Cycloaddition Products from (1-Diazo-2-oxoalkyl)silanes and Cyclopropenes. A Silatropic 2,3-Diazabicyclo[3.1.0]hex-3-ene/1,4-Dihydropyridazine Equilibrium☆

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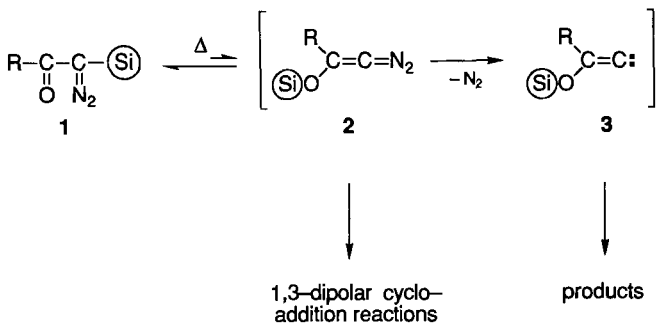
Received November 27, 1991

Key Words: (1-Diazo-2-oxoalkyl)silanes / Cyclopropenes / Cycloaddition / Silyl shift / Homopyrazole / 1,4-Dihydropyridazine isomerization

(1-Diazo-2-oxoalkyl)silanes **1a–h** react with cyclopropene **4** to form 2-silyl-2,3-diazabicyclo[3.1.0]hex-3-enes **5** and/or 1-silyl-1,4-dihydropyridazines **6**. In most cases, a temperature- and solvent-dependent equilibrium **5** ⇄ **6** maintained by an $N \rightarrow N'$ silyl shift exists in solution. With cyclopropene **10**, only the 1-silyl-1,4-dihydropyridazines **11** are obtained. None of the 1:1 adducts corresponds to the product expected from a [3 + 2] cycloaddition reaction between the components. Evidence is presented that 1-diazo-2-siloxy-1-alkenes **2** are initially formed from **1** by a 1,3-($C \rightarrow O$) silyl shift and are then trapped by the cyclopropene in a 1,3-dipolar cycloaddition reaction.

(1-Diazo-2-oxoalkyl)silanes **1** easily isomerize to 1-diazo-2-siloxy-1-alkenes **2** by a 1,3-($C \rightarrow O$) silyl migration. The resulting cumulenic diazo compounds **2** cannot be isolated, since they lose N_2 instantaneously under the reaction conditions (typically 30–80°C), and products derived from the resulting alkylidene carbenes **3** are obtained[1]. In the presence of an excess of a reactive dipolarophile, diazoalkenes **2** may be trapped, however, in a 1,3-dipolar cycloaddition reaction, even though the equilibrium **1** ⇄ **2** lies far on the left-hand side[2]. With dipolarophiles such as *N*-phenyl maleimide and norbornene, the genuine [3 + 2] cycloaddition products arising from **2** are isolated.



Lahti and Berson have provided evidence that 1-diazo-2-methyl-1-propene can be trapped by cycloaddition to 3,3-dimethyl-1-cyclopropene[3]; in that case, however, the primary [3 + 2] cycloaddition product was not obtained but rather a rearranged isomer thereof. Cyclopropenes are also known to serve as dipolarophiles for diazoalkanes[4–7], diazoacetates[7,8], and diazophosphoryl compounds[6,8]. Considering the thermal equilibrium between the 1,3-dipolar diazo species **1** and **2**, we decided to examine whether cyclopropenes would be able to trap the minor structural isomer **2** in the presence of the diazocarbonyl compound **1**.

Results

(1-Diazo-2-oxoalkyl)silanes **1a–h** were heated at the temperature and time intervals specified in Table 1 in the presence of excess cyclopropene **4**. Because of the volatility of **4** (b.p. 14°C), the reactions at 90°C were carried out in a pressure tube. In all cases, 2,3-diazabicyclo[3.1.0]hex-3-enes ("homopyrazoles") **5** and/or 1,4-dihydropyridazines **6** were isolated as the main or exclusive products (Scheme 1 and Table 1). The N–Si bond in both **5** and **6** is easily cleaved by water; therefore, some material was lost on chromatographic workup, even if this was done by rather fast Lobar column chromatography. The particularly labile 1,4-dihydro-1-silylpyridazine **6h** was deliberately hydrolyzed to furnish 1,4-dihydropyridazine **9**. Remarkably, the thermal decomposition of **1a–h**, which occurs *under the same reaction conditions* in the absence of cyclopropene **4**, was suppressed totally or to a large extent, so that the products derived from alkylidenecarbenes **3**, namely siloxyalkynes **7**[1a] (R =

Table 1. Reaction conditions, products, and yields for Scheme 1

1, 5-8	R	(Si)	Reaction Conditions	%5 [a]	%6 [a]	%7	%8
a	*t*Bu	Si*i*Pr$_3$	90°C/4h	76		–	–
b	*t*Bu	SiPh$_2$*t*Bu	90°C/2h		62	–	–
c	*t*Bu	SiMe$_2$*t*Bu	90°C/4h	67 (**5+6**)		–	–
d	*i*Pr	Si*i*Pr$_3$	90°C/6h	46 (**5+6**)		–	8
e	Me	Si*i*Pr$_3$	90°C/4h	30 (**5+6**)		–	24
f	C_6H_5	Si*i*Pr$_3$	36°C/4h		55	[b]	–
g	C_6H_4-4-OMe	Si*i*Pr$_3$	90°C/4h		33	[b]	–
h	C_6H_4-4-NO_2	Si*i*Pr$_3$	36°C/4h		68	[b]	–

[a] Yields of isolated products are given. In solution, a temperature- and solvent-dependent equilibrium **5** ⇄ **6** exists in all cases except for **5a**. – [b] In the reaction mixture, the alkyne is detected by IR [ν(C≡C) = 2260–2265 cm^{-1} [1a,22]], but it is lost during chromatographic workup.

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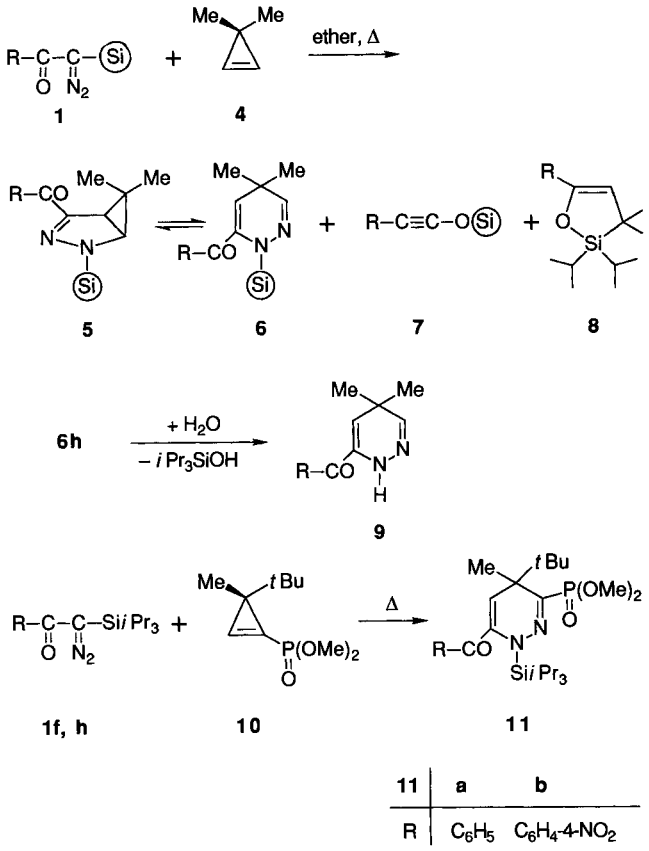
aryl) or 1-oxa-2-sila-4-cyclopentenes **8**[1c] (R = alkyl) were obtained only as by-products. The case of **1f** may be an exception: According to the IR spectrum of the reaction mixture, a quite significant amount of **7a** was formed, but since this product was lost because of hydrolysis during chromatographic workup, its yield cannot be given.

