Unimolecular Rearrangement Reactions in Silylpyrazolones—A Theoretical Approach

Stefan Schmatz[†]

Institut für Physikalische Chemie der Universität Göttingen, Tammannstrasse 6, D-37077 Göttingen, Germany

Received September 13, 2001

Due to the easy migration of silyl groups, the chemistry of silylpyrazolones exhibits various unimolecular reaction channels not encountered in conventional pyrazolone chemistry. The unimolecular rearrangement process starting from the CH form of *N*-(trimethylsilyl)-pyrazolone (which is primarily formed in the intramolecular condensation reaction of silylhydrazones) is investigated by density functional (B3LYP) and ab initio (MP2) calculations. The transition states are discussed in detail. First, the organosilyl group migrates from the nitrogen atom to the oxygen atom (1,3-Si shift). The second and third steps consist of two consecutive 1,2-H shifts from the carbon to the nitrogen atom. The barriers for the hydrogen migrations determine the overall classical barrier. In comparison to the reactant CH form, the most stable isomer *O*-silylpyrazolone is lower in energy by 5 kcal mol^{-1}. This finding is in agreement with the experimental result. The calculated structure of this isomer is compared with X-ray diffraction data. The OH and NH forms of *N*-(trimethylsilyl)-pyrazolone are slightly higher in energy than the CH form.

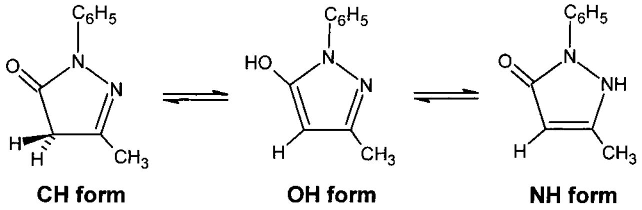
1. Introduction

5-Pyrazolones are very important in pharmaceutics (e.g., phenazones) and serve as precursors for dyes, pigments, and pesticides. They can be prepared by condensation of organohydrazines and acetoacetic ethyl esters to form hydrazones which undergo intramolecular condensation when heated above 100 °C.[1]

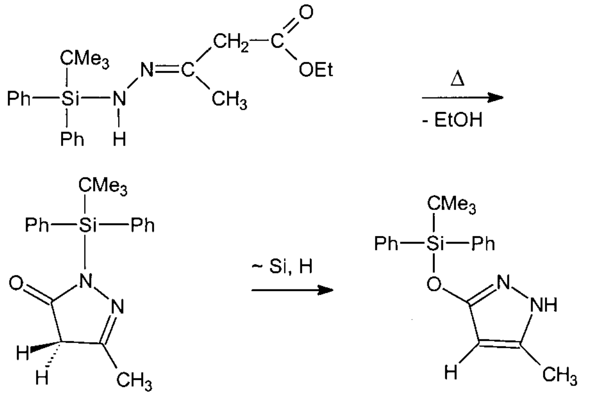
The pyrrole-type hydrogen atom in pyrazolones is particularly mobile. 1-Substituted 5-pyrazolones can exist in three possible tautomeric forms (Scheme 1).[1,2] For example, in the case of 3-methyl-1-phenyl-5-pyrazolone, the CH form is stable in nonpolar solvents, whereas in aqueous solution the NH (90%) and OH (10%) forms coexist in equilibrium.[1]

Silylhydrazones are prepared by condensation of tris(organyl)silylhydrazines and acetoacetic ethyl esters. Cis/trans mixtures of silylhydrazones are obtained, where the trans configuration is preferred for sterical reasons. When heated above 240 °C, ethanol and *N*-silylpyrazolones are formed by intramolecular condensation. After 1,3-N,O-silyl group migration an *O*-silylpyrazolone is obtained (Scheme 2)[3,4] The solid *O*-(organosilyl)pyrazolones are stable toward oxygen and water. The CH form (Scheme 1) could not be isolated. The OH and NH forms (Scheme 1) were not detectable either.

Scheme 1



Scheme 2



It is well-known that silyl groups in neutral and anionic molecules can undergo easy migrations.[5−8] This has been applied to the synthesis of isomeric compounds as well as to stabilizing elements in lower coordination.[9,10] It is a unique feature in silylpyrazolone chemistry that additional isomers exist which are unknown

---

[†] E-mail: sschmat@gwdg.de.

(1) Jackson, A. H. In *Comprehensive Organic Chemistry: The Synthesis and Reactions of Organic Compounds*; Pergamon Press: Oxford, U.K., 1979; Vol. 4 (Heterocyclic Compounds).

(2) Minkin, V. I.; Olekhnovic, L. P.; Zhdanov, Yu. A. *Molecular Design of Tautomeric Compounds*; Reidel: Dordrecht, The Netherlands, 1988.

(3) Witte-Abel, H.; Drost, C.; Klingebiel, U.; Noltemeyer, M. *J. Organomet. Chem.* **1999**, *585*, 341.

