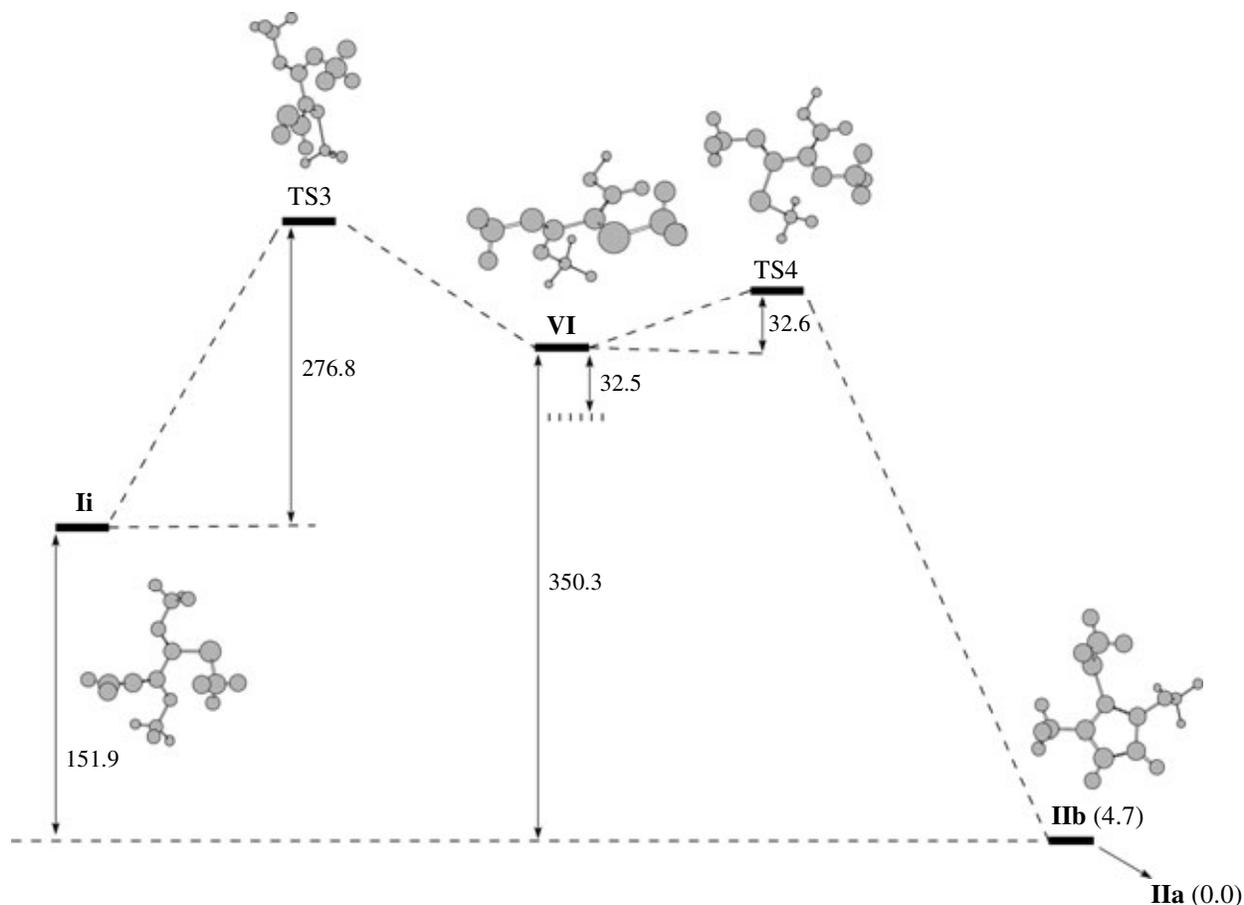
Fig. 4. Path (2). Schematic profile of the pyrrole ring closure of azatriene **I**, initiated by 1,2-hydride shift (the triplet state is shown with a hashed bar).

