Acetylene—allene rearrangement of propargyl systems X—CH_2—C≡CH (X = H, Me, NMe_2, OMe, F, SMe): an *ab initio* study

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Acetylene—allene rearrangement in propargyl systems $XCH_2CH{\equiv}CH$ (X = H, Me, NMe_2, OMe, F, and SMe) was studied using the *ab initio* approach. The relative stabilities of the starting and final propyne structures and the corresponding allenes as well as the structure of intermediate carbanions were considered. *n*-π-Conjugation was shown to dominate in allene stabilization while the inductive effect of heteroatomic substituents makes at least comparable contribution to stabilization (or destabilization) of the propynyl structure. In particular, relative instability of 1-methoxypropyne can be rationalized by high electronegativity of O atom, which leads to dramatic decrease in the total electron density in the region of the neighboring C≡C triple bond. The influence of substituents on the mobility of the migrating proton was considered for the gas phase and with solvation effects included. Calculations involving electron correlation at the MP2 level of theory were shown to be insufficient for correct reproduction of the energy differences between the corresponding propynes and allene structures. The results of MP4 calculations with inclusion of ZPE correction are in good agreement with the available experimental data.

Key words: propyne, but-1(2)-yne, dimethylprop-1(2)-ynylamine, 1(3)-methoxypropyne, 1(3)-methylthiopropyne, allene, buta-1,2-diene, dimethylpropa-1,2-dienylamine, 1-methoxypropa-1,2-diene, 1-methylthiopropa-1,2-diene, relative stability, rearrangement, *ab initio* calculations.

Prototropic acetylene—allene isomerization has gained increasing importance as an advantageous tool in organic synthesis,[1—4] though this reaction only begins to unveil its potentialities. Recently,[5] it was shown that alkoxy-1,2-dienes synthesized using prototropic isomerization of propargyl ethers as well as other allenes are convenient building blocks for the synthesis of pyrroles, dihydropyridines, and other heterocycles with heteroatomic substituents. Deeper insight into the mechanism of prototropic acetylene—allene isomerization will favor both the development of theoretical foundations of the chemistry of dicoordinated carbon and wider use of this reaction in organic synthesis.

Migration of the triple bond in alkynes was first studied by A. E. Favorsky.[6,7] The triple bond migration toward the middle position involving intermediate formation of corresponding allene compounds or emergence of the system of conjugated double bonds is thermodynamically favorable for 1-alkynes. Such transformations occur with particular ease in the presence of superbases.[1,3,8—11] When superbasic reagents can metallate acetylenes (*viz.*, Na,[6,7] alkali metal amides,[2] $KNH(CH_2)_3NH_2$ [12,13]), isomerization into terminal acetylenes occurs due to the formation of acetylides MC≡CR (M = Li, Na, K).

Migration of the triple bond in systems with heteroatomic substituents has been less studied. In particular, thermodynamic aspects of the rearrangement are still to be clarified. Acetylene hydrocarbons are usually more stable than the corresponding allene isomers; however, the reverse is often observed in heteropropargyl systems. For instance, alkylpropargyl ethers easily rearrange into alkylallenyl ethers under the action of superbases.[1,3,8—11] Usually, the isomerization products contain negligible amounts of 1-alkoxypropynes,[1] which points that the α,β-acetylene isomers are less thermodynamically favorable.

The mechanism of 1,3-hydrogen shift in propargyl systems in the presence of bases has been the subject of intense experimental research. In particular, an intermolecular mechanism of proton transfer involving the formation of stable anionic intermediates was proposed

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 713—720, May, 2002.

1066-5285/02/5105-774 $27.00

in studies of isomerization of acetylene acids under the action of KOH.[14] Intramolecular mechanism of proton transfer was also suggested[15] for isomerization of 1,3,3-triphenylpropyne in the presence of trimethylenediamine. Unusually high rate of alkyne isomerization under the action of a potassium salt of 1,3-diaminopropane, $KNH(CH_2)_3NH_2$,[10,11] was rationalized in terms of concerted proton transfer *via* cyclic transition state (TS). Recently,[16] we studied an analogous mechanism of prototropic rearrangement of the propyne molecule in the presence of hydroxide ion and showed that propyne can undergo isomerization into allene *via* the formation of intermediate complex of allenide ion with water molecule. The results of experimental studies[17] of the mechanism of acetylene—allene isomerization in the presence of $KNH(CH_2)_3NH_2$ indicated that the reaction involves (at least in part) the formation of particular anionic intermediates rather than proceeds by a concerted mechanism.