Scheme 1. For reaction conditions, products and yields, see Table 1



11	a	b
R	C_6H_5	C_6H_4-4-NO_2

In solution, compounds **5** and **6** are in equilibrium (see below); in the absence of solvent, either a liquid mixture of **5** and **6** or only one of the two structural isomers is obtained (homopyrazole: **5a**; 1,4-dihydropyridazines: **6b,f–h**; see Table 1). As an example, the IR spectra of dihydropyridazine **6b** in the solid state and after dissolving in $CHCl_3$ (→ mixture of **5b** and **6b**) are reproduced in Figure 1.

Whereas the identity of the 1,4-dihydropyridazines **6** has been firmly established by an X-ray crystal structure analysis of **6b** (see below), the following spectroscopic features serve to distinguish homopyrazoles **5** from the bicyclic constitutional isomers **12** and **13** (i.e. the direct products of a [3 + 2] cycloaddition reaction of either **1** or **2** with cyclopropene **4**): The silylenol ether form **13** is excluded because both IR ($\tilde{\nu}$ = 1620–1660 cm^{-1}) and ^{13}C-NMR spectra ($\delta \cong 201$; δ = 185.5 for **5h**) indicate the presence of a carbonyl group. A decision between **5** and **12** in favor of **5** is based on the low value of $\nu(C=O)$, which points to a conjugated carbonyl group, and a ^{13}C-NMR signal at δ = 147.4–149.3, which is in the expected range for C=N in **5** but much too low for C-3 in **12**. The ^{29}Si-NMR signal of **5a** (δ = 11.5 in C_6D_6) may also support the assignment[9]. The two methyl groups at C-6 of **5** are involved in an exchange process (see below); since their NMR signals are coalesced at the recording temperature, they are not detected. For the cyclopropane carbon atom C-6, a ^{13}C-NMR signal at δ = 5.5–6.8 is obtained. Since these values appeared to be at an unusually high field even for a cyclopropane carbon atom bearing two methyl groups, we have synthesized as a model compound homopyrazole **14** by the azomethine imine route developed by Visser and Smael[10]. In the ^{13}C-NMR spectrum, we find $\delta(CMe_2)$ at δ = 8.2 which is in sufficient agreement with the values mentioned above; moreover, the other signals of the bicyclic framework in **5** and **14** also compare very well.

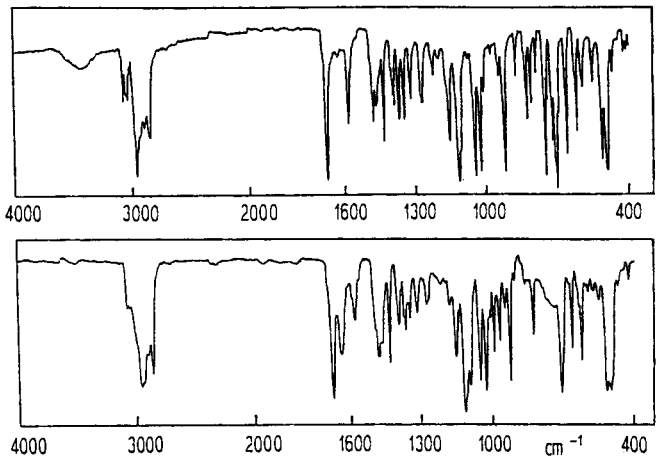
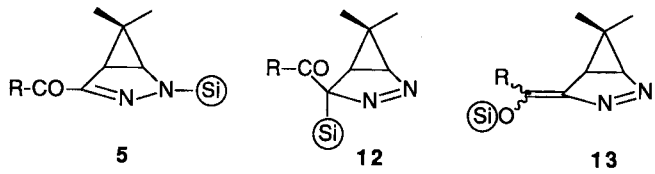
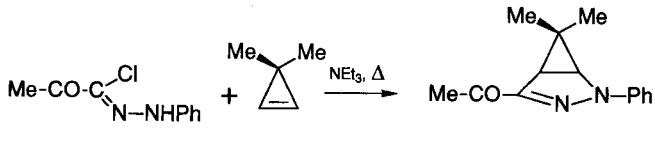


Figure 1. Top: IR spectrum of pure **6b** in the solid state (KBr pellet). – Bottom: IR spectrum after dissolving **6b** in $CHCl_3$ (mixture of **5b** and **6b**)





Cyclopropenes bearing an electron-withdrawing group at the double bond are particularly suitable reaction partners for diazo dipoles[6,8]. In fact, when diazo compounds **1f,h** are heated in the presence of cyclopropene-1-phosphonate **10**[11] (Scheme 1), a faster reaction than in the presence of cyclopropene **4** occurred. The dimethyl 1,4-dihydropyridazine-3-phosphonates **11a,b** were the sole products isolated; in contrast to the related 1,4-dihydropyridazines **6**, no equilibrium between **11** and a homopyrazole analogous to **5** could be detected. The position of the PO substituent follows from a comparison of the ^1H-NMR spectra of **6** and **11**: For **11a,b**, the signal attributed to 5-H [δ = 4.96 ± 0.02, $^4J(P,H)$ = 8.4 Hz] is still present, whereas the low-field signal attributed to 3-H in **11** (δ = 6.43–6.55) has disappeared. No matter whether diazocarbonyl compound **1** or

diazoalkene **2** has been trapped by cyclopropene **10** in the first place, the substituent pattern of **11a,b** indicates that the regioselectivity of the [3 + 2] cycloaddition to the unsymmetrically substituted double bond of **10** is the one expected from frontier orbital considerations[12].

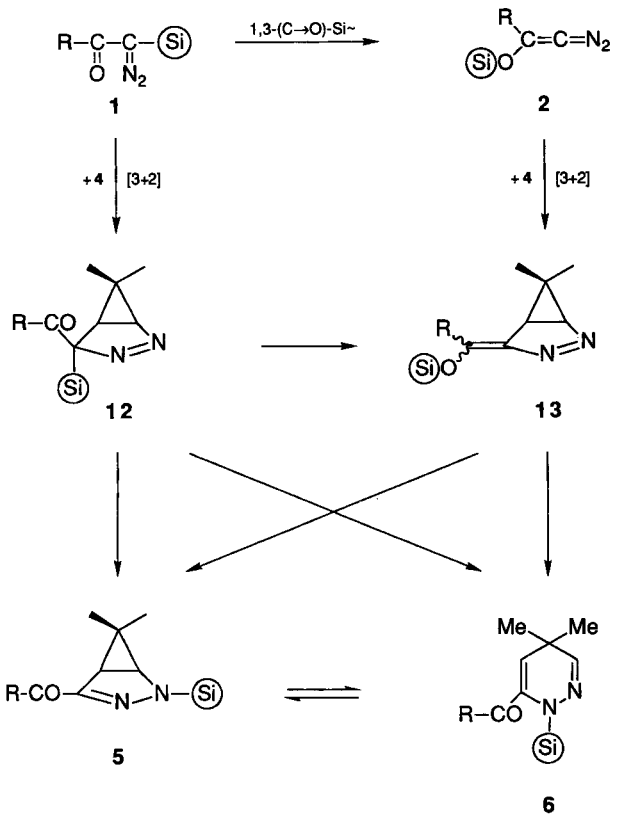
Mechanistic Considerations

Compounds **5**, **6**, and **11** are obviously not the primary products resulting from a cycloaddition reaction of either diazocarbonyl compounds **1** or diazoalkenes **2** with cyclopropenes **4** and **10**. Possible reaction pathways leading to homopyrazoles **5** and/or 1,4-dihydropyridazines **6** must include one of these products (**12** or **13**), however. Both **12** and **13** could isomerize to the final products by migration of the silyl group (Scheme 2).