structural reorganization in the transition **Ii**→TS1 is flattening of the molecular skeleton with respect to heavy atoms, including methyl carbon centers. The structure of TS1 is perfectly planar, and its configuration remains unchanged along the transition TS1→**V**. The interatomic distance between the N and C atoms participating in the formation of new bond in TS1 is 1.983 Å. According to [9], the corresponding value for unsubstituted pyrrole is 1.884 Å. The transition state is considerably less polar than the initial state; however, the subsequent stabilization as structure **V** leads to sharp increase in polarity (Table 2). The 4,5-hydride shift in intermediate **V** is characterized by an activation barrier of 61.5 kJ/mol (TS1; Figs. 2, 3). As a result, the final structure is **IIa** where the methoxy group is coplanar to the pyrrole ring. Unlike the transition **I**→TS1→**V**, the polarity of the critical states along the transition **V**→TS2→**II** decreases monotonically. Therefore, in going to a polar condensed phase, the energy of TS1 in reaction (1) is expected to increase while the energy of TS2 should decrease. On the

whole, the heat balance in reaction (1) is 156.6 kJ/mol. According to the calculations, the contribution of the triplet channel to the rearrangement of carbenoid intermediate **V** is much smaller than that of the singlet channel (Fig. 2).

All rotational isomers of azatriene **I** shown in Fig. 1 are capable of being involved in the pyrrole cyclization according to path (2) with almost equal probabilities. The first stage of this process, i.e., 1,2-hydride shift in the allene fragment is rate-determining (Fig. 4). Its energy of activation amounts to 262.2 kJ/mol. The next stable structure is carbenoid species **VI** which occupies potential well with a depth of 78.4 kJ/mol (singlet state). Ring closure occurs through transition state TS4 (Fig. 5) with an activation barrier of 32.6 kJ/mol. The final stationary state has structure **IIb** with orthogonal arrangement of the methoxy group with respect to the pyrrole ring (Fig. 5). The energy of structure **IIb** is higher by 4.7 kJ/mol than that of pyrrole **IIa**.

The degree of charge separation at the critical points of the potential energy surface increases for the