(4) Gellermann, E.; Klingebiel, U.; Schäfer, M. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1131.

(5) Bailey, R. E.; West, R. *J. Am. Chem. Soc.* **1964**, *86*, 5369.

(6) Boudjouk, P.; West, R. *Intra-Sci. Chem. Rep.* **1973**, *7*, 65.

(7) West, R.; Boudjouk, P. *J. Am. Chem. Soc.* **1973**, *95*, 3987.

(8) Reetz, M. T. *Adv. Organomet. Chem.* **1977**, *16*, 33.

(9) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71.

(10) Becker, G. *Z. Anorg. Allg. Chem.* **1976**, *423*, 242.

10.1021/om010826p CCC: $22.00
Publication on Web 01/31/2002

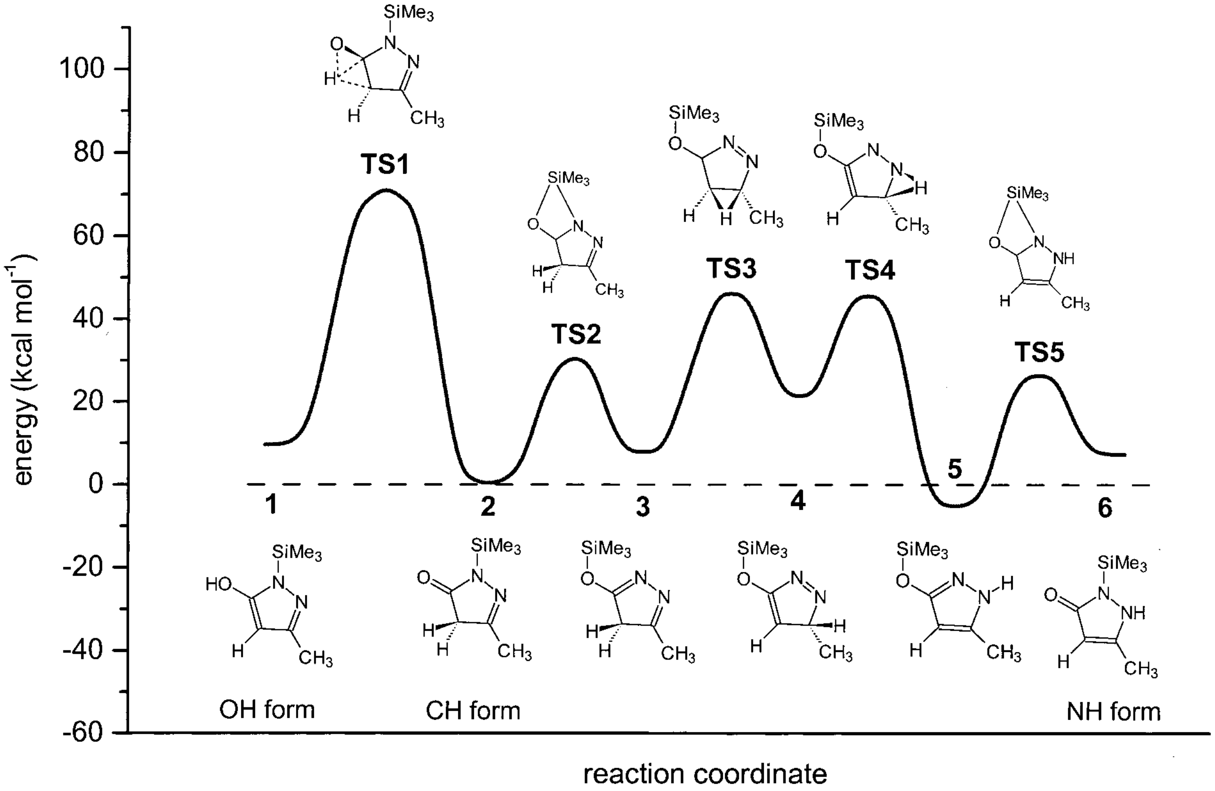


Figure 1. Potential energy diagram (schematic) for the isomers of the *O*-(trimethylsilyl)-3-methyl-5-pyrazolone system. The abscissa does not correspond to any well-defined reaction coordinate. Energetic differences are taken from B3LYP/6-31G(d)-calculations (see the text). The Lewis formulas of the six isomers and five transition states are also shown in this figure. The CH form **2** is the primarily formed product (see Scheme 2). The experimentally isolated species **5** is the most stable structure.

in conventional pyrazolone chemistry. The NH hydrogen in *O*-silylpyrazolones is acidic and can be substituted by electrophilic agents.[3]

In a recent series of papers[11−13] unimolecular expansion reactions of rings containing nitrogen and silicon atoms were reported. Reaction mechanisms have been suggested which are supported by density functional (DFT) calculations. The isomerizations proceed either via a single transition state[11,13] or via more than one transition state[12,13] involving stable intermediate species. Large-amplitude motions play a crucial role in the unimolecular rearrangement processes.