Although there is no definite proof, we assume the reaction sequence **1** → **2** → **13** → **6** ⇄ **5** for the following reasons: (a) In contrast to the silyl-diazoketones **1a–h**, ethyl diazo(triisopropylsilyl)acetate does not react with cyclopropenes **4** (90°C/12 d) and **10** (36°C/20 h). This difference can neither be attributed to steric effects nor to major electronic changes (simple diazoacetic esters do undergo a 1,3-dipolar cycloaddition to both **4**[7] and **10**[6a,8] at room temperature). We assume that both, the silyl-diazoketones and the silyl-diazoester, are unreactive towards **4** and **10** because of strong shielding of the diazo dipole by the bulky silyl substituent. However, in contrast to the silyl-diazoester[13], the silyl-diazoketones can rearrange under the reaction conditions by a 1,3-(*C* → *O*) silyl shift to form the cumulenic diazo compounds **2**[2] which can undergo the [3 + 2] cycloaddition through a transition state with much less steric strain. Had the cycloaddition reaction **1** + **4** → **12** taken place, one might have expected **12** to undergo a [3 + 2] cycloreversion reaction to an allyldiazomethane derivative, as has been observed for other 4-acceptor-substituted 2,3-diazabicyclo[3.1.0]hex-3-enes[7,8]. The isomerization reaction **12** → **13** seems feasible, but one should remember that a ketosilane → silylenol ether rearrangement typically occurs at more elevated temperatures (120–150°C)[14].

For the isomerization of **13** to the final products, the route **13** → **5** seems less likely than **13** → **6**. In the latter case, the 1,7-(*O* → *N*) silyl shift can be looked at as a sigmatropic rearrangement involving eight atoms. However, the actual

Scheme 2



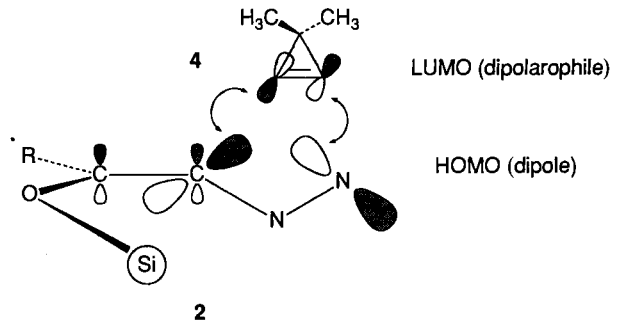


Figure 2. Cycloaddition of diazoalkenes **2** to cyclopropene **4**: Geometry of the approach of the reactants and HOMO-LUMO interaction

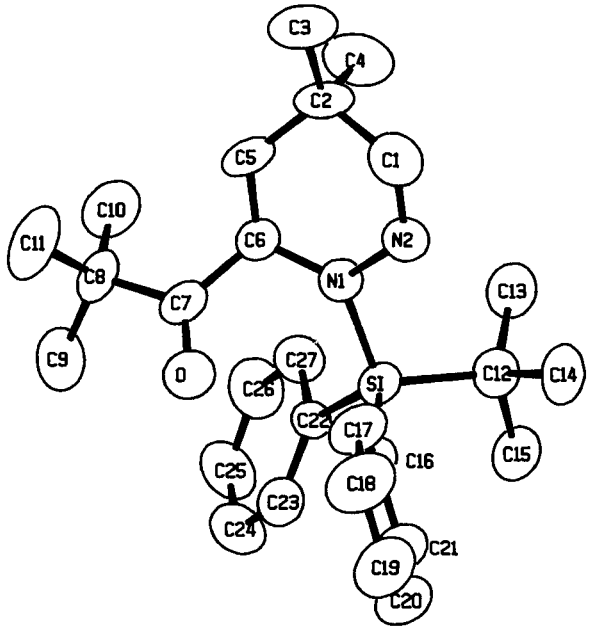


Figure 3. Plot of **6b** in the solid state. Selected bond distances [Å] and bond angles [°]: Si–N(1) 1.753(3), N(1)–N(2) 1.409(4), N(2)–C(1) 1.262(5), C(1)–C(2) 1.507(6), C(2)–C(5) 1.472(6), C(5)–C(6) 1.308(5), C(6)–N(1) 1.409(5), C(6)–C(7) 1.498(5); Si–N(1)–N(2) 108.7(3), Si–N(1)–C(6) 133.7(3), N(2)–N(1)–C(6) 116.4(3), C(5)–C(6)–N(1) 121.5(4), C(5)–C(6)–C(7) 123.8(4), N(1)–C(6)–C(7) 113.7(4). Torsion angles [°]: N(1)–N(2)–C(1)–C(2) –5.4, C(2)–C(5)–C(6)–N(1) 5.8, C(2)–C(5)–C(6)–C(7) 173.5, Si–N(1)–C(6)–C(7) 18.8, *N(1)–C(6)–C(7)–O* 32.7, C(5)–C(6)–C(7)–O –135.9

silyl group migration can occur in an easy-to-realize five-membered array provided that the *exo* double bond has the *Z* configuration. This is in fact the configuration which has been observed in the cycloadducts of **2** to norbornene and *N*-phenylmaleimide[2]. It results from the most favored geometry of approach of the cycloaddition partners **2** and **4**, since the opposite face of the diazo dipole of **2** is sterically more shielded by the bulky silyl group (Figure 2).

Crystal Structure Analysis of 1,4-Dihydropyridazine 6b

The crystal and molecular structure was determined by X-ray diffraction. Figure 3 shows a plot of the molecule. The heterocycle assumes a boat structure, some characteristic features of which are given in Figure 4.

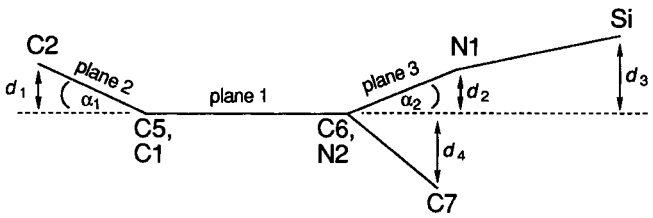


Figure 4. Parameters defining the boat form of the 1,4-dihydropyridazine ring of **6b**. Plane 1: C1–N2–C6–C5 (deviations of individual atoms: ±0.003 Å); plane 2: C1–C2–C5; plane 3: N2–N1–C6. α_1 = 23.6°; α_2 = 18.6°; d_1 = 0.355 Å; d_2 = 0.236 Å; d_3 = 0.483 Å; d_4 = −0.485 Å

The steric interaction between the bulky $SiPh_2tBu$ group at N1 and the acyl group at C6 has been reduced by adequate adaptations of the bond angles and torsion angles involved. Most significantly, the silyl group is bent away from the neighboring substituent, as the enlarged bond angle C6–N1–Si [133.7(3)°] shows. The corresponding widening of the angle N1–C6–C7 has not occurred, however. On the contrary, this angle [113.7(4)°] is much smaller than the exocyclic angle at the sterically unbiased side of C6 [angle C5–C6–C7: 123.8(4)°]. The Si···O distance [3.025(3) Å] does not suggest a particular attractive interaction between these two atoms.