TS3

VI

TS4

IIb
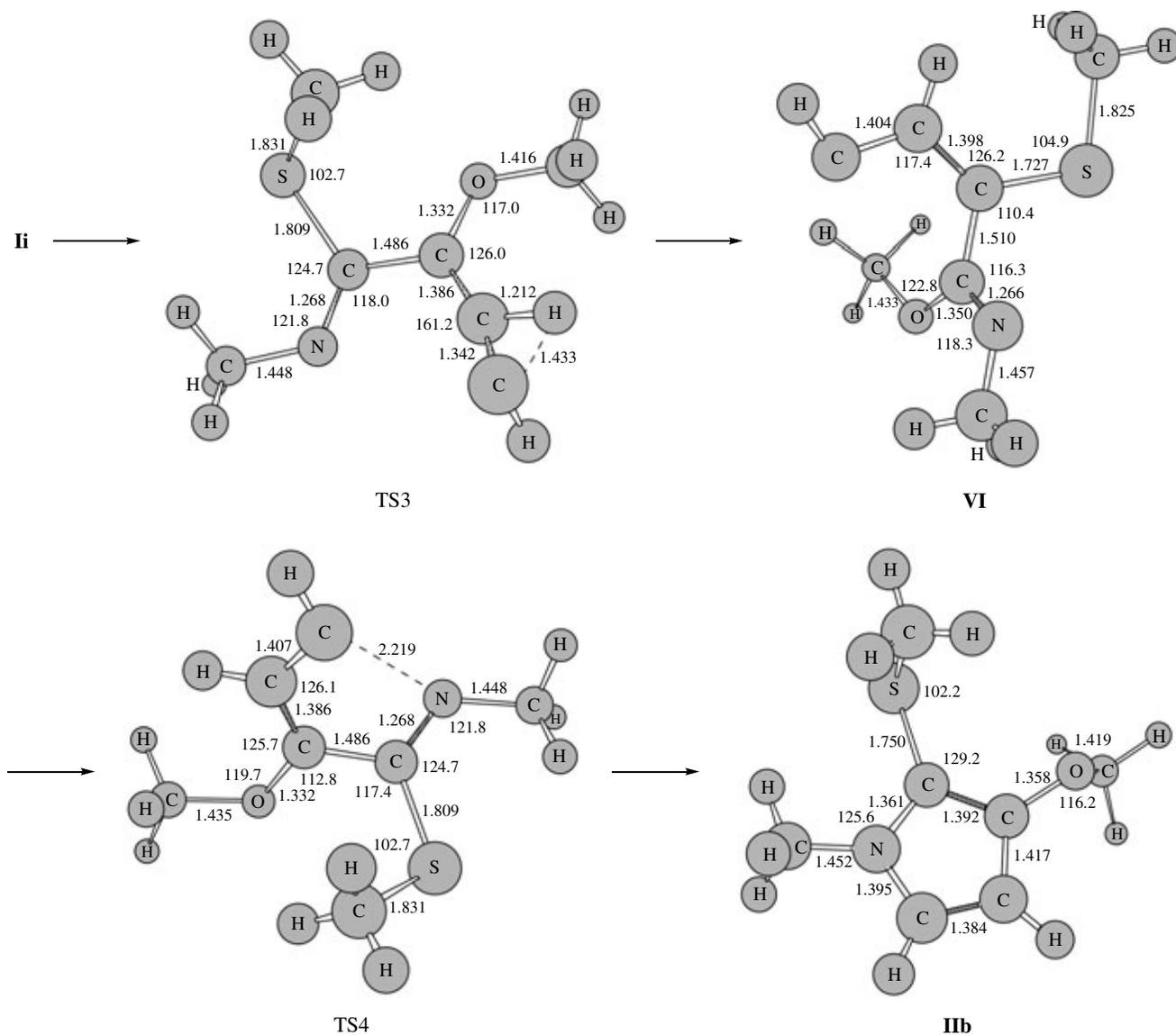
Fig. 5. Path (2). Molecular structures and principal geometric parameters of carbenoid intermediate **VI**, product **IIb**, and transition states TS3 and TS4.

transition $I \rightarrow VI$ and decreases along the transition $VI \rightarrow II$. Unlike carbene intermediate **V** in reaction (1), intermediate **VI** in reaction (2) is more stable in the triplet state (32.5 kJ/mol). Analysis of the gradient path in the transitions $I(^3V) \rightarrow TS3(^3V)$ and $VI(^3V) \rightarrow TS4(^3V)$ gives an insignificant decrease in the energy of activation, by 7.1 and 11.3 kJ/mol, respectively. These data suggest that the existence of lower triplet channel in the pyrrole ring closure of azatriene **I** according to path (2) does not increase the contribution of the latter to an appreciable extent relative to path (1). Thus cyclization path (2) may operate either when the reaction mixture contains no rotational states like **Ii** or in protic media where less energy-consuming

formation of intermediate **VI** is possible due to collective proton exchange between compound **I** and the nearest solvate environment.