An important factor affecting the ease of acetylene—allene rearrangement under base catalysis is the mobility of the migrating H atom. In the case of the same base, the mobility should be determined by the ease of proton abstraction, *i.e.*, by the stability of carbanions formed. Currently, reliable estimates of proton abstraction energies are lack even for the simplest system containing three carbon atoms, C_3H_4. The experimental energy of proton abstraction from the allene molecule is 381.4±3.1 kcal mol^{-1},[18] while the energy of proton abstraction from the sp^3-hybridized C atom in the propyne molecule was estimated at 381.1±2.1 kcal mol^{-1}.[18] Taking into account that (i) both reactions result in the same anion and (ii) the propyne molecule is 0.9±0.5 kcal mol^{-1} more stable than the allene molecule,[19] one should admit that these experimental values are somewhat inconsistent with each other. Moreover, a theoretical study[20] of the propyne and allene anions showed that, contrary to common opinion, the latter is more stable in the gas phase.

The aim of this work was to perform an *ab initio* study of the substituent effect on the relative stability of isomerization products in the propargyl systems X—CH_2—C≡CH (X = H, Me, NMe_2, OMe, F, SMe) and on the proton abstraction energy in the formation of anions appearing in the course of prototropic rearrangements.

Calculation Procedure

In the case of propyne and but-1-yne the ratio of possible isomers has been well studied experimentally, and these data can be used for assessing the calculation procedure. The propyne molecule is 0.9±0.5 kcal mol^{-1} more stable than the allene molecule.[19] The but-1-yne molecule is 0.71 kcal mol^{-1} energetically less favorable than the corresponding allene isomer; isomerization of the latter into but-2-yne leads to further decrease in energy (by 4.8 kcal mol^{-1}).[21,22]

Previously,[23] we studied migration of the double bond in heteroallylic systems. The relative energies of isomers calculated in the RHF approximation with inclusion of correlation corrections at the second-order Møller—Plesset level of perturbation theory (MP2) with the 6-31+G* basis set were found to be in good agreement with the experiment. Moreover, these values are well reproduced in the one-electron approximation; the inclusion of correlation effects has strong effect only on the TS energies. The absolute values of the energies of proton abstraction from the sp^3-hybridized C atom in the allyl systems are somewhat overestimated; however, the corresponding relative energies in the series propane, propene, 3-methoxypropene, and 3-methylthiopropene are reproduced with an error of at most 1 kcal mol^{-1}.

Unfortunately, we found that this computational procedure is inapplicable to heteropropargyl systems.

Calculations in the RHF/6-31+G* approximation provided a qualitatively correct reproduction of the relative energies of isomers in the propyne and but-1-yne series (Table 1). According to calculations, the propyne molecule is more stable than allene molecule, which is in agreement with the experimental data.[19,24] The energy difference between these structures calculated in this approximation is 1.81 kcal mol^{-1}, which is somewhat larger than the experimental value.[19] The ratio of the calculated total energies of the but-1-yne and buta-1,2-diene molecules correctly points to preferableness of the allene structure; however, the energy difference between these molecules (−0.15 kcal mol^{-1}) is lower than the experimental value (−0.71 kcal mol^{-1}).[21]

The inclusion of correlation energy at the MP2 level of theory unexpectedly did us a disservice. According to calculations, isomerization of propyne into allene is accompanied by a 3.28 kcal mol^{-1} increase in the energy of the system, which is even more far from the experimental value. Even poorer agreement with the experimental data was found when estimating the relative stability of but-1-yne isomers.

Table 1. Experimental and calculated energies of propyne—allene rearrangement (ΔE_1), proton abstraction from allene molecule (ΔE_2), and isomerization of but-1-yne into buta-1,2-diene (ΔE_3) and but-2-yne (ΔE_4)

Method	ΔE_1	ΔE_2	ΔE_3	ΔE_4
	kcal mol^{-1}			
Calculations				
ZPE	−0.38	−9.00	−0.46	−0.38
RHF	1.81	397.87	−0.15	−5.81
RHF+ZPE	1.43	388.87	−0.61	−6.20
MP2	3.28	388.70	1.04	−4.37
MP2+ZPE	2.90	379.70	0.58	−4.75
MP4	0.91	390.70	−1.18	−4.43
MP4+ZPE	0.52	381.70	−1.63	−4.81
G1	0.79	381.23	−1.61	—
G2	0.77	381.50	−1.53	—
Experiment	0.9±0.5 [19]	381.4±3.1 [18]	−0.71 [21]	−4.80 [21]

The energy of proton abstraction from the allene molecule obtained in the RHF approximation is strongly overestimated. Calculations at the MP2 level of theory led to some decrease in energy, which is nevertheless 7.3 kcal mol^{-1} higher than the experimental value.

These drawbacks required a search for a more reliable computational cost efficient procedure.

