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Investigation of Addition Mechanism of Diazoles to Vinylorganosilanes by Methods of Quantum Chemistry

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Abstract—The behavior of pyrazole and imidazole in the reactions with vinyltrimethoxysilane and vinylsilatrane in the presence of the catalytic amount of lithium was studied by the B3LYP/6-311G(d,p) method. It is established that these processes are accompanied by the formation of lithium salts of diazoles. These substances exist in the planar and pyramidal forms in which lithium atom is bound with all atoms of the aromatic ring. Thermodynamic parameters of the process are considered, and the transition states and potential barriers are found in the approximation of isolated molecules.

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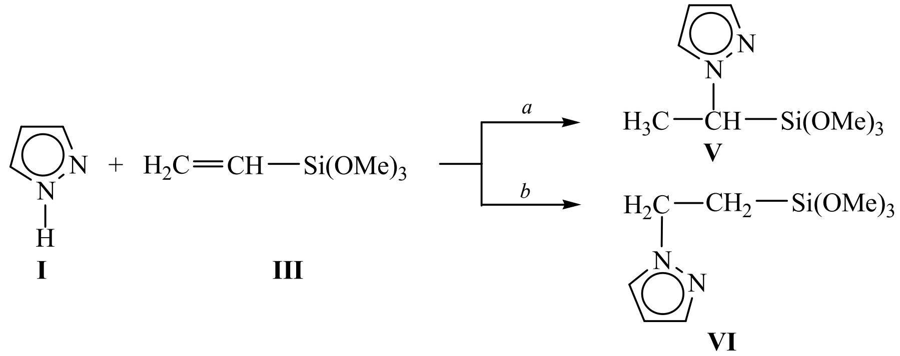
Mechanisms of diazoles (pyrazole **I** and imidazole **II**) addition to vinyl- and ethynylsilanes [1, 2] were not specially studied up till now.

We have carried out quantum-chemical studies of this reaction by the B3LYP/6-311G(d,p) approximation [3] by an example of model pairs of reagents like pyrazole **I**/vinyltrimethoxysilane **III** and pyrazole **I**/vinylsilatrane **IV** and for comparison including imidazole **II** which permitted explaining some experimental results.

Formally, the reaction may take two pathways with the formation of α-adduct **V** or β-adduct **VI**.

Scheme 1.



In the case of pyrazole **I** enthalpies of the reactions *a* and *b* are –72.9 and –72.0 kJ mol^{-1}, and Gibbs energies, –18.0 and –16.7 kJ mol^{-1} respectively. Both directions are thermodynamically permitted with almost the same probability. The Gibbs energy of product **V** is only by 1.3 kJ mol^{-1} lower than that of product **VI**. In the case of imidazole **II** enthalpies of the reactions of the types (a) and (b) are –62.4 and –66.2 kJ mol^{-1} and Gibbs energies, –7.5 and –12.6 kJ mol^{-1} respectively. Hence, the reaction with

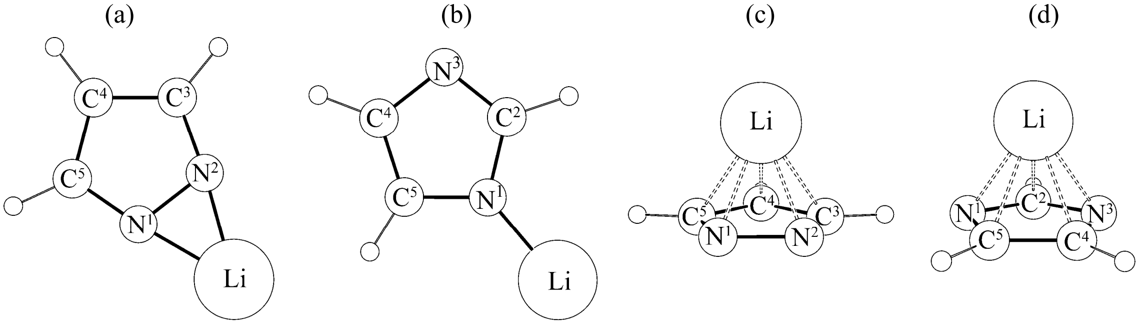


Fig. 1. Molecular structures of monomer forms of lithium salts of (a, c) pyrazole and (b, d) imidazole. B3LYP/6-311G(d,p).

pyrazole is more thermodynamically favorable than with imidazole.