In this article we present a thorough quantum-chemical study of the unimolecular isomerization pathways of silylpyrazolones, with particular emphasis on reaction mechanisms and transition states.

2. Methodology

The calculations are performed for isolated molecules, i.e., molecules in the gas phase which may well be compared with experimental results in aprotic polar and in nonpolar solvents. In protic solvents, however, tautomerism is mediated by intermolecular mechanisms which are not a subject of this work.[2] To reduce the computational expense, the calculations were performed for derivatives of (trimethylsilyl)hydrazine instead of those of (di-*tert*-butylphenylsilyl)hydrazine.[3] Hence, we study the isomerizations of *O*-(trimethysilyl)-3-methyl-5-pyrazolone (**5**).

The structures of the stationary points **1**−**6** and **TS1**−**TS5** (see Figure 1) were optimized using Becke's three-parameter hybrid method B3LYP with Becke's exchange functional[14] and the correlation functional of Lee, Yang, and Parr.[15] The 6-31G(d) basis set was employed in the DFT calculations; it comprises 197 contracted Gaussian type orbitals (cGTOs) for $C_7H_{14}N_2OSi$. To characterize the stationary points (minima or first-order saddle points) on the potential energy hypersurface (PES), the Hessian matrices at these points were calculated. The energies were further corrected for zero-point vibrational effects (harmonic level; imaginary frequencies not included) which, however, are usually only of minor importance in isomerization reactions. The TS routine of GAUSSIAN98[16] and the intrinsic reaction coordinate (IRC) method[17,18] were employed for the calculation of the transition state (first-order saddle point) geometries.

The nomenclature of the ring atoms used in this work is given in Chart 1.

3. Results and Discussion

The calculated geometries of the 11 stationary points **1**−**6** and **TS1**−**TS5** are contained in Table 1 and

---

(11) Gellermann, E.; Klingebiel, U.; Noltemeyer, M.; Schmatz, S. *J. Am. Chem. Soc.* **2001**, *123*, 378.

(12) Schmatz, S. *J. Phys. Chem. A* **2001**, *105*, 3875.

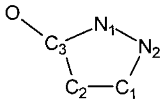
(13) Klingebiel, U.; Schmatz, S.; Gellermann, E.; Drost, C.; Noltemeyer, M. *Monatsh. Chem.* **2001**, *137*, 1105.

(14) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(15) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

Chart 1



displayed graphically in Figure 2. The energetics of the isomers are given in Table 2 and in Figure 1.

Local Minima on the PES. We start our analysis with the CH form of the 1-silylpyrazolone **2** and define the corresponding energy at zero. This species is primarily formed in the intramolecular condensation reaction of the silylhydrazone (see Scheme 2). The C=O double bond (122.1 pm) has the shortest C−O distance of all structures considered in this work. The same holds for the N(2)−C(1) bond, which is calculated to be 128.9 pm. The C(2)−C(3) bond (153.1 pm) is the longest endocyclic distance encountered in this system. The exocyclic N−Si bond measures 180.6 pm. The five-membered ring defines a plane of symmetry, and the molecule belongs to point group C_s. The π-system includes six electrons delocalized over five atoms.

As in 1-arylpyrazolones the system can isomerize from the CH form via **TS1** into the OH form **1**, which is located 9.6 kcal mol^{-1} higher in energy than **2**. The C−O bond is elongated by 14.1 pm, indicating a single bond. The C(2)−C(3) bond is contracted by 15.3 pm compared to **2**. The C(1)−C(2) bond is shortened by 8.2 pm and adopts a value between a single and a double bond. The other geometrical parameters change only slightly compared to **2**. The O−H bond distance amounts to 96.9 pm. The OH hydrogen atom is coplanar with the ring, and the system exhibits C_s symmetry. The OH form is aromatic, with six π-electrons being delocalized over six atoms.

In silylpyrazolones the CH form can isomerize by 1,3-silyl migration from the nitrogen to the oxygen atom via a four-center transition state (**TS2**). Isomer **3** (point group C_s) shows the largest N−N distance (143.6 pm) of all structures investigated in this work. Because the nitrogen atom N(1) now has only two neighboring atoms, it can form a double bond with the nitrogen atom N(2). Accidentally, the B3LYP results for both C=N double bonds amount to 129.1 pm. The C−C bond lengths are rather similar to each other (150.7 pm for C(1)−C(2) and 150.4 pm for C(2)−C(3)). The new O−Si bond measures 173.0 pm. The endocyclic C−C−C angle (97.8°) is smallest in species **3**. Structure **3** lies 7.7 kcal mol^{-1} above the CH form **2** and is energetically very similar to the OH structure **1** and the NH form **6** (see below). Four π-electrons are delocalized over four atoms.

