

## Multiple bond migration with participation of a protophilic agent

### 5.\* Double bond migration in heteroallylic systems

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The pathways of migration of the double bond in heteroallylic systems  $XCH_2CH=CH_2$  ( $X = NMe_2, OMe, PMe_2$ , and  $SMe$ ) with participation of hydroxide ion were investigated by the *ab initio* RHF/6-31+G\* and MP2/6-31+G\* methods. The results are compared with those of analogous calculations of the systems with  $X = H, Me$ . Conformational isomerism of the initial molecules and reaction products, as well as the structure of intermediate carbanions, are considered. Increased acidity of compounds containing atoms of the third-row elements is explained in terms of a negative hyperconjugation model. 1,3-Hydrogen shift with participation of hydroxide ion in the systems  $XCH_2CH=CH_2$  results in double bond migration toward substituent X to form 1-hetero-1-propenes  $XCH=CHMe$ . Comparison of the energies of the final products indicates thermodynamic preferableness of the formation of *E*-isomers. At the same time, in the case of substituents with atoms of the second-row elements the interaction of  $\sigma$ -bonds of the substituents and the p-AO of the terminal C atom additionally stabilizes *Z*-isomers of the carbanions and can be the reason for preferable kinetically controlled formation of these isomers. If the substituents contain atoms of the third-row elements, the formation of *E*-isomers of 1-hetero-1-propenes becomes both kinetically and thermodynamically predominant.

**Key words:** propene, but-1(2)-ene, 1-(dimethylamino)prop-1(2)-ene, 1-methoxyprop-1(2)-ene, 1-(dimethylphosphino)prop-1(2)-ene, 1-methylthioprop-1(2)-ene, 1,3-hydrogen shift, carbanion, acidity, hydroxide ion, reaction mechanism, *ab initio* quantum-chemical calculations.

Previously,<sup>1–4</sup> we studied the mechanism of migration of the double bond in the molecules of propene and its methoxy and methylthio derivatives in the presence of hydroxide ion and showed that 1,3-hydrogen shift can occur *via* the formation of an intermediate complex of the three-carbon system with the water molecule, *i.e.*, formally without exchange of the migrating proton with the medium. In all cases the energies of transition states determining the activation barriers on the pathways of migration of the double bond appeared to be lower than those of the reagents, reaction products, and the systems that formed from anions and the water molecule. This suggests that the direction of the double bond migration will be determined by the energy difference between the initial reagents and final products.

Migration of the double bond in a heteroallylic system  $XCH_2CH=CH_2$  with a substituent at the  $sp^3$ -hybridized carbon atom results in *Z*- and *E*-isomers of 1-heteroprop-1-enes ( $XCH=CHMe$ ). As a rule, *E*-isomers are more

thermodynamically stable and dominate in equilibrium mixtures.<sup>5–13</sup> At the same time, in the case of, *e.g.*, alkyl substituents, the formation rate of *Z*-isomers is usually higher than that of *E*-isomers and isomerization in the presence of catalysts results mostly in *Z*-alkenes.<sup>5,6</sup> For substituted propenes in which the allyl group is bonded to a N or O atom, the preferable kinetically controlled formation of *Z*-isomers is also initially observed. Then conversion occurs of *Z*- into *E*-isomers until the establishment of thermodynamic equilibrium.<sup>7–13</sup> Assuming that prototropic rearrangement begins with proton abstraction from the  $sp^3$ -hybridized carbon atom, it can be suggested that the preferableness of kinetically controlled formation of *E*- or *Z*-alkenes is determined by the relative stability of the corresponding carbanions.

The aim of this work was to study (i) the structure and relative stability of substituted propenes  $XCH_2CH=CH_2$  ( $X = H, Me, NMe_2, OMe, PMe_2, SMe$ ) and corresponding carbanions and (ii) the substituent effect on the direction and thermal effect of isomerization of the allylic system.

\* For Parts 1–4, see Refs. 1–4.