In practice, the addition of diazoles to $VinSiR_3$ is carried out in the presence of a catalytic amount of lithium [1]. It probably leads to the formation of lithium salts of pyrazole and imidazole (Fig. 1). According to our calculations the molecules of diazoles and their lithium salts form stable associates which in the course of the addition reaction decompose probably to give individual molecules.

The calculations show that lithium salts of diazoles can exist in the planar (Figs. 1a, 1b) and the pyramidal (Figs. 1c, 1d) form. In the latter case the lithium atom is bound to all the atoms of the aromatic ring.

In the case of pyrazole the planar form of its lithium salt is by 49.0 kJ mol^{-1} more favorable in energy than the pyramidal one. In the case of imidazolyllithium the energy of pyramidal form is by 36.4 kJ mol^{-1} lower as compared to the planar form.

It is seen from the table that lithium diazolides possess electronic parameters significantly differing from the starting pyrazole and imidazole. The substitution with lithium of the hydrogen atom in the NH group of the pyrazole molecule leads to an increase in

Values of HOMO and LUMO and atomic charges in the molecules of pyrazole, imidazole, and their lithium salts

Parameter	Pyrazole	Pyrazole lithium salt (planar form)	Parameter	Imidazole	Imidazole lithium salt (pyramidal form)
E(HOMO), eV	–6.87	–5.90	*E*(HOMO), eV	–6.38	–6.65
E(LUMO), eV	+0.35	–1.11	*E*(LUMO), eV	+0.59	–1.26
Atomic charges according to Mulliken					
N^1	–0.2338	–0.3045	N^1	–0.2982	–0.2916
N^2	–0.2054	–0.3045	N^3	–0.3279	–0.2916
C^3	+0.0730	+0.0879	C^2	+0.1519	+0.0387
C^4	–0.3060	–0.3105	C^4	+0.0004	–0.0675
C^5	+0.1282	+0.0879	C^5	–0.0728	–0.0675
Li	–	+0.4921	Li	–	+0.3613
Atomic charges according to Bader [4, 5]					
N^1	–0.7440	–0.8944	N^1	–1.1636	–1.1211
N^2	–0.6340	–0.8944	N^3	–1.0580	–1.1211
C^3	+0.4834	+0.4411	C^2	+0.9457	+0.7412
C^4	–0.0353	–0.0655	C^4	+0.3994	+0.2440
C^5	+0.3782	+0.4411	C^5	+0.3234	+0.2440
Li	–	+0.9091	Li	–	+0.8868