Via an 1,2-hydrogen shift (**TS3**) between the carbon atoms C(2) and C(1), species **4** is obtained. Relative to the CH form **2**, this structure has a high energy (21.1 kcal mol^{-1}) which is due to the exocyclic methyl group being no longer coplanar with the ring and the +I effect of the methyl group being absent in this structure. The π-system comprises only four electrons, which are delocalized over four atoms. The C−Me distance is larger by more than 3 pm compared to all other isomers, and the N(2)−C(1)−C(2) angle (104.1°) is the smallest observed. The N−N bond distance (125.9 pm) clearly indicates a double bond. The same holds for the C(2)−C(3) bond (134.7 pm). The N(1)−C(3) distance (143.8 pm) is longest in the species.

By a further 1,2-hydrogen shift (**TS4**) the NH form of the *O*-silylpyrazolone **5** is obtained. In agreement with the experimental result,[3] this is the most stable isomer of the system (−5.2 kcal mol^{-1} with respect to the CH form **2**). In contrast, in the absence of polar solvents the CH form is the most stable species in arylpyrazolones. In silylpyrazolones a new absolute minimum arises with a NH functionality. This structure should not be confused with the NH form of arylpyrazolones, because the keto group is not existent in **5**. The N(1)−N(2)−C(1) angle is widened to 113.5°. The ring exhibits C_s symmetry. Six π-electrons are delocalized over the five-membered ring, and the condition for aromaticity is fulfilled.

Structure **5**, with a di-*tert*-butylphenylsilyl group instead of a trimethylsilyl group, has been characterized by X-ray diffraction.[3] It is evident that the endocyclic bond lengths lie between typical values of single and double bonds, indicating the aromaticity of the five-membered ring, which is planar with a sum of angles of 540°. The endocyclic (and exocyclic C−O) bond distances and angles agree well with the experimental result[3] (given in parentheses): r(N(1)−N(2)) = 136.6 pm (137.4), r(N(2)−C(1)) = 136.0 pm (134.4), r(C(1)−C(2)) = 138.8 pm (137.1), r(C(2)−C(3)) = 141.7 pm (140.0), r(C(3)−N(1)) = 133.0 pm (132.3), r(C−O) = 134.8 pm (135.4); α(C(2)−C(3)−N(1)) = 112.3° (112.7°), α(C(3)−N(1)−N(2)) = 103.6° (103.2°), α(N(1)−N(2)−C(1)) = 113.5° (112.7°), α(N(2)−C(1)−C(2)) = 105.8° (106.6°), α(C(1)−C(2)−C(3)) = 104.8° (104.7°). The B3LYP Si−O distance is calculated to be 171.5 pm, whereas the experimental result amounts to 166.26 pm and the C−O−Si angle from X-ray diffraction (135.2°) is almost 9° wider than the calculated angle (126.4°). The difference appears partly to be due to the shallow potential for bending the oxygen valence angle and partly due to the fact that different substituents are involved in theory and experiment. The bulky *tert*-butyl and phenyl groups widen the angle and the electron-withdrawing effect of the phenyl group further polarizes the silicon atom and increases the Si−O bond strength.

Finally, **5** has the possibility to undergo a further 1,3-silyl migration (**TS5**) to yield the NH form of the silylpyrazolone **6**, which can be compared with the corresponding structure known from conventional pyrazolone chemistry. It is energetically located at 7.3 kcal mol^{-1} above the CH form **2**. Despite the fact that the sum of endocyclic angles amounts to almost 540°, the ring is not planar and does not exhibit C_s symmetry. The NH nitrogen atom is sp^3-hybridized, and the hydrogen is tilted out of the ring plane by about 45°.

Transition States. The saddle point between the primary CH form **2** and the OH form **1** is governed by the motion of a hydrogen atom from the carbon site C(2) to the oxygen atom. The reduced mass corresponding to the normal mode with imaginary harmonic wavenumber amounts to 1.097 amu, which is essentially the mass of a hydrogen atom. The O−H bond distance amounts to 137.3 pm, which is 40.4 pm longer than in **1**. The distance H−C(2) is calculated to be 147.5 pm.

---

(17) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.
(18) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

Table 1. B3LYP/6-31G(d) Equilibrium Geometries of the 11 Stationary Points[a]