### Calculation procedure

Calculations were carried out following the known procedure.<sup>2-4</sup> The geometry of the structures under study was optimized by the restricted Hartree–Fock (RHF) method in the 6-31+G\* basis set. The energies were calculated at the second-order Møller–Plesset (MP2) level of perturbation theory using the GAMESS program package.<sup>14</sup>

### Results and Discussion

**Initial compounds.** Allylic systems  $\text{XCH}_2\text{—CH=CH}_2$  (X = H (1), Me (2), NMe<sub>2</sub> (3), OMe (4), PMe<sub>2</sub> (5), SMe (6)) were considered as initial reagents. Characteristic of molecule **1** is a cisoid conformation with respect to rotation about the C(2)—C(3) bond. Despite a rather short distance between H atoms (2.277 Å in the equilibrium structure; in this case, the C—C—C bond angle increases to 125.3°), it is this conformation that corresponds to a minimum on the potential curve of internal rotation in the propene molecule since it corresponds to minimum repulsion between the electrons of the C—H  $\sigma$ -bonds and the C(1)=C(2)  $\pi$ -bond. The repulsion is maximum in the staggered conformation (with a HC(3)C(2)C(1) dihedral angle of 60°) corresponding to the transition state. According to our calculations, the barrier to internal rotation in molecule **1** is ~2.0 kcal mol<sup>-1</sup>.

The cisoid conformation is also characteristic of the molecules of other compounds under study. Substituents can be either in *cis*- or in *gauche*-position with respect to the vinyl group. Hereafter, the *cis*- and *gauche*-conformers will be denoted **a** and **b**, respectively.

*gauche*-Conformers of the molecules are more energetically preferable for all substituents (Table 1). At the same time, it should be noted that the energies of the conformers are close. Among the systems with substituents containing atoms of the second-row (third-row)

elements, the largest energy differences are observed for **3** (**5**). This can be due to the fact that the methyl groups in conformers **3a** and **5a** "are forced" to be in eclipsed position with respect to H atoms at the C(3) atom. Steric hindrances in the molecules of these compounds are responsible for rather large deviations of the XC(1)C(2)C(3) dihedral angles from zero. The larger deviation observed for molecule **5a** can be explained by the larger size of the P atom compared to that of the N atom.

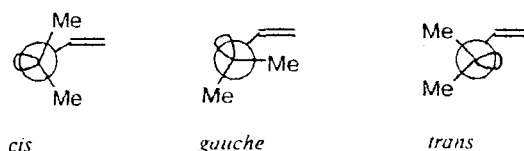
Transitions from *gauche*- to *cis*-conformations of molecules **3** and **5** also require the overcoming of higher energy barriers (see Table 1). This can be explained by additional steric hindrances due to the presence of two methyl groups at the heteroatom (X). Transition **3b**→**3a** can occur only in the case of simultaneous concerted rotation about the C(2)—C(3) and C(3)—N bonds. The energy barrier to rearrangement **5b**→**5a** is lower than for system **3** since the C—P bond is longer than the C—N bond.

The 1,3-hydrogen shift mechanism studied in this work implies that the reaction begins with attack of the base on the proton at the C(3) atom in the *gauche*-position. Taking molecule **4** as an example, it was shown<sup>3</sup> that the hydroxide ion attacks conformer **4a** (**4b**) to give *Z*- or *E*-isomers of 3-methoxyprop-1-ene, respectively. Analysis of the energy differences between *cis*- and *gauche*-conformers of all the above-mentioned initial structures suggests that migration of the double bond toward the substituent results in preferable formation of *E*-isomers.

**Reaction products.** 1,3-Hydrogen shift under the action of base results in 1-substituted prop-1-enes  $\text{X—CH=CH—CH}_3$  (**1c**–**6c**, substituents X correspond to those in compounds **1**–**6**) that can exist as *E*- and *Z*-isomers. In addition, rotamers can exist in systems **3c**–**6c** due to rotation about the C(1)—X bond.

The potential curves of internal rotation<sup>4</sup> in the molecules of *E*- and *Z*-isomers of compounds **4c** and **6c** show that obvious steric hindrances "force" the *Z*-isomers to exist only in *s-gauche*-conformation, whereas both *E*-isomers can exist in two rotameric forms. *s-cis*-Conformer of 1-methoxyprop-1-ene and *s-gauche*-rotamer of its sulfur-containing analog are the most stable.