Dynamic Processes: Ring Inversion of Homopyrazoles 5 and Silatropic Equilibrium 5 ⇄ 6

Ring Inversion: For all homopyrazoles **5**, a fast exchange of the *exo*-6- and *endo*-6-methyl groups is observed by NMR spectroscopy. At probe temperature (ca. 35°C), only one signal for the two methyl groups is observed in the ^{1}H-NMR spectrum (200 MHz), whereas no signal at all is found in the ^{13}C-NMR spectrum (50 MHz). For **5a** and **5d**, the rate of exchange at the coalescence temperature has been obtained (Table 2).

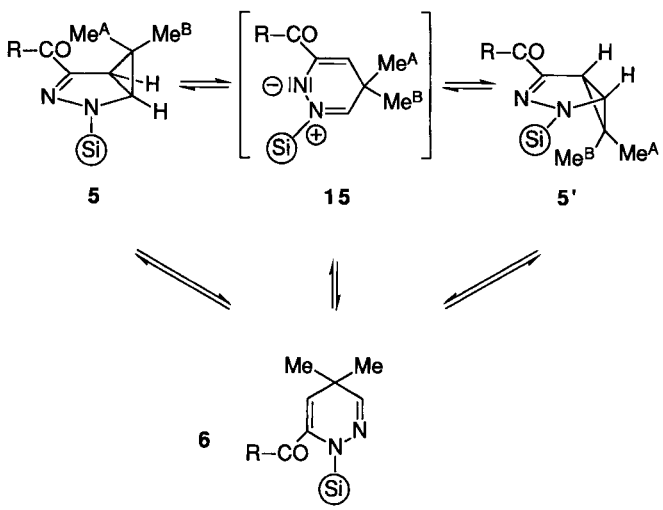
The exchange phenomenon is due to a ring inversion of the bicyclic skeleton, which has been detected before in other homopyrazoles[10] as well as in homopyrrole[16], homofurane[16,17], and homothiophene[16] systems. According to investigations by Klärner and Schröer[16], such ring inversions occur by a sequence of two disrotatory electrocyclic processes, in which the central cyclopropane bond is broken and formed again[18]. Thus, the topomerization **5** ⇄ **5'** occurs via the monocyclic *N*-vinylazomethine imine intermediate **15** (Scheme 3). The alternative pathway **5** ⇄ **6** ⇄ **5'** can be excluded, since in contrast to the exchange process discussed the isomerization **5** ⇄ **6** is slow on the NMR time scale, even at higher temperatures (see below). The $\Delta G_c^{\ddagger}$ values for the ring inversion (Table 2) are very similar to those found for 6,6-dimethyl-2,4-diphenyl-2,3-diazabicyclo[3.1.0]hex-3-ene[10]; it is known, that only strongly electron-withdrawing substituents at N2 slow down the electrocyclic ring opening of homopyrazoles[10] and homopyrroles[19].

Table 2. Rate (k_c) and $\Delta G_c^{\ddagger}$ value at coalescence temperature T_c for the exchange process *endo*-6-Me ⇄ *exo*-6-Me in **5a,h**

5	Solvent	T_c [K]	$\Delta\nu$ [a] [Hz]	k_c [b] [s^{-1}]	$\Delta G_c^{\ddagger}$ [kJ mol^{-1}]
a	CD_2Cl_2	258	108.9	242	51.1
	[D$_8$]toluene	248	53.2	116	50.5
h	[D$_8$]toluene	263	38.4	85	54.5

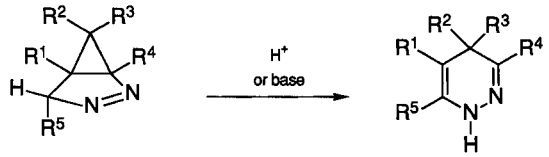
[a] Separation of ^{1}H-NMR signals of the two methyl groups at the coalescence temperature recorded at 200 MHz. – [b] $k_c = 2.22 \cdot \Delta\nu$; see ref.[15].

Scheme 3



Silatropic Equilibrium **5** ⇄ **6**: In solution, an equilibrium maintained by an $N \rightarrow N'$ silyl shift exists between homopyrazoles **5** and 1,4-dihydropyridazines **6** (Scheme 1 and Table 1). This is a unique equilibrium, since homopyrazoles and 1,4-dihydropyridazines have never been reported to coexist. 2-H-2,3-diazabicyclo[3.1.0]hex-3-enes are not known, and their 4-H tautomers **16** are isomerized to 1,4-dihydropyridazines **17** irreversibly under the influence of acids or bases[4,5b,6–8].

The effects of the substituent pattern, the solvent, and the temperature on the equilibrium concentration of **5** and **6** have been investigated. As for the influence of the substit-



16 **17**

uents (Table 3), one notes steric and electronic effects. Since steric interactions between the vicinal acyl and silyl groups exist in the 1,4-dihydropyridazines **6** (compare the crystal structure of **6b**, see above), the monocyclic isomer is increasingly destabilized, the more bulky these substituents are. The only apparent irregularity is represented by the pair **5b**/**6b**, which according to this rationalization should rank second in Table 3. The destabilization of the bicyclic isomer by a 4-methoxybenzoyl group as compared to benzoyl and 4-nitrobenzoyl groups is certainly due to an electronic effect, but we do not have an obvious explanation. As a hypothesis, we propose that in the case of **6g** (which has the most electron-rich carbonyl oxygen), an attractive Si···O interaction stabilizes the monocyclic isomer. Although we have not found such an interaction in the crystal structure of **6b**, it could exist in **6g** since the aryl group exhibits less steric bulk than a *t*Bu group; therefore, the torsion angle between C=C and C=O could more easily adopt a value which brings the carbonyl oxygen closer to the silicon atom than in the case of **6b**.

Table 3. Isomer ratio **5**:**6** (determined by ^{1}H-NMR spectroscopy in $CDCl_3$ at 35°C) in the order of decreasing amount of homopyrazole **5**

5, 6	R	(Si)	Ratio 5 : 6
a	*t*Bu	Si*i*Pr$_3$	>97 : 3 [a]
c	*t*Bu	SiMe$_2$*t*Bu	52 : 48
d	*i*Pr	Si*i*Pr$_3$	45 : 55
e	Me	Si*i*Pr$_3$	35 : 65
b	*t*Bu	SiPh$_2$*t*Bu	30 : 70
h	C$_6$H$_4$–4–NO$_2$	Si*i*Pr$_3$	30 : 70
f	C$_6$H$_5$	Si*i*Pr$_3$	10 : 90
g	C$_6$H$_4$–4–OMe	Si*i*Pr$_3$	<3 : 97 [a]

[a] Only one isomer detected.