	1	**TS1**	**2**	**TS2**	**3**	**TS3**	**4**	**TS4**	**5**	**TS5**	**6**
r(N(1)−N(2))	138.7	142.7	140.8	141.1	143.6	133.5	125.9	133.3	136.3	137.7	141.7
r(N(2)−C(1))	132.7	131.2	128.9	129.4	129.1	136.5	148.7	146.0	136.0	136.9	139.4
r(C(1)−C(2))	142.2	145.7	150.4	152.4	150.7	148.5	149.1	140.6	138.3	138.4	135.6
r(C(2)−C(3))	137.8	143.6	153.1	150.4	150.4	140.4	134.7	139.4	141.7	142.5	146.1
r(C(3)−N(1))	136.1	134.5	138.6	130.8	129.1	134.7	143.8	135.7	133.0	133.6	140.6
r(N(1)−Si)	180.4	181.1	180.6	213.0						209.4	180.0
r(C(1)−CH_3)	149.9	149.6	149.4	149.4	149.5	150.3	153.6	150.4	149.6	149.6	149.6
r(C(2)−H(1))	108.2	108.9	109.7	109.7	109.7	108.1	108.0	108.0	108.0	108.0	108.0
r(C(2)−H(2))		147.5	109.7	109.7	109.7	138.4					
r(O−Si)				205.9	173.0	171.7	171.6	171.8	171.5	200.6	
r(N(2)−H)							206.4	131.6	100.8	101.0	101.8
r(C(1)−H)						125.4	110.2	129.2			
r(C(3)−O)	136.2	130.3	122.1	127.8	133.1	134.1	133.3	133.6	134.8	129.6	123.1
α(C(3)−N(1)−N(2))	109.5	108.6	112.0	111.8	107.9	110.4	110.5	108.7	103.6	107.2	108.7
α(N(1)−N(2)−C(1))	105.8	107.2	108.9	107.5	109.7	109.0	109.5	107.4	113.5	109.2	107.0
α(N(2)−C(1)−C(2))	111.8	112.2	112.5	112.6	111.6	107.8	104.1	107.4	105.8	108.4	110.0
α(C(1)−C(2)−C(3))	103.7	101.7	101.2	98.1	97.8	102.3	105.5	104.3	104.8	104.9	108.3
α(C(2)−C(3)−N(1))	109.2	110.3	105.4	109.9	112.9	110.4	110.3	112.0	112.3	109.9	105.3
α(C(3)−O−Si)	65.0	55.2	62.6	93.6	124.4	125.5	128.1	126.3	126.4	94.8	64.5
α(C(3)−N(1)−Si)	130.2	130.8	125.9	89.5	61.6	61.5	62.3	62.4	62.0	89.6	123.7
E (+ 749 E_h)	−0.436 128	−0.336 932	−0.451 499	−0.402 271	−0.439 138	−0.377 954	−0.415 939	−0.378 467	−0.459 747	−0.409 298	−0.439 834
ΔE	9.6	71.9	0.0	30.9	7.7	46.2	21.1	45.8	−5.2	26.4	7.3
ω_{TS}		2146.5 i		221.3 i		1232.4 i		1416.4 i		205.2 i	
μ		1.0967		8.5786		1.3954		1.2694		7.4345	
E_{zp}	128.6	124.5	128.4	128.0	128.1	126.0	128.3	125.8	129.0	128.6	128.9

[a] Bond lengths r are given in pm and bond angles α in deg (for the numbering of the atoms, see Chart 1). Absolute energies E are given in E_h. The saddle points are further characterized by the imaginary harmonic wavenumbers ω_{TS} (in cm^{-1}) and the corresponding reduced masses μ (in amu). The energy differences with respect to **2**, ΔE, and the zero point vibrational energies E_{zp} (at harmonic level; imaginary frequencies not included) are given in kcal mol^{-1}.