Analogously, three rotameric forms of **3c** and **5c** can be considered (here, the notations given below take into account the direction of the bisectrix of the MeNMe angle):



*cis*-Rotamers of both *E*- and *Z*-isomers of compounds **3c** and **5c** are characterized by the maximum repulsion between the electrons of two X—C  $\sigma$ -bonds and a  $\pi$ -bond. *Z*-Isomers are also characterized by

**Table 1.** Energy differences ( $\Delta E/\text{kcal mol}^{-1}$ ) between *cis*- and *gauche*-conformers of  $\text{XCH}_2\text{CH=CH}_2$  molecules, barriers to internal rotation for transitions between *gauche*-conformers ( $\Delta E_{gg}^\ddagger/\text{kcal mol}^{-1}$ ) and from *gauche*- to *cis*-conformers ( $\Delta E_{gc}^\ddagger/\text{kcal mol}^{-1}$ ), and the XC(3)C(2)C(1) dihedral angles ( $\alpha/\text{deg}$ )

Compound	X	Conformer	$\Delta E$	$\Delta E_{gg}^\ddagger$	$\Delta E_{gc}^\ddagger$	$\alpha$
<b>1</b>	H		0.0	2.1	2.1	0.0
<b>2a</b>	Me	<i>cis</i>				0.0
<b>2b</b>	Me	<i>gauche</i>	-0.8	2.2	2.6	120.7
<b>3a</b>	NMe <sub>2</sub>	<i>cis</i>				15.5
<b>3b</b>	NMe <sub>2</sub>	<i>gauche</i>	-1.6	3.0	7.6	131.1
<b>4a</b>	OMe	<i>cis</i>				0.0
<b>4b</b>	OMe	<i>gauche</i>	-0.1	1.3	3.1	130.0
<b>5a</b>	PMe <sub>2</sub>	<i>cis</i>				18.0
<b>5b</b>	PMe <sub>2</sub>	<i>gauche</i>	-2.5	3.4	4.4	117.5
<b>6a</b>	SMe	<i>cis</i>				0.0
<b>6b</b>	SMe	<i>gauche</i>	-1.9	2.8	2.4	115.9

the greatest steric hindrances. Because of this, *cis*-structures correspond to maxima of the potential curves of internal rotation, i.e., to the barriers to transitions between two *gauche*-conformations. Among all considered isomers of molecules **3c** and **5c**, only the *E*-isomer of compound **3c** exists in *gauche*-conformation. *trans*-Positioning of two methyl groups with respect to the double bond is preferable for the rest three conformers (Table 2).

For all compounds studied in this work, the double bond migration from terminal position toward the substituent is accompanied by a decrease in the total energy (Table 3). Migration of the double bond in alkenes to the middle part of the chain is usually explained in terms of additional stabilization due to  $\sigma,\pi$ -conjugation. Indeed, the composition of molecular orbitals (MOs) of **2c** (Fig. 1) indicates a rather strong  $\sigma-\pi$ -interaction. Obvious steric hindrances make the *Z*-isomer of compound **2c** less favorable than the *E*-isomer.

Migration of the double bond toward the substituent containing a heteroatom with the lone electron pairs (LEP) is usually explained by involvement of the LEP in conjugation with the  $\pi$ -system.<sup>6</sup> Among all the compounds considered, only the *E*-isomer of **4c** has a structure in which the LEP of the O atom can strongly interact with the  $\pi$ -system. The thermal effect of the formation of this compound is maximum. The highest occupied molecular orbital (HOMO) of the *E*-isomer of compound **4c** with an energy of  $-0.329$  au is mainly localized on the C(1)=C(2)  $\pi$ -bond, contains a small contribution ( $\sim 15\%$ ) of the LEP orbital of the O atom (Fig. 2), and is an antibonding orbital toward the O—

C(1) bond. Because of partial displacement of the electron density from the C(1)=C(2) bond and additional C(1)—O antibonding interaction, the HOMO energy of the *E*-isomer of **4c** is 1.1 eV higher than that of isomer **4b**. Additional C(1)—O bonding interaction appearing as a result of conjugation between the methoxy group and allylic  $\pi$ -system manifests itself in the composition of the  $3a''$  MO with an energy of  $-0.498$  au (see Fig. 2). This MO is composed of the p-AO of the O atom (36%) and AOs of the methyl group of the substituent (50%) and the nearest C(1) (13%) and C(2) atoms. Such additional bonding results in shortening of the C(1)—O bond from 1.393 to 1.346 Å on going from **4b** to **4c**.