Table 4. Isomer ratio **5h**:**6h** in different solvents at 35°C (determined by ^{1}H-NMR spectroscopy)

Solvent	E_T^N [20]	5h : 6h
C_6D_6	0.111	14 : 86
$CDCl_3$	0.256	30 : 70
$CDCl_2$	0.309	26 : 74
[D$_6$]acetone	0.355	23 : 77
CD_3CN	0.460	19 : 81
CD_3NO_2	0.481	18 : 82

The effect of the solvent on the equilibrium **5h** ⇄ **6h** is given in Table 4. With the exception of benzene, the amount of the monocyclic isomer **6h** increases with the solvent polarity. In fact, the following linear correlation between the equilibrium constant K and Reichardt's[20] normalized solvent polarity parameter E_T^N has been found (correlation coefficient r = 0.9991):

$$K = (-1.33 \pm 0.09) + (9.68 \pm 0.24) \cdot E_T^N$$

In benzene solution, the amount of **6h** is much higher than expected based on the solvent polarity. We assume that solute-solvent complexes preferentially exist for the monocyclic isomer, the overall shape of which is flatter than that of the homopyrazole **5h**.

The temperature dependence of the equilibrium **5h** ⇄ **6h** has been determined in [D$_6$]toluene between 248 and 368 K. Over this range, the equilibrium constant K = [**6h**]/[**5h**] drops from 11.05 to 3.64. From the relationship

$$\ln K = \Delta S^0/R - (\Delta H^0/R) \cdot T^{-1}$$

the following thermodynamic parameters of the equilibrium were obtained (nine different temperatures; correlation coefficient r = 0.993):

$$\Delta H^0(\mathbf{6h}-\mathbf{5h}) = -7.5 \pm 0.4\,\text{kJ mol}^{-1}$$
$$\Delta S^0(\mathbf{6h}-\mathbf{5h}) = -9.6 \pm 1.3\,\text{J mol}^{-1}$$
$$\Delta G^0_{298}(\mathbf{6h}-\mathbf{5h}) = -4.6 \pm 0.8\,\text{kJ mol}^{-1}$$

According to these values, the monocyclic isomer **6h** is energetically more favored, but less so at higher temperatures because of the entropy term. In other words, homopyrazole **5h** has the higher enthalpy because of ring strain, but the vibrational and rotational mobility of the acyl and silyl groups at elevated temperature is less restricted in **5h** as compared to **6h**, where the 1,2-disubstitution causes considerable steric hindrance.

The activation parameters of the isomerization **5h** → **6h** could not be determined by dynamic NMR spectroscopy, since the process remains slow on the NMR time scale at least up to 95°C. In mechanistic terms, the interconversion of **5** and **6** could occur either through a direct sigmatropic 1,5-homodienyl silyl shift or via the azomethine imine intermediate **15** (Scheme 3), which would isomerize reversibly to **6** by a 1,2-($N \rightarrow N'$) silyl migration. In the latter case, **15** would be the common intermediate of the ring inversion **5** ⇄ **5′** and of the isomerization **5** ⇄ **6**, whereby the electrocyclization occurs much faster than the 1,2-silyl migration. An isomerization similar to **15** → **6**, namely (irreversible) 1,2-proton shift in cyclic *N*-vinylazomethine imines, has been proposed[21] and is probably also operating in the acid-catalyzed rearrangement **16** → **17**. However, the experimental facts available so far do not allow to distinguish between the two mechanistic proposals.

This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*. R.M. gratefully acknowledges the receipt of a graduate fellowship from the *Fonds der Chemischen Industrie*. We also want to express our thanks to Professor *P. Binger* (Mülheim/Ruhr) for a gift of 3,3-dimethyl-1-cyclopropene in the early stages of our investigations.

Experimental

IR: Perkin-Elmer IR 397. – ^{1}H NMR: Varian EM 390 (90 MHz), Bruker WP 200 (200 MHz), Bruker AM 400 (400 MHz); internal

standard TMS (δ = 0) or $CHCl_3$ (δ = 7.24). – ^{13}C NMR: Bruker WP 200 (50.28 MHz), Bruker AM 400 (100.61 MHz); internal standard TMS (δ = 0) or $CDCl_3$ (δ = 77.0). The solvent used for recording all NMR spectra was $CDCl_3$. – Melting points: Copper block, temperatures given are not calibrated. – Distillations: Büchi Kugelrohr distillation apparatus, temperatures given are those of the heating mantle. – Elemental analyses: Perkin-Elmer EA 2400. Elemental analyses of compounds **5** and **6**, in some cases, were not satisfactory because of their high hydrolytic lability and the failure to completely purify them by column chromatography or by kugelrohr distillation. – All reactions were carried out in anhydrous solvents under argon, using rigorously dried glassware. – Column chromatography: Merck Lobar columns, LiChroprep Si-60, 40–63 µm. – (1-Diazo-2-oxoalkyl)silanes **1a–c**, **3–g**[1], **1h**[22] were prepared according to literature procedures.

1-Diazo-3-methyl-1-(triisopropylsilyl)-2-butanone (**1d**) was prepared according to ref.[1b]; yellow oil (75%). – IR (film): $\tilde{\nu}$ = 2061 cm^{-1} (vs, C=N_2), 1635 (s, C=O). – ^1H NMR (90 MHz): δ = 1.03 (d, ^3J = 6.0 Hz, SiCHMe_2), 1.15 (d, ^3J = 6.6 Hz, CHMe_2), 1.35 (sept, ^3J = 6.0 Hz, SiCHMe$_2$), 3.03 (sept, ^3J = 6.6 Hz, CHMe$_2$).

$C_{14}H_{28}N_2OSi$ (268.5) Calcd. C 62.61 H 10.53 N 10.43
Found C 62.2 H 10.57 N 8.5

Thermolysis of **1a–e,h** *in the Presence of Cyclopropene* **4**

General Procedure: A solution of the appropriate (1-diazo-2-oxoalkyl)silane **1** in anhydrous ether (20 ml) is placed in a high-pressure Schlenk tube, chilled to 0°C and a 2–15-fold excess of precooled 3,3-dimethyl-1-cyclopropene (**4**)[23] is added. The Schlenk tube is closed tightly and heated at 90°C for a time interval specified below. The solvent and the excess of **4** are removed at 20°C/14 mbar, and the residue is subjected to further purification.

4-(2,2-Dimethyl-1-oxopropyl)-6,6-dimethyl-2-triisopropylsilyl-2,3-diazabicyclo[3.1.0]hex-3-ene (**5a**): From **1a** (0.71 g, 2.50 mmol) and **4** (0.34 g, 5.00 mmol), 4 h; purification by Lobar column chromatography (ether/petroleum ether, 1:1 v/v); kugelrohr distillation at 200°C/0.01 mbar; light-yellow oil (0.66 g, 76%). – IR (film): $\tilde{\nu}$ = 1642 cm^{-1} (s, C=O). – ^1H NMR (90 MHz): δ = 0.83 (s, CMe_2), 1.07–1.57 (m, SiiPr$_3$), 1.30 (s, tBu), 2.92 (d, ^3J = 6.7 Hz, 5-H), 3.58 (d, ^3J = 6.7 Hz, 1-H). – ^{13}C NMR (50.3 MHz): δ = 5.9 (s, CMe_2), 11.7 (d, SiCH), 17.7 (q, SiCHMe_2), 27.7 (q, CMe_3), 38.9 (d, ^1J = 175.1 Hz, C-5), 43.3 (s, CMe_3), 58.0 (d, ^1J = 180.5 Hz, C-1), 147.6 (s, C=N), 201.6 (s, C=O).