We calculated the propyne and allene molecules and the allenide ion in the framework of combined G1 and G2 procedures and obtained good agreement between the calculated relative energies of both molecules and the deprotonation energy of allene and the experimental data (see Table 1). However, routine calculations using these procedures and, moreover, simulation of isomerization with partial optimization of geometry seem to be impossible. Detailed analysis showed that inclusion of correlation effects at the MP2 level of theory affects the total energies of the propyne and allene molecules in different manner and leads to overestimation of the relative energy of allene. This trend also holds for MP4 calculations; however, it is much less pronounced. It is also noteworthy that the magnitude of changes in the zero-point vibrational energy (ZPE) on going from propyne to allene is relatively small (no greater than 0.5 kcal mol^{-1}); however, this correction can be as high as ~10 kcal mol^{-1} when calculating the proton affinity energy of the allenide anion.

The inclusion of ZPE correction makes the estimates obtained in the RHF approximation somewhat better; however, the differences between the calculated and experimental data remain rather large. The proton affinity energy of the allenide ion obtained from MP2 calculations with inclusion of ZPE correction is in good agreement with the experimental value; on the other hand, the relative energy of the allene structure remains strongly overestimated. Calculations at the MP4 level of theory with inclusion of correlation effects correctly reproduce the relative energies of the propyne and allene molecules and the proton affinity energy of the anion if corrected for ZPE (see Table 1). Great importance of taking into account this value for correct reproduction of the proton affinity energies of acetylene and allene anions was pointed out earlier in studies of the relative stabilities of these structures.[20]

For butyne, MP4//6-31+G* calculations qualitatively correctly reproduce the relative energies of the molecules in the series but-2-yne < buta-1,2-diene < but-1-yne (see Table 1). The energy difference between but-1-yne and but-2-yne is in excellent agreement with the experiment. On the other hand, the relative stability of buta-1,2-diene is somewhat overestimated. In should be noted that overestimation of the stability of the allene structure is also typical of the G1 and G2 procedures.

In the text below, we discuss the results obtained with full optimization of the geometry and inclusion of ZPE correction in the RHF/6-31+G* approximation. The total energies were refined at the MP4 level of theory. To include the solvation effects, geometry optimization and calculations of ZPE corrections for the anions under study were carried out in the framework of the Kirkwood—Onsager model[25—27] and the total energies were obtained from MP4 calculations in the framework of the IEFPCM continuum model.[28,29] In both models, the solvent parameters corresponded to DMSO. Analysis of the electron density distribution was carried out in the framework of the "atom in molecule" (AIM) method.[30,31]

Calculations were performed using the GAMESS [32] and GAUSSIAN-98 program packages.[33]

Results and Discussion

Acetylene—allene rearrangement

$$X{-}CH_2{-}C{\equiv}CH \rightleftharpoons X{-}CH{-}C{=}CH_2 \rightleftharpoons X{-}C{\equiv}CH{-}Me$$

in the gas phase was studied taking the systems with substituents X = H, Me, NMe_2, OMe, and SMe as examples. Only the most stable conformers (Fig. 1) were considered.

For but-1-yne molecule, a staggered conformation with respect to the C(3)—C(4) bond is the most preferable. The optimum structures of 3-methoxypropyne and its thioanalog are characterized by C_s symmetry and the C(2)—C(3)—O(S)—C and C(3)—O(S)—C—H dihedral angles of 180°. This orientation corresponds to the weakest repulsion between the LEPs of the heteroatoms and the C—H σ-bonds.

We had to consider at least two conformations of the buta-1,2-diene molecule with different positions of the Me group, namely, the cisoid and transoid structures characterized by the C(2)—C(3)—C(4)—H dihedral angle of 0 and 180°, respectively. The energy difference between these structures is 1.38 kcal mol^{-1}; however, the transoid structure with higher energy corresponds to a TS rather than a minimum on the potential energy surface. Analogous picture is observed for propene molecule. The barrier is usually associated with mutual repulsion between the C—H bonds and π-electrons of the C=C bond.

Only the most stable[34] *s-cis*-conformers of 1-methoxypropa-1,2-diene and 1-methylthiopropa-1,2-diene molecules were considered.

The most stable conformer of but-2-yne molecule has a D_{3h} symmetry. Finally, the most stable conformations of 1-methoxypropyne and 1-methylthiopropyne molecules with C_s symmetry are characterized *trans*-position of one proton of the Me group substituent relative to the C(1) atom.

Among all compounds studied in this work, only for the propyne molecule passage from the structure with terminal triple bond to the allene structure is accompanied by an increase in the total energy (Table 2).