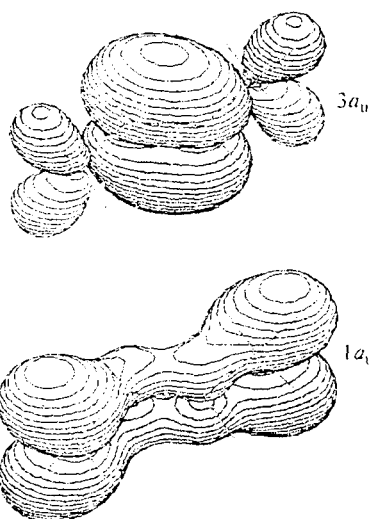


Fig. 1. The  $1a_u$  MO ( $\epsilon = -0.574$  au) and the  $3a_u$  HOMO ( $\epsilon = -0.344$  au) of the *E*-but-2-ene molecule. The contour lines are drawn with an increment of 0.04.

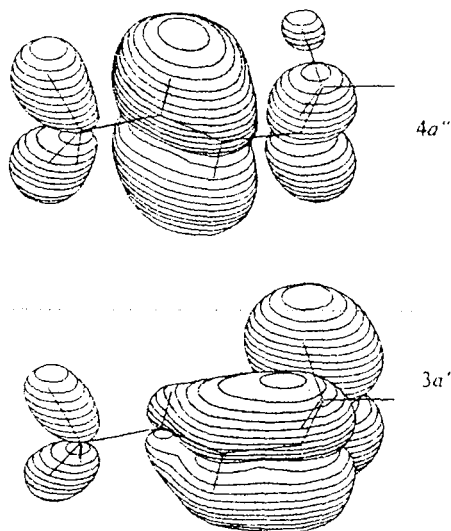


Fig. 2. The  $4a''$  HOMO ( $\epsilon = -0.329$  au) and the  $3a''$  MO ( $\epsilon = -0.498$  au) of the *E*-1-methoxyprop-1-ene molecule. The contour lines are drawn with an increment of 0.04.

**Table 2.** Energy differences ( $\Delta E_{ig}/\text{kcal mol}^{-1}$ ) between *gauche*- and *trans*-conformers of  $\text{XCH}=\text{CH}_2\text{Me}$  molecules and barriers to *gauche*—*trans*-transitions ( $\Delta E_{gt}/\text{kcal mol}^{-1}$ ) and to *gauche*—*cis*—*gauche*-transitions ( $\Delta E_{ggt}/\text{kcal mol}^{-1}$ )

Compound	X	$\Delta E_{ig}$	$\Delta E_{gt}$	$\Delta E_{ggt}$
<i>E</i> - <b>3c</b>	NMe <sub>2</sub>	−2.7	3.6	6.3
<i>Z</i> - <b>3c</b>	NMe <sub>2</sub>	2.1	0.4	3.2
<i>E</i> - <b>5c</b>	PMe <sub>2</sub>	2.0	0.7	1.9
<i>Z</i> - <b>5c</b>	PMe <sub>2</sub>	5.6	1.0	0.7

**Table 3.** Relative energies of transitions from *gauche*- $\text{XCH}_2\text{CH}=\text{CH}_2$  to *E*- $\text{XCH}=\text{CHMe}$  ( $\Delta E_E/\text{kcal mol}^{-1}$ ) and to *Z*- $\text{XCH}=\text{CHMe}$  ( $\Delta E_Z/\text{kcal mol}^{-1}$ ) calculated by the RHF/6-31+G\* (RHF) and MP2/6-31+G\*/RHF/6-31+G\* (MP2) methods

Compound	X	$\Delta E_E$		$\Delta E_Z$	
		RHF	MP2	RHF	MP2
<b>1</b>	H	0	0	0	0
<b>2</b>	Me	−2.2	−2.4	−0.7	−0.9
<b>3</b>	NMe <sub>2</sub>	−4.6	−5.7	−1.6	−2.1
<b>4</b>	OMe	−3.8	−5.9	−3.2	−4.8
<b>5</b>	PMe <sub>2</sub>	−3.1	−2.8	−1.3	−1.3
<b>6</b>	SMc	−3.2	−4.0	−1.9	−3.8