Finally, let us consider the third hypothetical channel for the formation of pyrrole structure from compound **I** through acetylenic isomer **VII** [path (3) in Scheme 2]. According to the calculations, intramolecular acetylene–allene rearrangement of buta-2,3-dieneimidothioate **I** into but-3-ynimidothioate **VII** is characterized by a high activation barrier due to symmetry-forbidden suprafacial 1,3-hydride shifts [11]. Therefore, accumulation of but-3-ynimidothioate **VII** is formally possible only during the synthesis of compound **I** or as a result of intermolecular prototropic
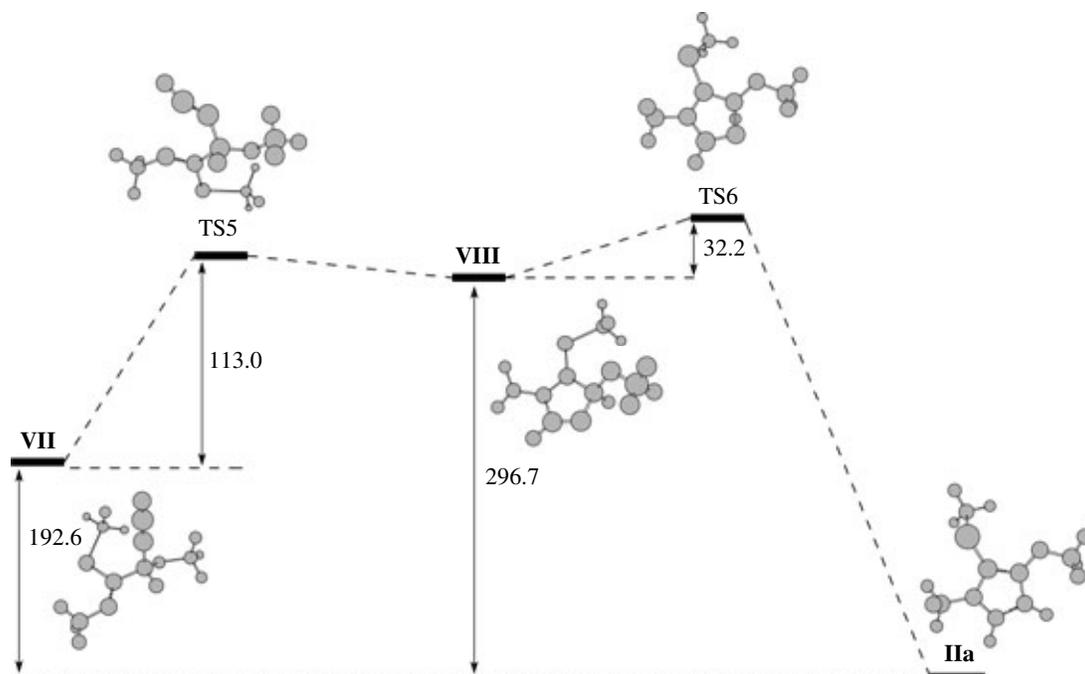
Fig. 6. Path (3). Schematic profile of the pyrrole ring closure of azatriene **I** through acetylenic structure **VII**.
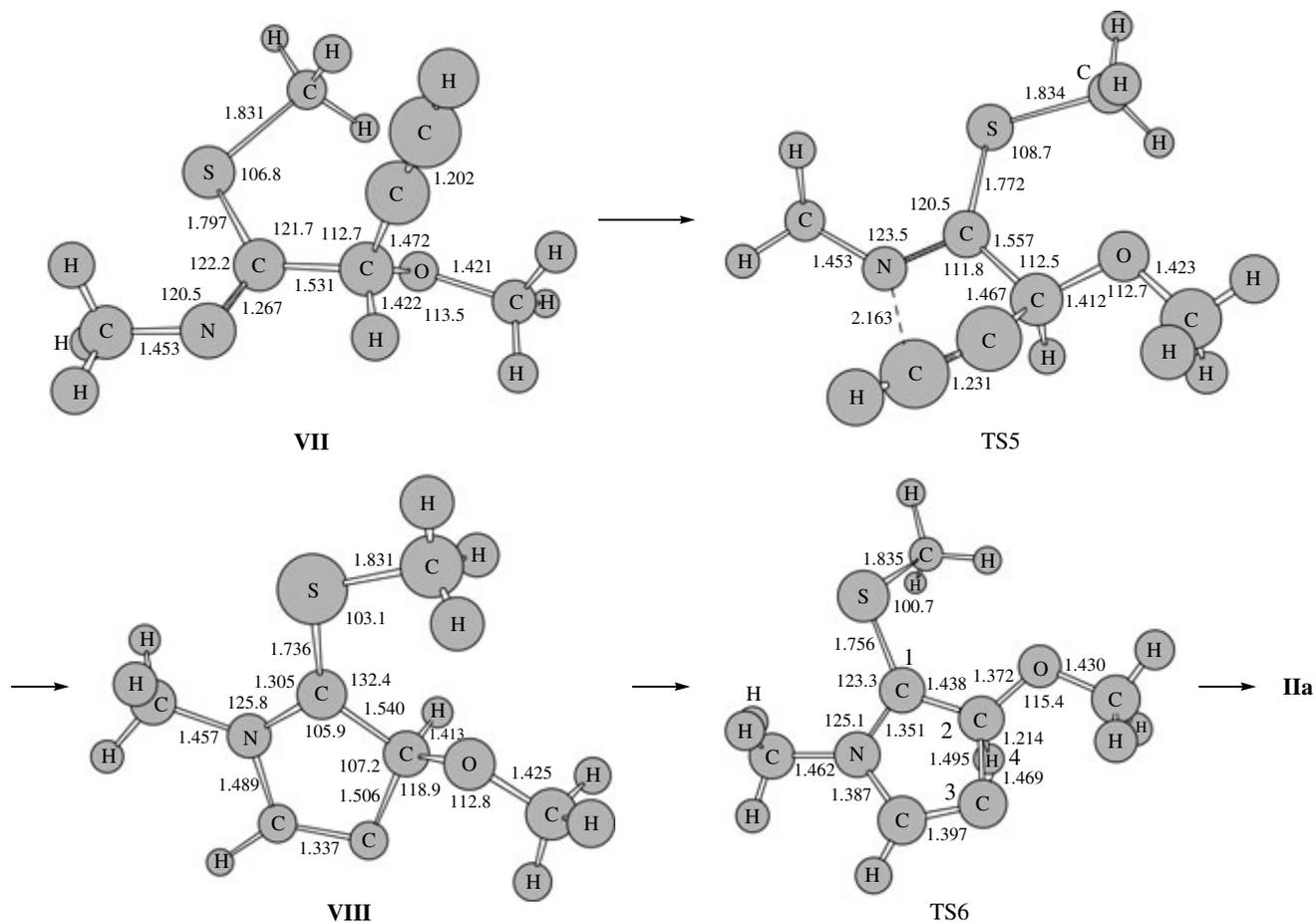
Fig. 7. Path (3). Molecular structures and principal geometric parameters of intermediates **VII** and **VIII** and transition states TS5 and TS6 (the torsion angle *1-2-3-4* in TS6 is 97.2°).