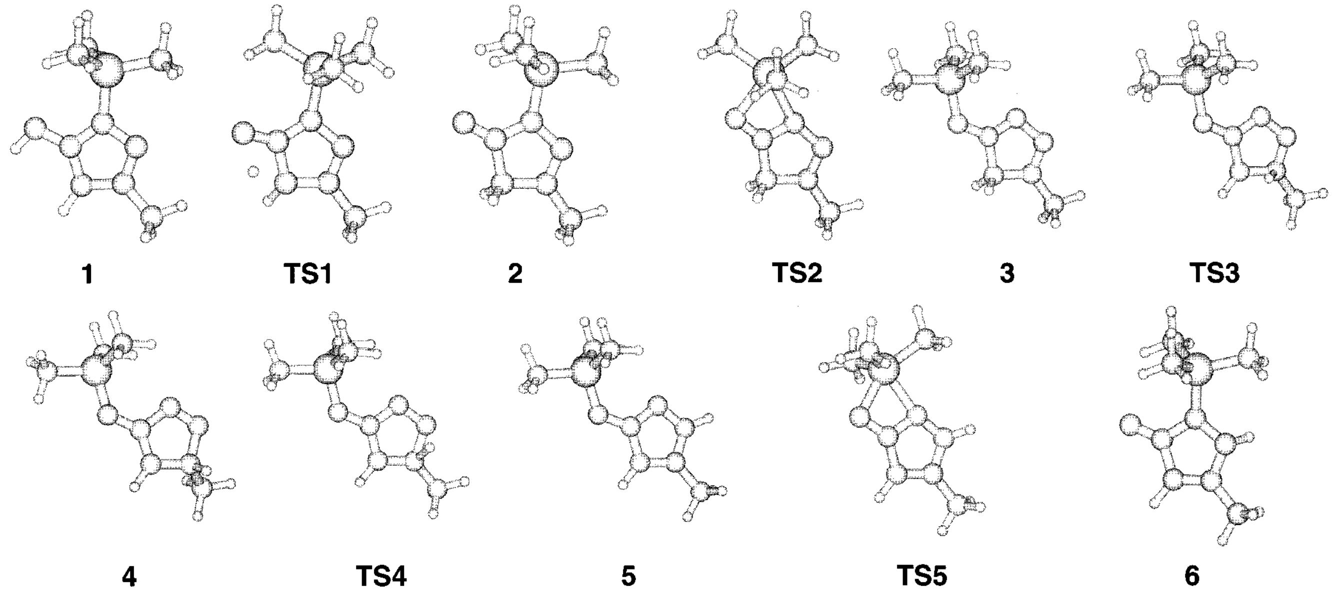


Figure 2. B3LYP/6-31G(d) structures of 11 stationary points on the *O*-(trimethylsilyl)-3-methyl-5-pyrazolone potential energy hypersurface (see the text).

Table 2. B3LYP/6-31G(d) and MP2 (with Different Basis Sets) Energies (in kcal mol^{-1}) of the 11 Stationary Points (Calculated at B3LYP/6-31G(d) Equilibrium Geometries)[a]

	1	TS1	2	TS2	3	TS3	4	TS4	5	TS5	6
B3LYP/6-31G(d)	9.6	71.9	0.0	30.9	7.7	46.2	21.1	45.8	−5.2	26.4	7.3
MP2/6-31G(d)	6.7	72.4	0.0	30.5	7.7	43.9	22.3	44.5	−5.9	26.6	9.2
MP2/6-31G(d,p)	4.0	70.3	0.0	30.3	7.8	42.5	22.0	42.6	−7.2	25.0	8.1
MP2/6-31+G(d,p)	2.5	68.5	0.0	30.0	7.8	41.8	21.7	42.1	−7.5	24.2	6.6
MP2/6-311+G(d,p)	1.7	68.0	0.0	31.9	9.8	42.4	23.1	42.8	−5.9	25.8	6.0
B3LYP/6-31G(d) + ΔE_{zp}	9.8	68.0	0.0	30.5	7.8	43.8	21.0	43.2	−4.6	26.6	7.8
MP2/6-311+G(d,p) + ΔE_{zp}	1.9	64.1	0.0	31.5	9.9	40.0	23.0	40.2	−5.3	26.0	6.5
$\Delta H_R°$(298 K)[b]	10.0		0.0		7.5		21.5		−4.4		7.9

[a] E(**2**) is set to zero for all methods/basis sets. [b] B3LYP/6-31G(d).

However, the migrating hydrogen atom is also interacting with the carbon site C(3), where the C(3)−H distance is only 4.2 pm longer compared to C(2)−H. The saddle point structure may be characterized as a four-center transition state. Both endocyclic carbon−carbon bond distances become appreciably smaller on going from **2** to **1**. The transition state **TS1** is closer to **1** than to **2**. The nonmigrating hydrogen atom and the oxygen atom are in a trans conformation enclosing a torsional angle of 63.1°. The reactive normal coordinate in **TS1** also includes the motion of the nonmigrating hydrogen atom into the plane of the ring. **TS1** is energetically located at 71.9 kcal mol^{-1} above the CH form **2**. The described 1,3-H-shift isomerization process is unimolecular. In the case of steric hindrance inhibiting intramolecular transitions, the proton may prefer the intermolecular migration mechanism. This tendency would be enhanced in the presence of protic solvents. In this case, the relatively high barrier to isomerization will become considerably lower. It should be noted that tunneling of the proton will play an important role in the isomerization dynamics.

From the intramolecular condensation of silylhydrazines, the CH form of the silylpyrazolone **2** is formed. The isomerization toward the most stable product **5** passes through the two intermediate structures **3** and **4** and the three saddle points **TS2**, **TS3**, and **TS4**. The B3LYP/6-31G* energetics of the minima and saddle points considered in this work are displayed schematically in Figure 1.

TS2 is located at 30.9 kcal mol^{-1} above the CH form. The structure is characterized by the 1,3-SiMe$_3$ shift from the nitrogen to the oxygen site. The Si−O (205.9 pm) and Si−N (213.0 pm) distances are almost equal in length. The acute angle at the silicon atom is calculated to be 62.5°, whereas the angle at the endocyclic carbon site (114.3°) indicates sp^2 hybridization of this atom. The remaining two angles are calculated to be 93.6° (Si−O−C) and 89.5° (Si−N−C). The sum of angles amounts to 360.9°, and the torsional angle θ(N(1)−C(3)−O−Si) is −2.7°. The bicyclic structure of the four-center transition state is almost coplanar. The reactive normal coordinate with an imaginary wavenumber of 221 cm^{-1} is described by a wagging motion of the trimethylsilyl moiety against the pyrazolone ring system. The corresponding reduced mass amounts to 8.58 amu.