In *E*-isomer of compound **3c**, the LEP axis deviates from the plane of the  $\pi$ -system by 16.5°, whereas the bonding angle at the N atom increases from 112° (in the initial form **3b**) to 117.2° and 114.6° for *cis*- and *gauche*-conformers, respectively. It is believed that the interaction of the LEP of the N atom with the  $\pi$ -system also will stabilize the double bond near the substituent. Indeed, the corresponding MOs of (*E*)-**3c** contain contributions of AO that can be assigned to the LEP orbital of the N atom and to orbitals of the C(1)=C(2)  $\pi$ -bond. In this molecule, the degree of the HOMO (with an energy of -0.297 au) localization on the C(1)=C(2) bond is only 60%, whereas the MO describing  $\pi$ -bonding of the substituent with the hydrocarbon fragment is strongly delocalized and is composed of AOs of all its atoms. It should be noted that an appreciable contribution to  $\pi$ -interaction comes from the AO of the N—CH<sub>3</sub>  $\sigma$ -bond (*gauche*). Despite unfavorable conditions for conjugation, the energy gain obtained for rearrangement **3b**→(*E*)-**3c** is close to that obtained for analogous rearrangement **4b**→(*E*)-**4c** (see Table 3).

The structures of *E*-isomers of compounds **5c** and **6c** and corresponding isomers of **3c** and **4c** are different. The LEP of the P atom in **5c** is in the plane of the three-carbon fragment and is not involved in  $\pi$ -conjugation. The HOMO of this molecule with an energy of -0.329 au is almost completely localized on the P atom (83%) and contains small contributions of AO of methyl groups of the substituent. The highest  $\pi$ -MO of molecule **5c** with an energy of -0.361 au, describing the C(1)=C(2)  $\pi$ -bond, is mainly (by 90%) localized on the propene fragment. Atomic orbitals of the P atom do not contribute to this  $\pi$ -MO, whereas AOs of methyl groups contribute appreciably. The MO with an energy of -0.466 au is responsible for additional C(1)—P bonding. It is composed of the AOs of methyl groups of the substituent (66%), the AO of the P atom (25%), and the p-AO of the C(1) atom (5%). Redistribution of the  $\pi$ -electron density results in shortening of the C—P bond from 1.868 Å (the C(3)—P bond in **5b**) to 1.829 Å (the C(1)—P bond in **5c**). The energy effect of stabilization of the double bond near the substituent is close to that of the methyl group in system **2c** (Table 3).

**Table 4.** Changes in the energy upon proton abstraction by hydroxide ion followed by the formation of *E*- and *Z*-anions [XCHCHCH<sub>2</sub>]<sup>-</sup> ( $\Delta E_{h-E}$  and  $\Delta E_{h-Z}$ ) and water molecule; energy differences between isomeric anions ( $\Delta E_{Z-E}$ )

Compound	X	$\Delta E_{h-E}$	$\Delta E_{h-Z}$	$\Delta E_{Z-E}$
		kcal mol <sup>-1</sup>		
1	H	6.9	6.9	0.0
2	Me	11.6	5.6	5.2
3	NMe <sub>2</sub>	8.5	2.4	4.7
4	OMe	7.5	4.4	2.9
5	PMe <sub>2</sub>	-8.6	-8.7	-0.8
6	SMe	-9.1	-9.6	0.2

The *E*-isomer of compound **6c** has a more complicated structure. The C(2)C(1)SCH<sub>3</sub> dihedral angle in this isomer is 127° and the direction of the LEP axis of the S atom is unfavorable for conjugation. Nevertheless, the electron density of the C(1)=C(2)  $\pi$ -bond in isomer **6c** is rather strongly delocalized. As in the case of system **5c**, the AOs of the S—Me bond contribute appreciably to the  $\pi$ -MO. Moreover, we failed in localizing the  $\pi$ -MO that could be mainly localized on the C(1) and C(2) atoms of this molecule. The HOMO is composed of the AOs of the S atom (62%), C(1) atom (13%), C(2) atom (18%), and to some extent of the AOs of the C(3) atom and those of the H atoms bonded to the C(3) atom. The other two MOs with energies of -0.386 and -0.447 au are also mainly composed of the AO of the S atom (by 40 and 50%, respectively). However, AOs of the three-carbon fragment and S—CH<sub>3</sub> bond also make rather large contributions to these MOs. The rather high energy of the double bond stabilization near the S atom corresponds to the interaction of the hydrocarbon  $\pi$ -system with the AOs of the S atom and S—CH<sub>3</sub>  $\sigma$ -bond. The contribution of the LEP is small because of its unfavorable position with respect to the  $\pi$ -system. Because of steric hindrances, *Z*-isomers of compounds **3c**–**6c** are less stable than the corresponding *E*-isomers (see Table 3). In all *Z*-isomers, the LEP of the heteroatom is not involved in conjugation.