shifts promoted by solvent molecules. Theoretically possible reaction (3), as well as reactions (1) and (2), consists of two stages (Fig. 6). The first stage is closure of but-3-ynimidothioate **VII** to give five-membered ring **VIII** with formation of a new N–C bond. It involves transition state TS5 with an activation barrier of 113.0 kJ/mol, which then stabilizes as local stationary state **VIII** (the depth of the potential well is 8.9 kJ/mol). The next stage, 3,4-hydride shift in intermediate **VIII** overcomes an activation barrier of 32.2 kJ/mol (TS6; Figs. 6, 7). As in reaction (1), the final structure is **IIa**. The total heat effect of reaction (3) amounts to 192.6 kJ/mol, i.e., it is comparable with that found for reaction (1) (156.6 kJ/mol).

However, acetylenic isomer **VII** is less thermodynamically stable than the allene structure ($\Delta H =$ 36.0 kJ/mol), and the probability for its formation is small. Therefore, it cannot be involved in the pyrrole ring closure to an appreciable extent, although the energy of activation of the transition **VII→IIa** is only slightly higher than that for reaction (1) (136.3 and 125.9 kJ/mol, respectively). Moreover, the conditions for accumulation of intermediate **VII** (see above) are not met. Compound **VII** was not identified among products of the reaction of 1-lithio-1-methoxyallene with methyl isothiocyanate and those obtained by thermally induced transformations of allenic imidothioate **I** under solvent-free conditions. Thus there are still no experimental proofs for participation of path (3) in the cyclization of azatriene **I** to pyrrole structure.