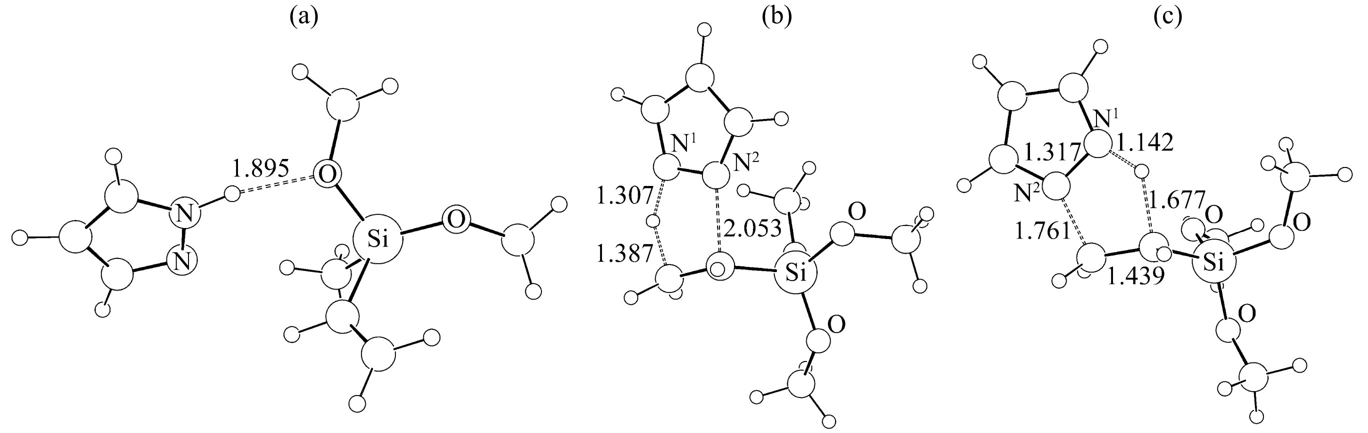


Fig. 2. (a) Molecular structure of prereaction complex of the reaction of pyrazole with vinyltrimethoxysilane and planar five-member transition states of this reaction: (b) reaction in α-position, (c) reaction in β-position, B3LYP/6-311G(d,p).

the nucleophilic properties of the molecule. It follows from the significant increase in the HOMO energy and the negative charge on the nitrogen atoms. It specially relates to the nitrogen atom directly bound with lithium.

Considering only the most favorable pyramidal form of the imidazole lithium salt we found that the transition of this substance to a lithium salt did not lead to an increase in the nucleophilic properties of the molecule. The HOMO energy even decreases to some extent as compared to the starting imidazole molecule, and the charges on nitrogen atoms vary insignificantly. It may be one of the factors governing the decreased activity of imidazole in the addition to vinyltrimethoxysilane as compared to pyrazole.

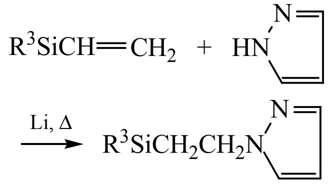
Nevertheless, the analysis of only electronic parameters of the ground state of starting molecules does not reflect probable reaction pathways and the conditions of their proceeding, as well as the probability of the reaction to follow some definite pathway if several of them exist. Therefore the search for transition states of the chemical reactions under study and their analysis was carried out.

It was found that for the directions *a* and *b* of these reactions the key factor determining the choice of a pathway is the value of the potential barrier of the reaction. For the calculation of these barriers thermodynamic parameters of prereaction complex (Fig. 2a) playing the role of reagent transforming in one of the probable transition states (Figs. 2b, 2c) were used.

Each of the transition states has one imaginary frequency, 1351i and 793i cm^{-1} for the addition to α- and β-position respectively.

The calculated activation enthalpies, $\Delta H^{\neq}$ of the reaction of N-alkylation of pyrazole with vinyltrimethoxysilane are 154.9 and 136.9 kJ mol^{-1} for the reactions in α- and β-positions respetively. If the planar form of lithium pyrazolide is used $\Delta H^{\neq}$ of the reaction of addition of pyrazole in the β-position of the vinyl group of Vin-Si(OCH$_3$)$_3$ is significantly lower and reaches only 80.8 kJ mol^{-1}.

The calculated data suggest the preferred addition of pyrazole to the vinyl groups of vinylsilanes contrary to the Markovnikov rule with the formation of *N*-[β-(silatranyl)ethyl]pyrazole. The calculated results were confirmed by practice.



R^3 = MeO, N(CH$_2$CH$_2$O)$_3$.

Therefore the search for the transition state of the lithium pyrazolide addition was carried out only for β-position of CH$_2$=CHSi(OMe)$_3$. The prereaction complex of this reaction includes the planar form of lithium pyrazolide because the pyramidal form in the course of complete optimization of molecular geometry undergoes spontaneous rearrangement to the planar one.