The best conditions for interaction of the LEP with the  $\pi$ -system are realized in system **4c**, in which the methyl group of the substituent deviates by 25° from the plane passing through the C(2), C(1), and O atoms. Despite the decrease in the resulting overlap, the composition of the HOMO of this molecule is much like that of the HOMO of the *E*-isomer and differs from the latter in some electron density redistribution between the C(1) and C(2) atoms resulting in equalization of their populations. The HOMO energies of both isomers are equal. The MO describing the C(1)—O bond contains additional contribution of the AO of the O—CH<sub>3</sub>  $\sigma$ -bond. A rather effective interaction of the AOs causes a decrease in the energy of the system by 4.8 kcal mol<sup>-1</sup> upon migration of the double bond to the heteroatom.

The scheme of the interaction of the  $\pi$ -system with the substituent changes only slightly on going from *E*- to *Z*-isomers of compounds **5c** and **6c**. In fact, the LEP of the P atom in the *Z*-isomer of **5c** is not involved in conjugation. As previously, the interaction between the  $\pi$ -orbitals of the propenyl fragment and the P—C  $\sigma$ -bonds remains a stabilizing factor. The corresponding MOs of the *E*- and *Z*-isomers of **5c** have equal energies and the same compositions. Analogously, the *E*- and *Z*-isomers of **6c** differ only in the value of the C(2)C(1)SCH<sub>3</sub> dihedral angle, which increases to 138° in the latter. Their MOs, whose compositions reflect the interaction between the double bond and the substituent, are close both qualitatively and quantitatively.

The most pronounced changes on going from the *E*- to *Z*-isomer are observed for compound **3c**. In

*E*-isomers, the methyl groups of the substituent are in *gauche*-position and the bond angles at the N atom are increased, thus providing conjugation of its LEP with the  $\pi$ -system. In *Z*-isomers of **3c**, the LEP of the N atom lies in the plane of the hydrocarbon fragment and is not involved in conjugation. The bond angles at the N atom (111.6°) are much larger than those at the P atom in compound **5c**, whereas the electron density of the N—C  $\sigma$ -bonds is shifted toward the N atom. This likely makes the  $\sigma$ — $\pi$ -interaction difficult. The  $\pi$ -bond orbitals in **3c** are virtually not mixed with AOs of the substituent, which results in an increase in the total energy of 3.6 kcal mol<sup>-1</sup> on going from *E*- to *Z*-isomer of compound **3c**.

According to the results obtained, migration of the double bond to the middle part of the chain is thermodynamically favorable for all the substituents considered, the *E*-isomers being more stable in all cases. Thus, the structure of both initial compounds and final products indicates preference for the formation of *E*-isomers of substituted propenes  $XCH=CHMe$ .

**Intermediate carbanions.** Both the conventional "intermolecular" mechanism of alkene isomerization<sup>15,16</sup> and the single-stage mechanism under consideration involve the formation of a carbanion upon proton abstraction by the base from the C atom near the double bond. In our case, the hydroxide ion serves as a base; therefore, one should compare the acidity of the initial compounds and that of the water molecule. It should also be taken into account that isomerization of initial structures of the types **a** and **b** following the single-stage mechanism under study results in *Z*- and *E*-anions, respectively.

According to calculations, the acidity of unsubstituted propene is lower than that of the water molecule. The estimate obtained is in good agreement with the data on the C—H acidity in the gas phase.<sup>17</sup> For all substituents X with atoms of the second-row elements (C, N, O), abstraction of a proton by hydroxide ion results in an increase in the total energy of the system (see Table 4). *Z*-Anions of **2–4** appeared to be more energetically preferable. The preferred order of their formation changes as follows:  $CH_3 > N(CH_3)_2 > OCH_3$ . These results are in good agreement with the ratio of *E*- and *Z*-isomers in kinetically controlled alkene isomerization reactions.<sup>5</sup>

Increased stability of the *Z*-isomer of the anion of **2** can be explained by analyzing the composition of its HOMO (Fig. 3). The HOMO is composed of the p-AOs of the C(1) and C(3) atoms and of the orbitals of the C—H  $\sigma$ -bonds of the methyl group, which favors the additional bonding interaction with the C(1) atom. No such bonding occurs in the *E*-isomer of the anion of **2** because the C(1) atom is too distant from the substituent.