To conclude, it should be noted that, among the three possible channels for the transformation of 1-aza-1,3,4-triene **I** into pyrrole **II**, path (1) implying formation of pyrrole ring via direct intramolecular nucleophilic attack by the nitrogen atom on the terminal allene carbon atom to give cyclic carbene species as key intermediate seems to be the most realistic.

REFERENCES

1. Shagun, V.A., Toryashinova, D-S.D., Nedolya, N.A., Tarasova, O.A., and Brandsma, L., *Russ. J. Org. Chem.*, 2004, vol. 40, p. 775.

2. Nedolya, N.A., *Ph. D. Thesis of Utrecht University*, Utrecht (The Netherlands), 1999.

3. Brandsma, L. and Nedolya, N.A., *Synthesis*, 2004, p. 735; Brandsma, L., *Eur. J. Org. Chem.*, 2001, p. 4569; Brandsma, L., Nedolya, N.A., Tarasova, O.A., and Trofimov, B.A., *Khim. Geterotsikl. Soedin.*, 2000, p. 1443; Nedolya, N.A., Brandsma, L., and Trofimov, B.A., *Khim. Geterotsikl. Soedin.*, 1996, p. 917; Nedolya, N.A., de Lang, R.-J., Brandsma, L., and Trofimov, B.A., *Abstracts of 11th Int. Conf. on Organic Synthesis*, Amsterdam, 1996, p. 251.

4. Nedolya, N.A., de Lang, R.-J., Brandsma, L., and Trofimov, B.A., *Russ. J. Org. Chem.*, 1997, vol. 33, p. 76; Nedolya, N.A., Brandsma, L., Zinov'eva, V.P., and Trofimov, B.A., *Russ. J. Org. Chem.*, 1997, vol. 33, p. 80.

5. Nedolya, N.A., Brandsma, L., Shlyakhtina, N.I., Fedorov, S.V., and Klyba, L.V., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 917; Nedolya, N.A., Schlyakhtina, N.I., Klyba, L.V., Ushakov, I.A., Fedorov, S.V., and Brandsma, L., *Tetrahedron Lett.*, 2002, vol. 43, p. 9679; Nedolya, N.A., Brandsma, L., Shlyakhtina, N.I., and Fedorov, S.V., *Khim. Geterotsikl. Soedin.*, 2002, p. 707; Shlyakhtina, N.I., Nedolya, N.A., and Brandsma, L., Abstracts of Papers, *V Molodezhnaya nauchnaya shkola-konferentsiya po organicheskoi khimii* (Vth Youth Scientific School–Conf. on Organic Chemistry), Yekaterinburg: Ural. Otd. Ross. Akad. Nauk, 2002, p. 496.

6. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, J.A., Jr., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., and Pople, J.A., *Gaussian 98, Revision B.03*, Pittsburgh PA: Gaussian, 2003.

7. Minyaev, R.M., *Usp. Khim.*, 1994, vol. 63, p. 933.

8. Tennant, J., *Comprehensive Organic Chemistry*, Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon, 1979, vol. 2. Translated under the title *Obshchaya organicheskaya khimiya*, Moscow: Khimiya, 1982, vol. 3, p. 476.

9. Mackie, J.C., Colket, M.B., Nelson, P.F., and Esler, M., *Int. J. Chem. Kinet.*, 1991, vol. 23, p. 733.

10. Bacskay, G.B., Martoprawiro, M., and Mackie, J.C., *Chem. Phys. Lett.*, 1999, vol. 300, p. 321.

11. Temnikova, T.I. and Semenov, S.N., *Molekulyarnye peregruppirovki v organicheskoi khimii* (Molecular Rearrangements in Organic Chemistry), Leningrad: Khimiya, 1983.