In the reaction of pyrazole with vinyltrimethoxysilane in the presence of catalytic amount of lithium during the formation of the structure of the prereaction

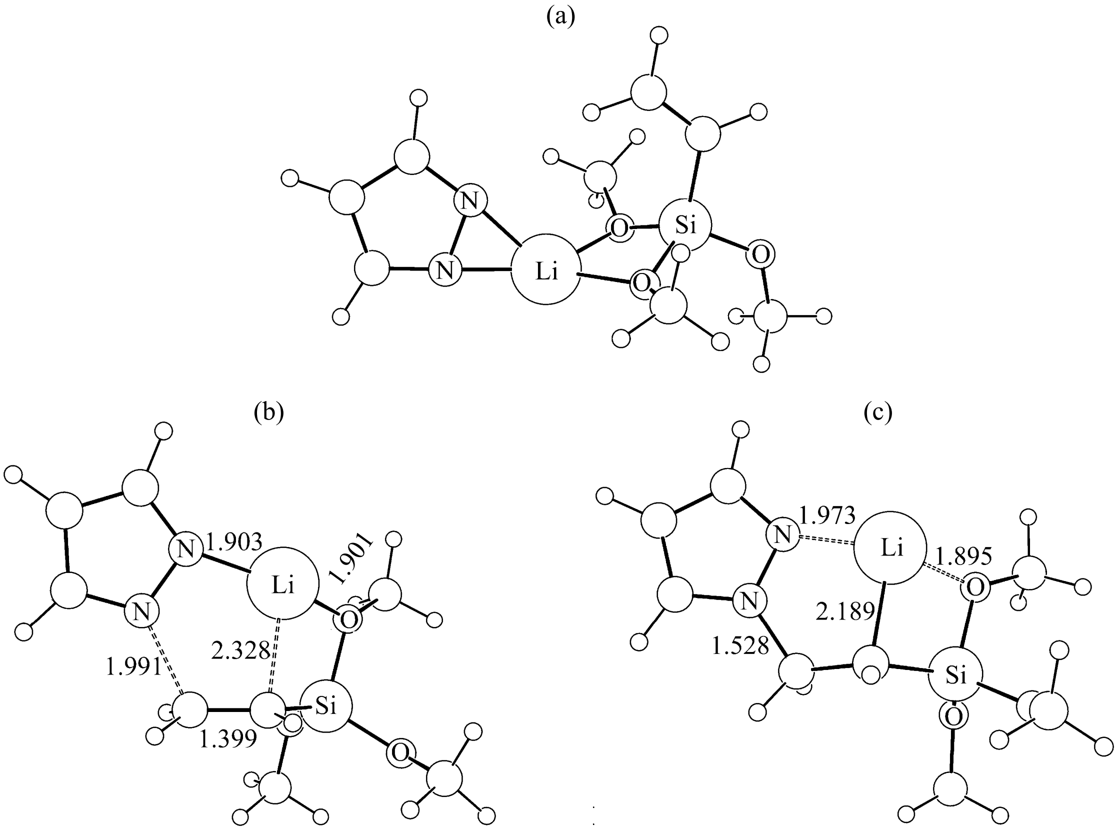


Fig. 3. Molecular structure of prereaction complex of the addition of lithium pyrazolide to the vinyl group of (a) Vin-Si(OMe)$_3$, (b) transition state of this reaction , and (c) the adduct, B3LYP/6-311G(d,p).

com-plex the coordination of nitrogen atoms with lithium is taken into account. Another factor facilitating the reaction progress is the additional solvation of the metal atom with oxygen atoms of methoxy groups if they are present in the starting vinylsilane. That is why for the calculation of potential barrier of this reaction the prereaction complex with the planar form of lithium pyrazolide presented in the Fig. 3a was chosen as a reagent.

Considering this circumstance the β-addition of lithium pyrazolide to the double bond of vinyltrimethoxysilane may include the molecular structure of the transition state presented in Fig. 3b

This structure of the transition state similarly to the prereaction complex takes into account the participation of coordination bonds between lithium and oxygen atoms.

In general, the decrease in the transition state energy and hence in the potential barrier of the reaction is observed. It is consistent with the experimental fact that the addition of the catalytic amount of lithium accelerates the addition of pyrazole. The calculation of the reaction coordinate for this transition state (IRC calculations) confirmed that it leads to the products and reagents of the addition reaction.