The reactive normal mode is depicted graphically in Figure 3. It can be seen from this figure that the five-membered ring approximately performs a rotation in a clockwise direction around an axis perpendicular to the ring plane. This axis intersects the plane very closely to carbon atom C(2), which is almost at rest, as can be seen from the small arrow in Figure 3. The silicon atom and two of the methyl groups migrate from N(1) to C(3). The third methyl group, which is perpendicular to the ring plane (see Figure 2), moves only very slightly during the passage of the transition state.

The transition state **TS3** connecting structures **3** and **4** corresponds to a 1,3-prototropic change. The proposed

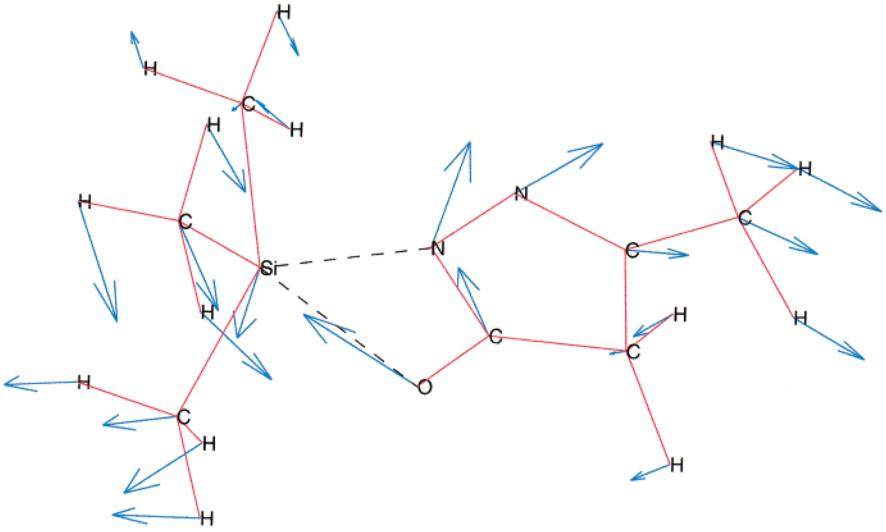


Figure 3. Reaction coordinate at saddle point **TS2**: i.e., the normal coordinate with the imaginary harmonic wavenumber (see the text). The dashed lines denote the two bonds being broken and formed, respectively.

unimolecular isomerization process can be substituted by a bimolecular mechanism involving protic solvent molecules. However, this pathway is not the subject of the present study. The saddle point **TS3** exhibits a three-center transition structure formed by the carbon atoms C(2) and C(3) and the migrating hydrogen atom. The distance between the proton and C(2) (125.4 pm) is shorter than the distance H−C(3) (138.4 pm), and the saddle point may be classified as a late transition state. The C(2)−H−C(3) angle is calculated to be 68.3°. The reactive normal coordinate is governed by the hydrogen migration (the corresponding reduced mass amounts to 1.40 amu) but includes substantial changes of the endocyclic bond lengths (except the C(1)−C(2) bond). The saddle point is energetically located at 46.2 kcal mol^{-1} above **2**.

The saddle point **TS4** describes the second 1,2-H shift. Also, this step can be afforded through an intermolecular pathway. In **TS4**, the proton migrates from the C(1) site to the nitrogen atom N(2). The three-center structure is rather similar to **TS3**: The C(1)−H distance amounts to 129.2 pm, and the N(2)−H distance is calculated to be 131.6 pm. The enclosed angle measures 68.1°. The saddle point is 45.8 kcal mol^{-1} higher in energy compared to the CH structure **2**, very similar to the energetics of **TS3**. The same holds for the reactive normal coordinate with corresponding reduced mass of 1.27 amu, which also in this case indicates the governing migration of the hydrogen atom. However, all five endocyclic bond lengths are subject to a change in the isomerization **4** → **5**.

It should be noted that tunneling is supposed to strongly influence the reaction dynamics of both 1,2-H shifts via **TS3** and **TS4**.

From the most stable species **5** a further 1,3-Si shift from the oxygen atom back to the nitrogen atom can occur. The structure of the saddle point **TS5** is rather similar to that of **TS2**. The O−Si−N angle is calculated to be 64.0°, and the O−C−N angle amounts to 111.3°. The sum of angles of the four-center transition state is 359.6° with a torsional angle θ(N(1)−C(3)−O−Si) = 5.8°. The bicyclic **TS5** is approximately coplanar. Moreover, it exhibits approximate C_s symmetry because one of the three methyl substituents of the silicon atom lies in the plane of the ring. In contrast, in **TS2** one of the three methyl groups is almost perpendicular to this plane (see Figure 2). The harmonic wavenumber of **TS5** amounts to 205 cm^{-1} with a corresponding reduced mass of 7.43 amu. The reaction coordinate corresponds to a wagging motion of the trimethylsilyl group and the ring, where the O−Si bond is broken and a new Si−N bond is formed.