Substituted allene structures were found to be more energetically favorable than the structures with terminal triple bond. In the case of buta-1,2-diene such a stabilization can be explained by occurrence of additional σ—π-interaction. This effect is manifested in changes in the atomic charges in the fragment containing three carbon atoms. Indeed, a charge of 0.260 au is transferred from the Me group to the C≡CH fragment in the propyne

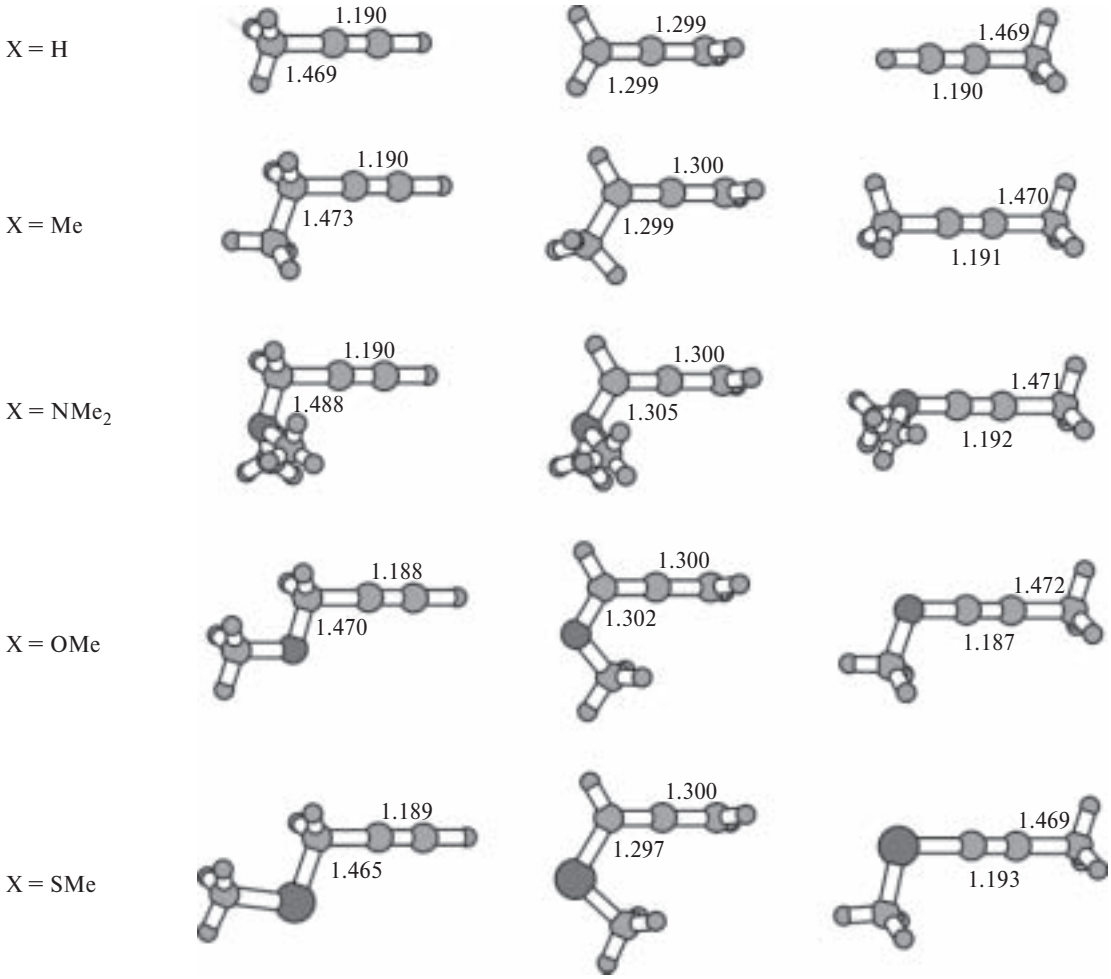

Fig. 1. Molecular structure of compounds $XCH_2—C≡CH$, $XCH=C=CH_2$, and $XC≡C—Me$. Shown are the carbon—carbon bond lengths (Å) in the fragment containing three carbon atoms.

molecule. In the but-1-yne molecule, the Et group has nearly the same effect (0.272 au) while the terminal Me group bears a charge of +0.050 au. On going from but-1-yne to buta-1,2-diene the charge on the Me group increases by 0.042 au. Finally, the but-2-yne molecule was found to be the most stable among all the isomers studied in this work due to the stabilizing effect of two Me groups transferring a charge of 0.238 au to the C≡C fragment each.

Table 2. Changes in energies (ΔE) on going from the propargyl structure $X—CH_2—C≡CH$ to allene and propynyl structures for the gas phase and with inclusion of solvent effects (figures in parentheses)

X	ΔE/kcal mol^{-1}	
	$X—CH=C=CH_2$	$X—C≡C—Me$
H	+0.52 (+1.33)	0 (0)
Me	−1.63 (−1.16)	−4.81 (−4.45)
NMe_2	−3.78 (−3.12)	−2.16 (−2.03)
OMe	−5.02 (−3.22)	+1.77 (+2.86)
SMe	−4.86 (−3.71)	−6.20 (−5.47)

Migration of the multiple bond in the fragment containing three carbon atoms toward the heteroatom is usually rationalized by additional conjugation of the LEP of the heteroatom with the π-system of the unsaturated fragment. The OMe and SMe groups are considered as π-electron donors. On going from 3-methylthiopropyne to 1-methylthiopropa-1,2-diene the charge on the substituent changes from 0.042 to 0.145 au. In contrast to this, passage from 3-methoxypropyne to 1-methoxypropa-1,2-diene is accompanied by an increase in the negative charge (from −0.638 to −0.651 au) on the methoxy group which acts as electron acceptor. However, based on the changes in the net charge on the substituent, we cannot estimate the extent and determine the direction of π-electron transfer and, consequently, assess stabilization of the system due to p—π-conjugation.