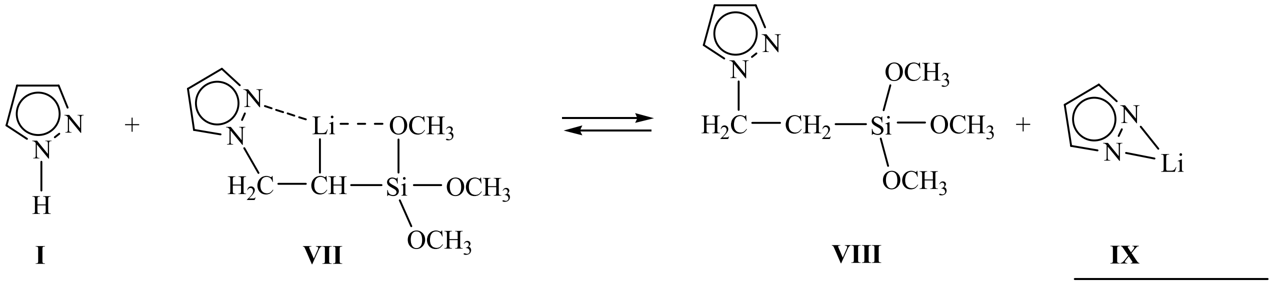
In Fig. 3c the optimal molecular structure of the product of β-addition of N-Li-pyrazole to vinyltrimethoxysilane is presented.

The structure shown in Fig. 3c is not the final reaction product. As lithium is added in catalytic amounts, lithium pyrazolide must be regenerated in the course of the process. For the evaluation of energy possibility of such transfer let us consider the equilibrium of Li/H exchange according to Scheme 2.

The enthalpy change in the course of this reaction ΔH = [H(**VIII**) + H(**IX**)] – [H(**I**) + H(**VII**)] = -32.7 kJ mol^{-1}, and the change in Gibbs energy ΔG = -35.2 kJ mol^{-1}.

Hence, the equilibrium of this reaction is shifted towards products **IX** and **VIII**. Consequently the

Scheme 2.



lithium atom splits from product **VII** and transfers to compound **IX** with pyrazole which again enters the reaction with the second molecule of vinyltrimethoxysilane. Hence, for supporting this reaction just the catalytic amount of lithium is necessary.

From the spatial arrangement of the transition state of the pyrazole molecule (Figs. 2b, 2c) it follows that the analogous explanation of imidazole addition is impossible. Five-membered reaction site in the transition state is a planar cyclic structure. One of the carbon atoms of the vinyl group adds the nitrogen atom N^2, while N^1 nitrogen atom lends the proton to another carbon atom. In the pyrazole molecule these atoms occupy neighboring positions, and the formation of the above-described ring is easy. In the imidazole molecule the nitrogen atoms are separated by a carbon. That is why N^1 nitrogen atom together with its proton is remote from the carbon atom which should accept this proton, and the addition does not take place.

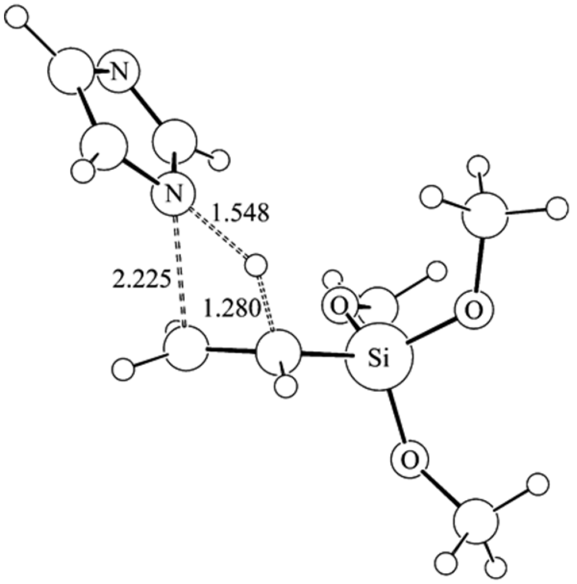


Fig. 4. Molecular structure of transition state of β-addition of imidazole to the molecule of vinyltrimethoxysilane (1815i cm^{-1}), B3LYP/6-311G(d,p).