It remains in question whether the isomerization process is indeed unimolecular, as described in Figure 1. Tautomerism often occurs when two species simultaneously exchange two protons, in particular when a six-membered cyclic transition state structure can be formed. This appears not to be possible for silylpyrazolones. Thus, the intermolecular reaction mechanisms should involve protic solvent molecules. Alternatively, the OH form of the silylpyrazolones may play an active role in these intermolecular processes. While the hydrogen shifts can also be afforded via intermolecular mechanisms, the silyl shifts are essentially unimolecular. This has been shown in appropriate experiments by Klingebiel et al.[19] When differently substituted silylpyrazolones were present in the reaction, no cross products could be detected.

MP2 Calculations. To assess the quality of the DFT results, second-order perturbation calculations according to Møller and Plesset (MP2) with the 6-31G(d) basis set were performed at the B3LYP/6-31G(d) geometries of the 11 stationary points. The results are given in Table 2. The energies of the CH form **2** are set to zero for all methods and basis sets. As in our previous work on silylhydrazine chemistry,[11,12] the MP2 results are in good agreement with the B3LYP/6-31G(d) calculations. The differences between the B3LYP and MP2 energies of six stationary points are below 1 kcal mol^{-1}; only for structure **1** and **TS3** is this difference above 2 kcal mol^{-1}.

The basis set dependence of the MP2 results has been studied at the B3LYP/6-31G(d) geometries. To study the influence of polarization functions on the hydrogen

---

[19] Klingebiel, U. Private communication.

nuclei, we made use of the 6-31G(d,p) basis set (239 cGTOs for $C_7H_{14}N_2OSi$). We then added diffuse functions (6-31+G(d,p); 283 cGTOs) to assess their influence on the saddle point structures. Finally, extra valence functions were added, yielding a basis set of triple-ζ quality (6-311+G(d,p); 334 cGTOs).

Polarization functions on hydrogen slightly lower the energy differences with respect to **2**, in particular for the structures involving a migrating hydrogen atom (**TS1**, **TS3**, **TS4**) and the structures containing an NH (**5**, **6**) or OH bond (**1**). The influence of additional basis functions is rather small, with the exception of the OH form **1**. Here, the energy is systematically decreased from 6.7 to 1.7 kcal mol^{-1}. The same behavior can be observed for the NH form **6**, and, less pronounced, for **TS1**. When the MP2/6-31G(d) and MP2/6-311+G(d,p) results for the most stable structure **5** are compared, it is evident that the small basis set calculation benefits from error compensation.

The influence of zero point vibrational energy is very small, with the exception of the three saddle points involving hydrogen migration. Here, the energy differences are lowered by 2.4 kcal mol^{-1} (**TS3**), 2.6 kcal mol^{-1} (**TS4**), and 3.9 kcal mol^{-1} (**TS1**). The reason is the strong decrease of the high frequencies of the CH, NH, and OH stretching vibrations in the transition states, which usually are on the order of 10 kcal mol^{-1} (e.g., in **TS1** the harmonic wavenumber of the hydrogen stretching vibration perpendicular to the reaction coordinate amounts to only 1764 cm^{-1}).

3. Conclusions

Silicon is normally much more reactive toward the hard Lewis base oxygen than toward the softer Lewis base nitrogen.[6] The silyl group tends to be attached to the most electronegative atom. The 1,3-silyl group migration from nitrogen to oxygen in silylpyrazolones is one more example for this rule. The chemistry of these compounds is richer in unimolecular isomerizations compared to conventional pyrazolones.

The complex unimolecular rearrangement process starting from the primarily formed CH form **2** can be described as follows: First, the organosilyl group migrates from the nitrogen atom to the oxygen atom (1,3-Si shift). The second and third steps consist in two consecutive 1,2-H shifts from the carbon site C(2) to nitrogen atom N(2). The barriers of the hydrogen migrations determine the overall classical barrier (42−46 kcal mol^{-1}) where, however, tunneling of the proton may play an important role in lowering the effective activation energy. In comparison to the reactant, the most stable isomer *O*-silylpyrazolone is lower in energy by 5 kcal mol^{-1}. The OH (**1**) and CH (**6**) forms known from conventional pyrazolone chemistry are higher in energy than both **2** and **5** and can be reached via a single transition state starting from **2** or **5**, respectively.

Acknowledgment. I am indebted to Prof. P. Botschwina for his support. Fruitful discussions with Prof. P. Botschwina, Prof. U. Klingebiel, and Dr. R. Oswald are gratefully acknowledged. Dr. Oswald in addition kindly prepared Figure 3. Most of the calculations were carried out at the Gesellschaft für wissenschaftliche Datenverarbeitung Göttingen (GWDG). Thanks are due to the Deutsche Forschungsgemeinschaft (through Sonderforschungsbereich 357 “Molekulare Mechanismen unimolekularer Prozesse”) for financial support.

OM010826P