In the framework of the AIM method information on the π-interactions can be obtained by analyzing the ellipticity of electron density distribution in the region of chemical bonds. In the unsubstituted allene molecule, two C=C bonds are characterized by equal ellipticities (0.538), which corresponds to two π-systems lying in the mutually orthogonal planes. Introduction of a π-donor substituent causes an increase in the π-electron density on the neighboring double bond and, hence, an increase in the ellipticity of this bond. Conjugation with C—H bonds of the terminal methylene group leads to partial equalization of the orthogonal components of the π-electron density in the region of the C=C bond that is distant from the substituent and, correspondingly, to a decrease in the ellipticity.

Both these effects were observed for all allenes studied in this work. For compounds X—C(1)H=C(2)=C(3)H_2 the ellipticity of the C(1)=C(2) bond is 0.538, 0.553, 0.574, 0.626, and 0.561 for X = H, Me, NMe_2, OMe, and SMe, respectively. The ellipticity of the C(2)=C(3) bond in the same molecules is 0.538, 0.536, 0.500, 0.476, and 0.501, respectively. These values are consistent with an increase in the π-donor ability of substituents: Me < SMe < < NMe_2 < OMe. However, the energy decreases in another manner on going from the propargyl structure to allene (see Table 2): Me < NMe_2 < SMe < OMe. The methoxy group possesses the strongest π-donor properties, thus providing the greatest stabilization of the allene structure; however, high electronegativity of O atom is simultaneously a reason for predominant shift of the σ-electron density toward the substituent and for an increase in the net negative charge on the substituent.

By and large, the stabilizing effect of conjugation of the multiple bond with the LEP of the heteroatom leads to a greater relative decrease in the total energy compared to the effect of the interaction with the Me group. This is responsible for substantial preferableness of the allene structure compared to the propargyl structure in the case of heteroatomic substituents, the effect of the methoxy group being more pronounced than that of the NMe_2 and SMe groups.

Further migration of the multiple bond in buta-1,2-diene molecule to give a but-2-yne molecule is accompanied by a decrease in energy by 3.18 kcal mol^{-1}. The triple bond in this molecule is stabilized by the interaction with σ-bonds of two Me groups. A charge of 0.238 au is transferred from each methyl group to the acetylene fragment (Table 3).

One can assume that Me groups attached to the C≡C bond in the 1-methoxypropyne and 1-methylthiopropyne molecules influence in a similar stabilizing manner. These molecules are characterized by small changes in the charge on the terminal Me group upon variation of the substituent (see Table 3). However, these molecules significantly differ in stability relative to the corresponding allenes.

Table 3. Mulliken charges on atoms and groups (q) for different structures with substituents X = H, Me, NMe_2, OMe, and SMe

Atom or group	q/au				
	H	Me	NMe_2	OMe	SMe
Starting structures (H—C≡C—CH_2—X)					
H	0.167	0.166		0.174	0.176
C≡C	−0.426	−0.447		−0.385	−0.388
CH_2	0.234	0.222		0.838	0.159
X	0.026	0.050		−0.638	0.042
Allene structures (H_2C(3)=C(2)=C(1)HX))					
H(3)	0.055	0.048	0.037	0.044	0.052
C(3)	0.421	0.404	0.369	0.353	0.413
C(2)	−1.060	−1.053	−0.743	−0.684	−0.857
C(1)	0.421	0.425	0.705	0.824	0.105
H(1)	0.055	0.037	0.044	0.071	0.080
X	0.055	0.092	−0.465	−0.651	0.145
Final structures (Me—C≡C—X)					
Me	0.260	0.238	0.229	0.255	0.263
C≡C	−0.426	−0.476	+0.252	0.425	−0.821
X	0.167	0.238	−0.495	−0.679	0.558

Isomerization of 1-methylthiopropa-1,2-diene into 1-methylthiopropyne is energetically favorable and is accompanied by a decrease in the total energy by 1.46 kcal mol^{-1}, which is in agreement with experimental data.[9] Assuming that conjugation of the π-system with the LEP of the heteroatom leads to overall stabilization of the system, one could expect that the methoxy group (a π-donor) will favor stabilization of the neighboring multiple bond at least to the same extent that the thiomethyl group does. Nevertheless, the total energy of the 1-methoxypropyne molecule exceeds the energy of not only the 1-methoxypropa-1,2-diene molecule (by 6.78 kcal mol^{-1}), but even the starting 3-methoxypropyne molecule (by 1.77 kcal mol^{-1}). This ratio of the energies of different isomers allows one to explain high selectivity of prototropic isomerization of propargyl ethers into allenyl ethers;[3–9] however, electronic factors responsible for relative instability of 1-methoxypropyne require more detailed studies.