Nevertheless, the addition of imidazole can proceed through the other type of the transition state (Fig. 4).

The potential barrier of the reaction $\Delta H^{\neq}$ for this transition state (the prereaction complex of imidazole with vinyltrimethoxysilane analogous to that presented in Fig. 2a is taken as a reagent) is +270.0 kJ mol^{-1} which is two times higher than the barrier of addition of pyrazole through the five-membered transition state. So the high value of the potential barrier is possibly due to the fact that in the transition state (Fig. 4) the loss of aromaticity occurs in the imidazole fragment. Besides, from the general considerations the four-membered transition state should be more strained than the five-membered one.

Similar to the case of pyrazole, the addition of lithium to the starting system leads to formation of prereaction complexes where the lithium atom is bound simultaneously with the atoms of diazole fragment and the oxygen atoms of the methoxy group of the vinyltrimethoxysilane molecule (Fig. 5). In this case two forms of prereaction complex with the planar form of lithium imidazolide (Fig. 5a) and the pyramidal one (Fig. 5c) may exist.

The prereaction complex with the pyramidal form of lithium imidazolide proves to be more favorable by energy. The total energy of this complex is by 10.5 kJ mol^{-1} less than the energy of the complex with the planar form. Therefore just the pyramidal complex was taken as the starting reagent for the calculation of the potential barrier in the lithium imidazolide addition to vinyltrimethoxysilane.

In the transition state of the reaction the lithium atom is bound not only to the nitrogen atom, but as well as in the prereactional complex, to all the atoms of the imidazole ring (Fig. 5c). In this case the potential barrier of the reaction $\Delta H^{\neq}$ = +99.6 kJ mol^{-1} which is higher than the barrier of addition of lithium