$C_{20}H_{38}N_2OSi$ (350.7) Calcd. C 68.49 H 10.94 N 7.99
Found C 68.0 H 10.73 N 7.1

2-(tert-Butyldiphenylsilyl)-4-(2,2-dimethyl-1-oxopropyl)-6,6-dimethyl-2,3-diazabicyclo[3.1.0]hex-3-ene (**5b**) *and 1-(tert-Butyldiphenylsilyl)-6-(2,2-dimethyl-1-oxopropyl)-1,4-dihydro-4,4-dimethylpyridazine* (**6b**): From **1b** (0.91 g, 2.50 mmol) and **4** (0.34 g, 5.00 mmol), 2 h. The residue is dissolved in ether (3 ml), and at 0°C a colorless precipitate is obtained. Recrystallization from toluene yields **6b** (0.67 g, 62%) as colorless crystals, m.p. 163–165°C. Dissolution of **6b** in organic solvents results in the formation of an equilibrium mixture of **5b** and **6b**. – Spectroscopic data for **5b**: IR ($CHCl_3$): $\tilde{\nu}$ = 1637 cm^{-1} (s, C=O). – ^1H NMR (90 MHz): δ = 0.75 (s, CMe_2), 0.92 (s, SitBu), 1.12 (s, COtBu), 2.83 (d, ^3J = 6.6 Hz, 5-H), 3.30 (d, ^3J = 6.6 Hz, 1-H), 7.25–7.78 (m, SiC_6H_5). – Spectroscopic data for **6b**: IR (KBr): $\tilde{\nu}$ = 1673 cm^{-1} (vs, C=O). – ^1H NMR (90 MHz): δ = 0.75 (s, SitBu), 0.92 (s, CMe_2), 1.18 (s, COtBu), 5.28 (d, $|^4J|$ = 2.3 Hz, 5-H), 6.55 (d, $|^4J|$ = 2.3 Hz, 3-H), 7.25–7.78 (m, SiC_6H_5).

$C_{27}H_{36}N_2OSi$ (432.7) Calcd. C 74.93 H 8.40 N 6.48
Found C 74.7 H 8.46 N 6.3

2-(tert-Butyldimethylsilyl)-4-(2,2-dimethyl-1-oxopropyl)-6,6-dimethyl-2,3-diazabicyclo[3.1.0]hex-3-ene (**5c**) *and 1-(tert-Butyldimethylsilyl)-6-(2,2-dimethyl-1-oxopropyl)-1,4-dihydro-4,4-dimethylpyridazine* (**6c**): From **1c** (0.60 g, 2.50 mmol) and **4** (0.34 g, 5.00 mmol), 4 h; purification by Lobar column chromatography (ether/petroleum ether, 1:1 v/v). A light-yellow oil (0.52 g, 67%) is obtained, which is very sensitive to moisture and decomposes on attempted kugelrohr distillation. – Spectroscopic data for **5c**: IR (film): $\tilde{\nu}$ = 1643 cm^{-1} (s, C=O). – ^1H NMR (90 MHz): δ = 0.23 (s, $SiMe_2$), 0.73 (s, CMe_2), 0.93 (s, SitBu), 1.23 (s, COtBu), 2.83 (d, ^3J = 6.6 Hz, 5-H), 3.49 (d, ^3J = 6.6 Hz, 1-H). – ^{13}C NMR (50.3 MHz): δ = –5.0 (q, $SiMe_2$), 5.5 (s, CMe_2), 18.4 (s, SiCMe_3), 25.9 (q, SiCMe_3), 27.7 (q, CMe_3), 38.9 (d, ^1J = 175.6 Hz, C-5), 43.4 (s, CMe_3), 57.2 (d, ^1J = 181.4 Hz, C-1), 147.4 (s, C=N), 201.7 (s, C=O). – Spectroscopic data for **6c**: IR (film): $\tilde{\nu}$ = 1678 cm^{-1} (vs, C=O). – ^1H NMR (90 MHz): δ = 0.12 (s, $SiMe_2$), 0.90 (s, SitBu), 1.03 (s, CMe_2), 1.23 (s, COtBu), 4.90 (d, $|^4J|$ = 2.3 Hz, 5-H), 6.37 (d, $|^4J|$ = 2.3 Hz, 3-H). – ^{13}C NMR (50.3 MHz): δ = –3.4 (q, $SiMe_2$), 19.6 (s, SiCMe_3), 27.1, 27.4 (2 q, SiCMe_3 and CMe_2), 28.5 (q, CMe_3), 29.3 (s, C-4), 43.9 (s, CMe_3), 110.3 (d, ^1J = 159.5, C-5), 138.6 (s, C-6), 143.0 (d, ^1J = 197.7 Hz, C-3), 207.3 (s, C=O).

6,6-Dimethyl-4-(2-methyl-1-oxopropyl)-2-(triisopropylsilyl)-2,3-diazabicyclo[3.1.0]hex-3-ene (**5d**), *1,4-Dihydro-4,4-dimethyl-6-(2-methyl-1-oxopropyl)-1-(triisopropylsilyl)pyridazine* (**6d**) *and 2,2,5-Triisopropyl-3,3-dimethyl-1-oxa-2-sila-4-cyclopentene* (**8d**): From **1d** (0.67 g, 2.50 mmol) and **4** (2.44 g, 35.82 mmol), 6 h. Purification by Lobar column chromatography (ether/petroleum ether, 1:1 v/v) yields an unseparable mixture of **5d**/**6d** and **8d** as a yellow oil [0.43 g; **5d**/**6d**:**8d** = 86:14 (^1H NMR), i.e. 46% of **5d**/**6d** and 8% of **8d**]. – Spectroscopic data for **5d**: IR (film): $\tilde{\nu}$ = 1660 cm^{-1} (s, C=O). – ^1H NMR (400 MHz): δ = 0.81 (s, CMe_2), 1.12 (d, ^3J = 6.9 Hz, CHMe_2), 1.13 (d, ^3J = 7.4 Hz, SiCHMe_2), 1.35 (sept, ^3J = 7.4 Hz, SiCHMe$_2$), 2.84 (d, ^3J = 6.6 Hz, C-5), 3.56 (sept, ^3J = 6.9 Hz, CHMe$_2$), 3.67 (d, ^3J = 6.6 Hz, C-1). – ^{13}C NMR (100.6 MHz): δ = 6.0 (s, CMe_2), 12.0 (d, SiCH), 17.9 (q, SiCHMe), 19.3 (q, CHMe), 34.5 (d, CHMe), 37.3 (d, ^1J = 176.3 Hz, C-5), 59.7 (d, ^1J = 180.9 Hz, C-1), 148.0 (s, C=N), 200.7 (s, C=O). – Spectroscopic data for **6d**: IR (film): $\tilde{\nu}$ = 1694 cm^{-1} (vs, C=O). – ^1H NMR (400 MHz): δ = 1.07 (d, ^3J = 7.5 Hz, SiCHMe_2), 1.10 (s, CMe_2), 1.14 (d, ^3J = 6.8 Hz, CHMe_2), 1.40 (sept, ^3J = 7.5 Hz, SiCHMe$_2$), 3.28 (sept, ^3J = 6.8 Hz, CHMe$_2$), 5.49 (d, $|^4J|$ = 2.1 Hz, 5-H), 6.42 (d, $|^4J|$ = 2.1 Hz, 3-H). – ^{13}C NMR (100.6 MHz): δ = 14.5 (d, SiCH), 19.0 (q,SiCHMe), 20.0 (q, CHMe), 26.0 (q, CMe_2), 30.5 (s, CMe_2), 35.0 (d, CHMe), 116.3 (d, ^1J = 165.2 Hz, C-5), 139.7 (s, C-6), 142.0 (d, ^1J = 181.1 Hz, C-1), 200.9 (s, C=O). – Spectroscopic data for **8d**: IR (film): $\tilde{\nu}$ = 1632 cm^{-1} (m, C=C). – ^1H NMR (90 MHz): δ = 1.0–1.2 (m, SiiPr$_2$, CMe_2 and CHMe_2), 2.30 (sept, CHMe$_2$), 4.40 (s, 4-H).