Analysis of the electron density distribution in the alkyne molecules by the AIM method is in most cases complicated by the presence of the so-called "non-nuclear attractors" in the region of the C≡C triple bond. The reasons for the appearance of non-nuclear attractors for diatomic homonuclear molecules were analyzed previously[35] and originate from specific features of the behavior of the valence AOs at internuclear distances shorter than a certain threshold value. In this connection we restricted our consideration of the total electron density on the C≡C fragments of the molecules under study (see Table 3). In the propyne and but-1-yne molecules, these populations are close and much higher than in the acety-

lene molecule (−0.351 au) due to the electron donor effect of neighboring alkyl groups. The C≡C fragments in the 3-methoxypropyne and 3-methylthiopropyne molecules are somewhat less populated. It is reasonable to assume that a stronger carbon—carbon bond corresponds to greater "saturation" of this fragment with electrons. Then, all things being equal, one should expect a more easy isomerization for 3-methoxypropyne and 3-methylthiopropyne.

Rearrangement of but-1-yne into but-2-yne is accompanied by an increase in the charge on the acetylene fragment by 0.029 au and by a decrease in energy by 4.81 kcal mol^{-1}. Even greater increase in the population of this fragment (by 0.433 au) and a greater decrease in energy (by 6.20 kcal mol^{-1}) occurs in the isomerization of 3-methylthiopropyne into 1-methylthiopropyne.

1-Methoxypropyne is thermodynamically unfavorable compared to 3-methoxypropyne. The total charge on the C≡C fragment of this molecule is positive (see Table 3). Consequently, the triple bond depleted of electrons becomes strongly destabilized. Similarly to 1-methoxypropa-1,2-diene (see above), the overall change in the charge in the 1-methoxypropyne molecule does not reflect the detailed picture of electron density redistribution caused by the interaction of the heteroatom with the neighboring π-system. Analysis of the Mulliken populations of the p_π-AOs of the C atoms involved in the triple bond (Table 4) shows that the π-bonds in the 1-methoxypropyne molecule are to the greatest extent "saturated" with electron density. However, the net Mulliken charge on the C≡C fragment is positive (the same result was obtained by the AIM method) due to displacement of the electrons of the σ-bond toward the electronegative O atom. It should be noted that the equilibrium length of this bond (1.187 Å) is somewhat smaller than in other molecules (see Fig. 1). This points to an increase in π-character of the triple bond due to weakening of the σ-component.

Analysis of the calculated Mulliken populations of the π-bonds (see Table 4) revealed transfer of the π-the electron density to the C_β atom, which increases in the order Me < SMe < OMe. Such a change in the π-electron density is consistent with the enhanced reactivity of the C_β atom in the acetylene derivatives toward electrophiles.

Table 4. Mulliken populations of π-bonds (Q_π); C(1) (Q_1) and C(2) (Q_2) atoms; and total populations of C≡C fragment ($Q_{C\equiv C}$) in different molecules

Molecule	Q_π	Q_1	Q_2	$Q_{C\equiv C}$
		au		
HC≡CH	4.000	0	0	−0.553
Me—C≡CH	4.010	0.048	−0.058	−0.371
Me—C≡C—Me	4.010	−0.005	−0.005	−0.152
Me—C≡C—OMe	4.129	−0.010	−0.119	+0.178
Me—C≡C—SMe	4.066	0.043	−0.109	−0.269

In contrast to the isomerization of propargyl ethers, prototropic isomerization of propargylamines under the action of superbases (KNH_2/Al_2O_3,[36] $KOBu^t$/DMSO [9]) leads to dialkylprop-1-inylamines. This is quite consistent with the above-mentioned regularities: the dimethylamino group (π-donor) favors displacement of the multiple bonds in the propargyl system toward the substituent and destabilizes the neighboring triple bond to a lesser extent due to lower electronegativity of nitrogen compared to oxygen. Indeed, the calculated energy of the allene structure, $Me_2N—CH=C=CH_2$, is 3.78 kcal mol^{-1} lower than the energy of the initial molecule, $Me_2N—CH_2—C\equiv CH$, and 1.62 kcal mol^{-1} lower than the energy of the final structure $Me_2N—C\equiv C—Me$. Similarly to O atom, the N atom depletes the neighboring triple bond population; however, this effect is much less pronounced: the charge on the C≡C fragment in the $Me_2N—C\equiv C—Me$ molecule is 0.252 au. Migration of the triple bond from terminal position toward the heteroatom is energetically favorable, namely, the energy difference between corresponding structures is 2.16 kcal mol^{-1}.