The *E*-anion of **3** has a  $C_s$  symmetry and the LEP of the N atom is in the plane of the hydrocarbon skeleton. In this case, both steric hindrances and the repulsion between the LEP and the excess electron density on the

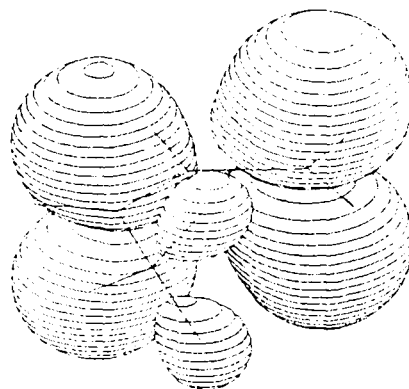
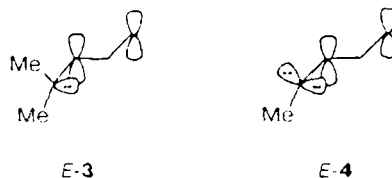
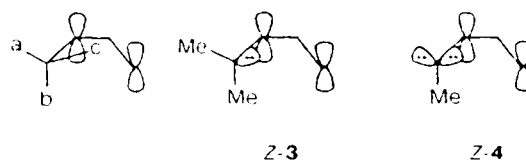


Fig. 3. The HOMO of *Z*-isomer of the but-1-ene anion. The contour lines are drawn with an increment of 0.04.

$p_z$ -AO of the C(3) atom are minimum. The C(2)C(3)OCH<sub>3</sub> dihedral angle in the *E*-anion of **4** is 111.1°. In this case, one of the equivalent LEPs is in the plane passing through the C(1), C(2), and C(3) atoms:



The spatial structure of the *Z*-anions of **3** and **4** is described by the other scheme:



In the *Z*-anion of **4**, position *b* is occupied by the methyl group while the equivalent LEPs are in positions *a* and *c*. In the *Z*-anion of **3**, the methyl groups are in positions *a* and *b*. In general, such a mutual arrangement of the Me—X  $\sigma$ -bonds, LEPs, and the  $p_z$ -AO of the C(3) atom is unfavorable. In the *Z*-anion of **4**, the directions coincide of the  $p_z$ -AO, the H<sub>3</sub>C—O  $\sigma$ -bond, and the direction along which the total electron density on two LEPs is maximum. This should result in a strong electron repulsion. The same is also valid for the *Z*-anion of **3**. However, the interaction with participation of the  $\sigma$ -bond of the N atom with the Me group in position *a* is expected to result in weaker repulsion than in the case of the interaction involving the LEP of the O atom in the *Z*-anion of **4**. At the same time, in both *Z*-anions the  $\sigma$ -bond of the heteroatom with the Me group in position *b* and the  $p$ -AO of the C(1) atom are collinear, the C(2)C(3)XCH<sub>3</sub> dihedral angle being equal to 89°. This spatial position of the substituent is favorable for additional long-range stabilizing interaction of

the X—CH<sub>3</sub>  $\sigma$ -bond with the p<sub>x</sub>-AO of the C(1) atom, thus resulting in a higher stability of the Z-anions of **3** and **4** compared to that of the E-anions. This interaction, which is more effective for the less polar C—N bond than for the C—O bond, as well as the above-mentioned strong repulsion between the two LEPs of the O atom and the electron density on the p<sub>x</sub>-AO of the C(3) atom are responsible for the larger energy difference between the E- and Z-anions of **3** compared to those of **4**. Thus, increased stabilization of Z-anions makes kinetically controlled formation of Z-isomers of propenes XCH=CHMe (X = Alk, Me<sub>2</sub>N, MeO) more probable.

A drastic increase in the acidity of the CH<sub>2</sub> group bonded to the substituent is observed in the systems XCH<sub>2</sub>CH=CH<sub>2</sub> containing substituents with atoms of the third-row elements. According to our results, the acidity of compounds **5** and **6** is higher than that of the water molecule, and the abstraction of a proton from these molecules by hydroxide ion is energetically more favorable (see Table 4). Previously,<sup>4</sup> we have considered differences in the acidity of molecules **4** and **6**. Based on the analysis of changes in the structural parameters and electron density distribution upon formation of anions, we concluded that stabilization of the carbanion of sulfur-containing compound **6** is due to the effect of negative hyperconjugation, which is not observed for **4**.