4-Acetyl-6,6-dimethyl-2-(triisopropylsilyl)-2,3-diazabicyclo[3.1.0]hex-3-ene (**5e**) *and 6-Acetyl-1,4-dihydro-4,4-dimethyl-1-(triisopropylsilyl)pyridazine* (**6e**): From **1e** (0.72 g, 3.00 mmol) and **4** (0.98 g, 14.38 mmol), 4 h. Purification by Lobar column chromatography (ether/petroleum ether, 6:4 v/v) yields an unseparable mixture of **5e**/**6e** and **8e** as a yellow oil [0.43 g; **5e**/**6e**:**8e** = 55:45 (^1H NMR), i.e. 30% of **5e**/**6e** and 24% of **8e**]. – Spectroscopic data for **5e**: IR (film): $\tilde{\nu}$ = 1653 cm^{-1} (s, C=O). – ^1H NMR (90 MHz): δ = 0.82 (s, CMe_2), 0.96–1.60 (m, SiiPr$_3$), 2.40 (s, COMe), 2.85 (d, ^3J = 6.8 Hz, 5-H), 3.70 (d, ^3J = 6.8 Hz, 1-H). – Spectroscopic data for **6e**: IR (film): $\tilde{\nu}$ = 1693 cm^{-1} (vs, C=O). – ^1H NMR (90 MHz): δ = 0.96–1.60 (m, SiiPr$_3$), 1.06 (s, CMe_2), 2.36 (s, COMe), 5.42 (d, $|^4J|$ = 2.1 Hz, 5-H), 6.42 (d, $|^4J|$ = 2.1 Hz, 3-H). – IR and ^1H-NMR data for **8e** correspond to the literature data[1c].

4-Benzoyl-6,6-dimethyl-2-(triisopropylsilyl)-2,3-diazabicyclo[3.1.0]hex-3-ene (**5f**) *and 6-Benzoyl-1,4-dihydro-4,4-dimethyl-1-*

(triisopropylsilyl)pyridazine (**6f**): To a chilled solution (0°C) of **1f** (2.42 g, 8.00 mmol) in ether (40 ml) is added precooled **4** (1.10 g, 16.00 mmol). The solution is refluxed at 36°C, the reflux condenser being cooled with methanol kept at −30°C. After 4 h, the solvent and the excess of **4** are removed at 20°C/14 mbar, and pentane (3 ml) is added to the remaining residue. On cooling to −78°C, a yellow precipitate forms which is recrystallized from ether/pentane to yield **6f** as yellow crystals (1.62 g, 55%), m.p. 89−92°C. In solution, an equilibrium between **5f** and **6f** exists. − Spectroscopic data for **5f**: ^{1}H NMR (90 MHz): δ = 0.90 (s, CMe_2), 1.05−1.58 (m, Si*i*Pr$_3$), 3.13 (d, ^3J = 6.6 Hz, 5-H), 3.73 (d, ^3J = 6.6 Hz, 1-H), 7.3−8.3 (m, C_6H_5). − Spectroscopic data for **6f**: IR (KBr): $\tilde{\nu}$ = 1662 cm^{-1} (s, C=O). − ^{1}H NMR (90 MHz): δ = 1.05−1.58 (m, Si*i*Pr$_3$), 1.15 (s, CMe_2), 5.00 (d, $|\,^4J\,|$ = 2.3 Hz, 5-H), 6.43 (d, $|\,^4J\,|$ = 2.3 Hz, 3-H), 7.33−7.95 (m, C_6H_5). − ^{13}C NMR (50.3 MHz): δ = 14.0 (d, SiCH), 19.0 (q, SiCH*Me*$_2$), 27.0 (q, C*Me*$_2$), 30.7 (s, *C*Me$_2$), 119.5 (d, ^1J = 168.2 Hz, C-5), 128.1 (d, *m*-C_6H_5), 129.9 (d, *o*-C_6H_5), 132.3 (d, *p*-C_6H_5), 137.7 (s, *i*-C_6H_5), 139.7 (s, C-6), 141.9 (d, ^1J = 181.1 Hz, C-3), 192.2 (s, C=O).

$C_{22}H_{34}N_2OSi$ (370.7) Calcd. C 71.28 H 9.26 N 7.56
Found C 71.0 H 9.14 N 7.4

1,4-Dihydro-6-(4-methoxybenzoyl)-4,4-dimethyl-1-(triisopropylsilyl)pyridazine (**6g**): From **1g** (1.35 g, 4.06 mmol) and **4** (0.80 g, 11.74 mmol), 4 h. Purification by Lobar column chromatography (ether/petroleum ether, 1:9 v/v) yields **6g** (0.53 g, 33%) as a red oil, which is very sensitive to moisture and decomposes on attempted kugelrohr distillation. − IR (film): $\tilde{\nu}$ = 1645 cm^{-1} (s, C=O). − ^{1}H NMR (90 MHz): δ = 0.94−1.52 (m, Si*i*Pr$_3$), 1.12 (s, CMe_2), 3.90 (s, OMe), 4.97 (d, $|\,^4J\,|$ = 2.2 Hz, 5-H), 6.45 (d, $|\,^4J\,|$ = 2.2 Hz, 3-H), 7.44 (AA′BB′ system, δ_A = 7.92, δ_B = 6.96, J_{AB} = 9.0 Hz, C_6H_4).