The results obtained show that the influence of heteroatomic substituents on the direction of migration of the multiple bonds in heteropropargyl systems is determined by both π-donor properties of the substituents and the effects associated with the electronegativity of heteroatoms. The electronegativity effects are less pronounced in the case of the double bond; however, they are distinctly manifested in violation of the order of the propargyl—allene isomerization energies in the series of substituents Me < NMe_2 < SMe < OMe due to the electron donor σ-effect of methylthio group and the σ-acceptor effect of dimethylamino group. For the triple bond, where the heteroatom is adjacent to the sp-hybridized C atom, the influence of inductive effect is more pronounced. In the case of methoxy group, the destabilizing inductive effect is stronger than the stabilizing effect of conjugation of the LEP with the ethynyl π-system. Even more dramatic example is provided by the $F—CH_2—C\equiv CH$ molecule with a strong electron acceptor substituent. Our calculations predict that isomerization of this molecule into corresponding allene structure is accompanied by an increase in energy by 0.09 kcal mol^{-1} and that the energy of propynyl structure is 12.79 kcal mol^{-1} higher than the that of the starting propargyl structure.

The solvation energies of all molecules calculated in the framework of the IEFPCM model with DMSO as solvent are low and vary between +1.48 kcal mol^{-1} for the allene molecule and −2.08 kcal mol^{-1} for the 3-methoxypropyne molecule, the allene structures being

Table 5. Calculated solvation energies in DMSO (ΔE_{solv}) for different structures with substituents X = H, Me, NMe_2, OMe, and SMe

Molecule	ΔE_{solv}/kcal mol^{-1}				
	H	Me	NMe_2	OMe	SMe
X—CH_2—C≡CH	0.58	0.05	−1.39	−2.08	−1.48
X—CH=C=CH_2	1.48	0.68	−0.74	−0.01	−0.17
X—C≡C—Me	0.58	0.28	−1.32	−0.86	−0.69

less stabilized by the solvent compared to corresponding acetylenes (Table 5). In the case of unsubstituted propyne, a possible reason for differences between the solvation energies of two isomers can be the zero dipole moment of allene molecule and, correspondingly, lesser extent of stabilization by the polar solvent. For all substituents, except for NMe_2, the largest calculated dipole moments and the highest solvation energies were obtained for 3-substituted propynes. However, this regularity is violated in the case of but-2-yne molecule with zero dipole moment, whose energy increases on going from the gas phase to solution to a lesser extent compared to the buta-1,2-diene molecule with nonzero dipole moment. The dipole moment of dimethylaminoprop-1-yne increases on going to the allene structure and varies only slightly upon further transformation into dimethylaminoprop-3-yne. Nevertheless, as for other substituents, the highest solvation energy corresponds to the structure with terminal triple bond while the lowest solvation energy corresponds to the allene structure. On the other hand, dimethylaminopropadiene is solvent stabilized to the greatest extent among the allene series.

The relative energies of isomers calculated with inclusion of solvation effects obey the same regularities as those observed for the gas phase (see Table 2). For all substituents studied in this work the energies of allene structures are lower than those of the compounds with terminal triple bond. As in the gas phase, further migration of the triple bond towards the substituent X is accompanied by a reduction of energy at X = Me, SMe, by an increase in energy on going from Me_2N—CH=C=CH_2 to Me_2N—C≡C—Me, and by substantial increase in energy upon the formation of MeO—C≡C—Me. The results obtained for the gas phase and with inclusion of solvation effects are close both qualitatively and quantitatively.

The ability of the propargyl system to undergo rearrangements depends on both the thermodynamic stability of isomers and the mobility of the corresponding protons. It is commonly accepted that the protons at sp-hybridized C atoms have the highest mobility in propargyl systems. However, high-level quantum-chemical calculations[20] and photoelectron spectroscopy data[37]

Table 6. Energies of proton abstraction (ΔE)[a] from the molecules of propyne and allene derivatives with substituents X = H, Me, OMe, and SMe

Molecule	ΔE^b/kcal mol^{-1}			
	H[c]	Me	OMe	SMe
XCH<u>H</u>–C≡CH	382.22 [381.1] (330.95)	382.71 (332.32)	377.28 (329.87)	365.70 (323.15)
X<u>C</u>H=C=CH_2	381.70 [381.4] (329.61)	383.30 (331.82)	381.57 (328.28)	369.66 (320.91)
XCH=C=CH<u>H</u>	381.70 (329.61)	384.35 (333.47)	382.30 (333.08)	370.56 (326.86)
X<u>C</u>≡C—CH_2<u>H</u>	382.22 (330.94)	386.47 (335.12)	374.78 (322.20)	370.99 (322.67)

[a] $\Delta E = E(HA) - E(A^-)$, where $E(HA)$ is the energy of the starting molecule and $E(A^-)$ is the energy of anion.
[b] Calculated for the gas phase and for solution in DMSO (figures in parentheses).
[c] Experimental values[18] are given in brackets.

indicated that in the gas phase the CH_2=C=CH$^-$ anion is 1.3 kcal mol^{-1} more stable than isomeric Me—C≡C$^-$ anion. Our calculations showed that the Me—C≡C$^-$ anion is more stable in the gas phase (by 3.34 kcal mol^{-1}) and that the inclusion of solvation effects makes this anion even more energetically favorable (by 18.43 kcal mol^{-1}), which is in agreement with the chemical properties of acetylene in solutions. Since the acetylene proton is not involved in the acetylene—allene rearrangement, no consideration was given to its abstraction.