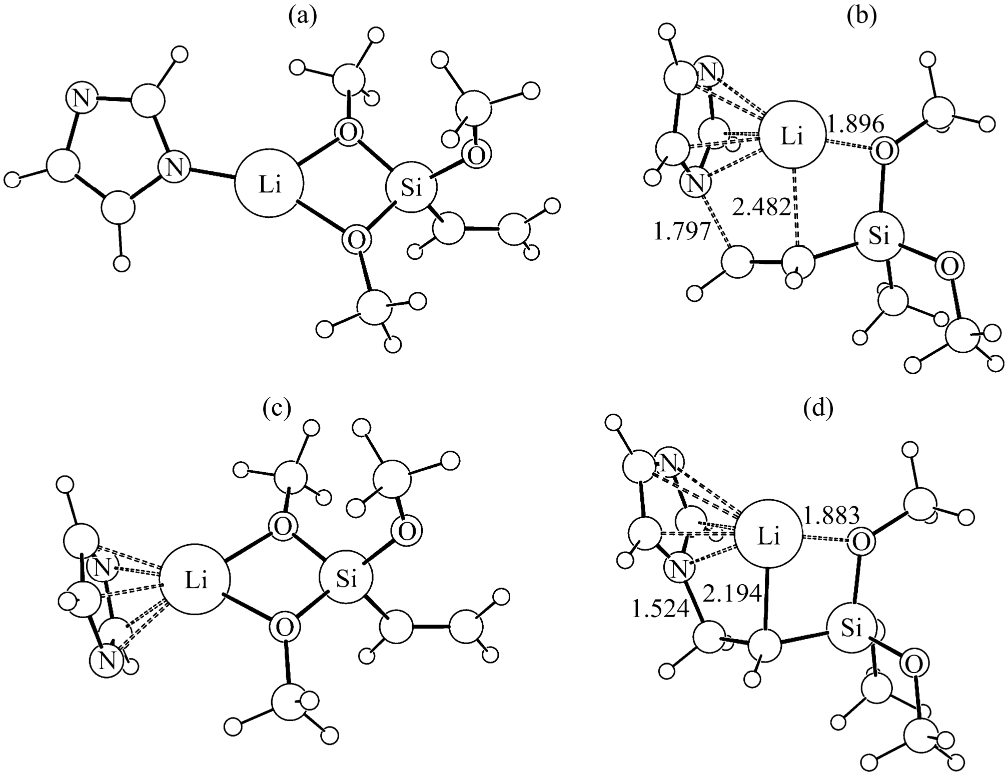


Fig. 5. Molecular structure of prereaction complexes in the reaction of β-addition of lithium imidazolide to vinyltrimethoxysilane: (a) planar form, (c) pyramidal form, (b) of the transition state of this reaction, and (d) of the adduct; B3LYP/5-311G(d,p).

pyrazolide to the same β-position of vinyl group of vinyltromethoxysilane. Hence, the addition of imidazole in the presence of lithium should proceed slower or at higher temperature.

Similarly to the case with pyrazole the adduct formed (Fig. 5d) is not the final reaction product.

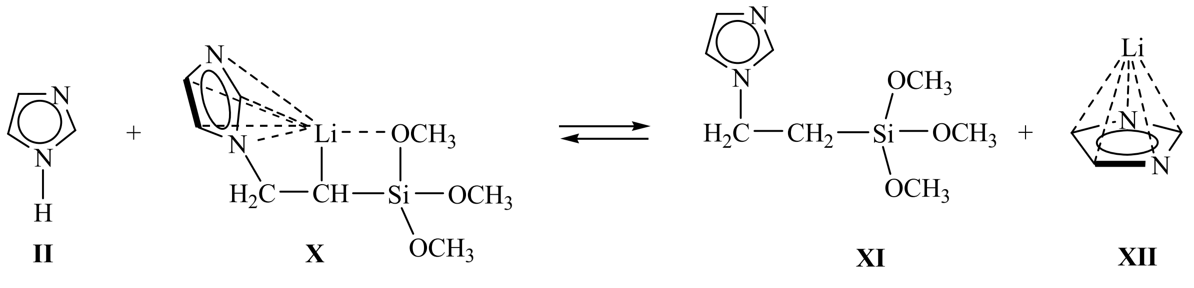
Let us consider the equilibrium (Scheme 3).

The enthalpy change in the course of this reaction: $\Delta H = [H(\mathbf{XI}) + H(\mathbf{XII})] - [H(\mathbf{II}) + H(\mathbf{X})] = -52.3$ kJ mol^{-1}. The change in Gibbs energy $\Delta G = -56.9$ kJ mol^{-1}.

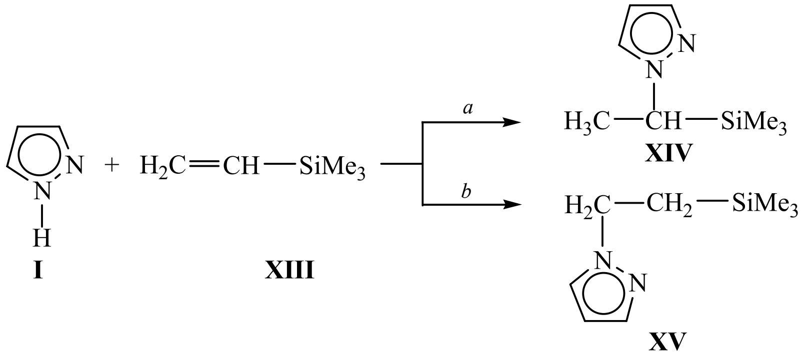
The negative value of Gibbs energy indicates that for the shift of equilibrium to the side of the products in the reaction with imidazole similarly to that with pyrazole only the catalytic amount of lithium is required.

Analogous studies were carried out for the process of addition of pyrazole and its lithium salt to vinylsilatrane Vin–Si(OCH_2CH_2)$_3$N. It was found that for this reaction the potential barriers are significantly lower as compared to that with vinyltrimethoxysilane. For example, $\Delta H^{\neq}$ of addition of pyrazole and its lithium salt to the β-position of the vinyl group of vinylsilatrane is +146.5 and +68.2 kJ mol^{-1} respectively.