The same regularities are also observed for compounds **3** and **5**. The formation of E-anions has virtually no effect on the N—C(3) and N—CH<sub>3</sub> interatomic distances in **3**, whereas the P—CH<sub>3</sub> bond in **5** is lengthened by 0.025 Å, thus becoming weakened, and the P—C(3) bond is shortened by 0.105 Å. Distributions of the excess negative charge in these anions are also different. The negative charge on the substituent in the E-anion of **3** increases by 0.143 au, of which 0.125 au is distributed over the Me groups. In the E-anion of **5**, the electron density is much more pronouncedly displaced toward the Me groups (0.187 au is thereon). On the whole, the dimethylphosphine substituent accepts a negative charge of 0.250 au. Thus, the increased acidity of compounds **5** and **6** can be explained in terms of a negative hyperconjugation model.

Unlike the anions of **3** and **4**, no preferableness of Z-isomers was revealed for the anions of **5** and **6** with atoms of the third-row elements (see Table 4). The RHF calculations for the anion of **6** predict equal energies of the isomers. The inclusion of correlation corrections results in a somewhat higher stability of the Z-isomer; however, the energy difference between the Z- and E-anions is only -0.2 kcal mol<sup>-1</sup>. For system **5**, both RHF and MP2 calculations indicate the preferred formation of the E-anion.

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According to the results obtained, the 1,3-hydrogen shift in heteroallylic systems in the presence of hydrox-

ide ion results in migration of the double bond toward the substituent. The energy differences between the final products indicate thermodynamically preferable formation of the E-1-heteroprop-1-enes. Realization of the mechanism of the double bond migration with participation of the H atom of the hydroxide ion studied in this work makes it possible to argue that the initial compounds also rearrange into E-isomers mostly. At the same time, additional stabilization of Z-isomers of carbanions due to the interaction of the  $\sigma$ -bonds of the substituent with the atoms of second-row elements can be the reason for preferable kinetically-controlled formation of Z-products. If the substituents contain the atoms of third-row elements, the formation of E-isomers of the final products seems to be more probable both kinetically and thermodynamically.

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## References

1. N. M. Vitkovskaya, V. B. Kobychev, A. B. Trofimov, and B. A. Trofimov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1772 [*Russ. Chem. Bull.*, 1997, **46**, 1677 (Engl. Transl.)].
2. N. M. Vitkovskaya, V. B. Kobychev, E. Yu. Larionova, and B. A. Trofimov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 35 [*Russ. Chem. Bull.*, 1999, **48**, 35 (Engl. Transl.)].
3. N. M. Vitkovskaya, V. B. Kobychev, E. Yu. Larionova, and B. A. Trofimov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 658 [*Russ. Chem. Bull.*, 1999, **48**, 653 (Engl. Transl.)].
4. V. B. Kobychev, N. M. Vitkovskaya, E. Yu. Larionova, N. S. Klyba, and B. A. Trofimov, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 407 [*Russ. Chem. Bull.*, 2000, **49**, 408 (Engl. Transl.)].
5. Yu. M. Zhorov, G. M. Panchenkov, and G. S. Volokhova, *Izomerizatsiya olefinov [Isomerization of Olefins]*, Khimiya, Moscow, 1977, 208 pp. (in Russian).
6. D. J. Cram, *Fundamentals of Carbanion Chemistry*, Academic Press, New York—London, 1965.
7. T. J. Prosser, *J. Am. Chem. Soc.*, 1961, **83**, 1701.
8. C. C. Price and W. H. Snyder, *J. Am. Chem. Soc.*, 1961, **83**, 1773.
9. J. Saner and H. Prah, *Chem. Ber.*, 1969, **102**, 1917.
10. A. Schouteeten and M. Julia, *Tetrahedron Lett.*, 1975, 607.
11. A. J. Hubert, *J. Chem. Soc.*, 1968, 2048.
12. R. A. Crellin and A. Ledwith, *Macromolecules*, 1975, **8**, 93.
13. M. Julia and A. Schouteeten, *Tetrahedron Lett.*, 1974, 3433.
14. M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupius, and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
15. T. I. Temnikova and S. N. Semenova, *Molekulyarnye peregrupirovki v organicheskoi khimii [Molecular Rearrangements in Organic Chemistry]*, Khimiya, Leningrad, 1983, 256 pp. (in Russian).
16. C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell Univ. Press, Ithaca, New York, 1953.
17. O. A. Reutov, I. P. Beletskaya, and K. P. Butin, *CH-Kisloty [CH Acids]*, Nauka, Moscow, 1980, 248 pp. (in Russian).