For propargyl systems, the energy of proton abstraction from sp^3-hybridized C atom in the gas phase (Table 6) decreases in the order Me > H > OMe > SMe. In the propyne molecule, methyl protons have much higher mobility than in the propene molecule for which the deprotonation energy is 390.7±2.1 kcal mol^{-1}.[38] Moreover, even for the but-1-yne molecule the calculated proton abstraction energy is lower than for water molecule (383.6 kcal mol^{-1} according to our calculations); introduction of OMe and especially SMe groups leads to further decrease in this energy.

On going from the propargyl systems X—CH_2—C≡CH to [XCHCCH]$^-$ anions the carbon—carbon bond lengths are equalized (Table 7). This is least pronounced in the system with X = SMe and most pronounced for X = OMe. The C(2)—C(1)—H bond angle is maximum in the [MeSCHCCH]$^-$ anion (124.3°) and minimum in the [MeOCHCCH]$^-$ anion (115.0°). In other words, the geometry of the [MeSCHCCH]$^-$ anion is the closest to that of the starting 3-methylthiopropyne molecule while the [MeOCHCCH]$^-$ anion is geometrically closest to the allene structure. In both anions, the Me group in the substituent is arranged in such a way that the C(2)—C(3)—O(S)—C(Me) dihedral angle is close to 90°,

Table 7. Changes in bond lengths (ΔR) and charges on atoms and atomic groups (Δq) on going from X—C(3)H_2—C(2)≡C(1)H molecules to $[XCHCCH]^-$ anions

Substituent X	ΔR/Å				Δq/au		
	C(2)—C(1)	C(3)—C(2)	C(3)—X	X—Me	X	O, S	Me
H	0.086	−0.124	—	—	−0.101	—	—
Me	0.093	−0.135	−0.019	—	−0.193	—	—
OMe	0.099	−0.143	0.017	−0.008	−0.084	−0.025	−0.058
SMe	0.073	−0.113	−0.058	0.011	−0.234	−0.088	−0.146

which can be explained by minimum repulsion between the LEP of heteroatoms and electrons of the π-bond of the hydrocarbon fragment similarly to the case of methoxypropene and methylthiopropene anions studied earlier.[23]

The formation of anions leads to concentration of the excess negative charge mainly on the atoms of the hydrocarbon fragment. The largest negative charge is transferred to the methylthio group, whereas the negative charge of the methoxy group increases only slightly (see Table 7). Recently,[23,39] we studied analogous distinctions between the structure and stability of anions containing OMe and SMe groups in allyl systems. Both the allyl and propargyl systems are characterized by rather high degree of transfer of the electron density to the Me group bonded to the S atom. The C(3)—S bond is appreciably shortened while the S—Me bond is lengthened. Thus, stabilization of anion in the presence of sulfur-containing substituent can be described in terms of resonance structures.

Considerable difference in the electronegativity of O and C atoms makes this stabilization in the system with methoxy group impossible.

When analyzing the changes in the deprotonation energies of allene compounds, one can see that the presence of methylthio group as before favors abstraction of a proton from both the C atom adjacent to the substituent and the distant (with respect to the substituent) C atom (see Table 6). On the other hand, the presence of methoxy group does not favor a decrease in the proton abstraction energy compared to the unsubstituted allene. It should also be noted that the lowest proton abstraction energy always corresponds to rearrangement of the propargyl system into allene structure; the only exception is the 3-methoxypropyne molecule which readily forms an anion that rearranges into 1-methoxypropa-1,2-diene. Because of this, further rearrangement of allene systems into propynyl systems under the action of bases can occur more slowly. Given several alternative channels of allene transformations (*e.g.*, dimerization), completion of the reaction requires large amounts of strong bases as in the case of, *e.g.*, isomerization of propargylamines into dialkylprop-1-ynylamines under the action of superbases.[36]

By and large, the above-mentioned regularities hold for calculations with inclusion of solvation effects. Similarly to gas-phase calculations, the energies of proton abstraction from sp^3-hybridized C atom decrease in order Me > H > OMe > SMe (see Table 6); however, the influence of substituents becomes less pronounced. The most important distinction from the results obtained for the gas phase is that the proton abstraction energies of propargyl—allene and allene—propynyl rearrangements are equalized after inclusion of solvation effects.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 98-03-33152a).

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Received February 27, 2001;
in revised form November 28, 2001