Scheme 3.



Scheme 4.



Note the significant change in the interatomic distance Si←:N of the silatrane fragment at the transition from prereaction complex to the transition state. For example, in the addition of pyrazole to Vin–Si$(OCH_2CH_2)_3N$ the Si←N interatomic distance in the silatrane fragment of prereaction complex is 2.565 Å while in the transition state of the reaction it is 2.839 Å. The same picture is observed in the course of the addition of lithium pyrazolide to vinylsilatrane: The interatomic distance Si←:N of the silatrane fragment in the prereaction complex is 2.623 Å while in the transition state it is 2.816 Å for the chosen approximation.

Hence, the nitrogen atom of the silatrane fragment in the transition states under consideration exists almost in the planar configuration.

In contrast to the above-described oxygen-containing silicon compounds alkenylsilanes do not react with diazoles. For example, it was established that vinyltrimethylsilane did not react with pyrazole [1]. The enthalpy and Gibbs energy of the pyrazole addition to the vinyl group of vinyltrimethylsilane (Scheme 4) favor the proceeding of this reaction to the side of the products. That means that thermodynamic factor is not the reason of different reactivity of vinyltrimethoxysilane and vinyltrimethylsilane.

The reaction enthalpy $\Delta H_\alpha = -67.8$ kJ mol^{-1}, $\Delta H_\beta = -69.5$ kJ mol^{-1}; Gibbs energy of the reaction is $\Delta G_\alpha = -16.7$ kJ mol^{-1}, $\Delta G_\beta = -16.7$ kJ mol^{-1}. Let us analyze the values of potential barriers for the addition of pyrazole and its lithium salt to the β-position of vinyl group of the vinyltrimethylsilane molecule.

The vinyltrimethylsilane does not form associates with strong hydrogen bond with the pyrazole molecule. That is why for the calculation of potential barrier of the reaction the reagent energy may be accepted to be the sum of energies of the isolated molecules of pyrazole and vinyltrimethylsilane. The transition state of the reaction of pyrazole molecule addition to the β-position of vinyl group of the vinyltrimethylsilane is completely analogous to the transition state presented in Fig. 2b and the activation enthalpy of this reaction is +118.1 kJ mol^{-1}.

In contrast to pyrazole its lithium salt forms the associate with the vinyltrimethylsilane molecule. Just this associate was taken as a reagent (prereaction complex) for the calculation of the potential barrier of the reaction of β-addition of lithium pyrazolide to vinyltrimethylsilane.

In the transition state of the reaction with vinyltrimethylsilane (imaginary frequency value is 247i cm^{-1}) the coordination of the lithium atom with oxygen observed for the case of vinyltrimethoxysilane is absent. Therefore no decrease in energy of the transition state is observed, and the activation enthalpy of the addition of lithium pyrazolide in this case is +91.3 kJ mol^{-1}.

Hence, the potential barriers of the addition of lithium diazolides to vinyltrimethoxysilane and vinyltrimethylsilane are as follows: +80.8 kJ mol^{-1} for the addition of pyrazole salt to the β-position of vinyltrimethoxysilane, +99.6 kJ mol^{-1} for the addition of imidazole salt to the β-position of vinyltrimethoxysilane, +91.3 kJ mol^{-1} for the addition of pyrazole salt to the β-position of vinyltrimethylsilane.

That means that evidently just the kinetic factor of the reaction determines the decreased activity of imidazole in such addition reactions and impedes the addition of pyrazole to vinyltrimethylsilane.

Low absolute values of the potential barriers are most probably caused by the limitations and incomepleteness of the chosen model of the reactions under consideration. Despite these faults the presented models adequately reflect the changes in the reaction barriers at the transition from pyrazole to imidazole and from vinyltrialkoxysilane to vinyltrialkylsilane. Besides, just the kinetic factor directs the addition of heteroaromatic ring to the β-position of the double bond.

Hence, the calculations performed agree well with the experimental data [1] which have shown that pyrazole is more reactive than imidazole in the addition to vinylsilanes.

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