6,6-Dimethyl-4-(4-nitrobenzoyl)-2-(triisopropylsilyl)-2,3-diazabicyclo[3.1.0]hex-3-ene (**5h**) *and 1,4-Dihydro-4,4-dimethyl-6-(4-nitrobenzoyl)-1-(triisopropylsilyl)pyridazine* (**6h**): A solution of **1h** (1.40 g, 4.00 mmol) in ether (40 ml) is chilled to 0°C and precooled **4** (0.55 g, 8.0 mmol) is added. The solution is refluxed at 36°C for 4 h, the reflux condenser being cooled with methanol kept at −30°C. The solvent and the excess of **4** are removed at 20°C/14 mbar, and the residual oil is purified by Lobar column chromatography ($CHCl_3$). Upon crystallization from ether/pentane, **6h** (1.13 g, 68%) is obtained as orange-red crystals, m.p. 98−101°C. In solution, an equilibrium mixture of isomers **5h** and **6h** is found. − Spectroscopic data of **5h**: IR ($CHCl_3$): $\tilde{\nu}$ = 1620 cm^{-1} (m, C=O), 1600 (s), 1523 (vs, NO_2), 1350 (vs, NO_2). − ^{1}H NMR (90 MHz): δ = 0.90 (s, CMe_2), 1.03−1.57 (m, Si*i*Pr$_3$), 3.12 (d, ^3J = 6.6 Hz, 5-H), 3.77 (d, ^3J = 6.6 Hz, 1-H), 8.27 (s, C_6H_4). − ^{13}C NMR (50.3 MHz): δ = 6.8 (s, CMe_2), 11.7 (d, SiCH), 17.7 (q, SiCH*Me*$_2$), 38.4 (d, ^1J = 173.9 Hz, C-5), 59.9 (d, ^1J = 182.2 Hz, C-1), 122.8 (d, *m*-C_6H_4), 131.0 (d, *o*-C_6H_4), 143.3 (s, *i*-C_6H_4), 149.3 (s, C=N), 149.4 (s, *p*-C_6H_4), 185.5 (s, C=O). − Spectroscopic data for **6h**: IR (KBr): $\tilde{\nu}$ = 1657 cm^{-1} (s, C=O), 1600 (s), 1523 (vs, NO_2), 1345 (vs, NO_2). − ^{1}H NMR (90 MHz): δ = 1.03−1.57 (m, Si*i*Pr$_3$), 1.13 (s, CMe_2), 4.97 (d, $|\,^4J\,|$ = 2.3 Hz, 5-H), 6.45 (d, $|\,^4J\,|$ = 2.3 Hz, 3-H), 7.95 and 8.33 (AA′BB′, J_{AB} = 9.0 Hz, C_6H_4). − ^{13}C NMR (50.3 MHz): δ = 13.7 (d, SiCH), 18.7 (q, SiCH*Me*$_2$), 26.6 (q, C*Me*$_2$), 30.8 (s, *C*Me$_2$), 121.5 (d, ^1J = 166.0 Hz, C-5), 123.5 (d, *m*-C_6H_4), 130.8 (d, *o*-C_6H_4), 139.8 (s, C-6), 142.2 (d, ^1J = 181.6 Hz, C-3), 143.1 (s, *i*-C_6H_4), 150.0 (s, *p*-C_6H_4), 190.5 (s, C=O).

$C_{22}H_{33}N_3O_3Si$ (415.7) Calcd. C 63.56 H 8.02 N 10.11
Found C 63.2 H 7.96 N 10.3

1,4-Dihydro-4,4-dimethyl-6-(4-nitrobenzoyl)pyridazine (**9**) *by Hydrolysis of* **6h**: A solution of **6h** (1.13 g, 2.72 mmol) in wet ether is stirred for 10 d. After removal of the solvent, an orange solid is obtained, which is recrystallized from ether/petroleum ether; orange powder (0.64 g, 94%), m.p. 153−155°C. − IR (KBr): $\tilde{\nu}$ = 3285 cm^{-1} (s, br, NH), 1646 (s, C=O), 1597 (s), 1525 (vs, NO_2), 1342 (vs, NO_2). − ^{1}H NMR ($CDCl_3$): δ = 1.20 (s, C*Me*$_2$), 5.20 [dd, $|\,^4J$(5-H,3-H)$\,|$ = $|\,^4J$(5-H,NH)$\,|$ = 2.3 Hz, 5-H], 6.35 (d, $|\,^4J\,|$ = 2.3 Hz, 3-H), 7.90 and 8.38 [AA′BB′, J_{AB} = 9.0 Hz, C_6H_4), 8.22 (broad, NH).

$C_{13}H_{13}N_3O_3$ (259.3) Calcd. C 60.21 H 5.06 N 16.21
Found C 60.0 H 5.03 N 16.1

Dimethyl 6-Benzoyl-4-tert-butyl-1,4-dihydro-4-methyl-1-(triisopropylsilyl)pyridazine-3-phosphonate (**11a**): A solution of **1f** (2.40 g, 7.93 mmol) in ether (10 ml) is added gradually to a refluxing solution of cyclopropene **10**[11] (3.30 g, 15.12 mmol) in ether (10 ml). After 2 h at reflux, the solvent is evaporated, and the residue is separated by Lobar column chromatography (ether). A yellow oil is obtained which slowly crystallizes. Recrystallization from ether/pentane yields a yellow powder (2.04 g, 49%), m.p. 108−111°C. − IR (KBr): $\tilde{\nu}$ = 1655 cm^{-1} (vs, C=O), 1246 (s, P=O), 1030 (vs, POMe). − ^{1}H NMR (90 MHz): δ = 1.10 (s, *t*Bu), 1.00−1.57 (m, Si*i*Pr$_3$), 1.35 (4-Me), 3.62 and 3.78 [2 d, ^3J(P,H) = 11.4 Hz, diastereotopic POMe$_2$], 4.98 [d, $|\,^4J$(P,H)$\,|$ = 8.4 Hz, 5-H], 7.40−7.93 (m, C_6H_5).

$C_{27}H_{45}N_2O_4PSi$ (520.8) Calcd. C 62.26 H 8.73 N 5.38
Found C 62.3 H 8.72 N 5.2

Dimethyl 4-tert-Butyl-1,4-dihydro-4-methyl-6-(4-nitrobenzoyl)-1-(triisopropylsilyl)pyridazine-3-phosphonate (**11b**): A solution of **1h** (1.14 g, 3.28 mmol) and **10** (0.75 g, 3.44 mmol) in benzene (10 ml) is refluxed for 1 h. The solvent is evaporated, and the residue is separated by column chromatography (ether). An orange-red oil is obtained which decomposes on attempted kugelrohr distillation. − IR (film): $\tilde{\nu}$ = 1667 cm^{-1} (s, C=O), 1597 (s), 1523 (s, NO_2), 1341 (s, NO_2), 1251 (vs, P=O), 1030 (vs, POMe). − ^{1}H NMR (90 MHz): δ = 1.03−1.43 (m, Si*i*Pr$_3$), 1.13 (s, *t*Bu), 1.37 (s, 4-Me), 3.65 and 3.81 [2 d, ^{3}J(P,H) = 11.4 Hz, diastereotopic PO*Me*$_2$), 4.94 (d, $|\,^4J$(P,H)$\,|$ = 8.4 Hz, 5-H), 7.98 and 8.37 (AA′BB′, J_{AB} = 9.0 Hz, C_6H_4). No correct elemental analysis was obtained.

4-Acetyl-6,6-dimethyl-2-phenyl-2,3-diazabicyclo[3.1.0]hex-3-ene (**14**): A solution of 2-oxo-*N*-phenylpropanehydrazonoyl chloride[24] (0.59 g, 3.00 mmol) in benzene (5 ml) and ether (10 ml) is placed in a Schlenk tube and cooled to 0°C. After addition of 3,3-dimethyl-1-cyclopropene (**4**)[23] (0.70 g, 10.24 mmol) and triethylamine (1.00 ml, 7.21 mmol), the tube is closed tightly and heated to 80°C for 2 h. On cooling to 0°C, a colorless precipitate of triethylammonium chloride forms which is filtered off. The solvent is evaporated, and the oily residue is subjected to Lobar column chromatography (ether/petroleum ether, 1:1 v/v). Compound **14** is isolated as a brown oil, from which an orange powder is obtained in pentane at −78°C; yield: 0.35 g (50%), m.p. 89−90°C. − IR (KBr): $\tilde{\nu}$ = 1650 cm^{-1} (vs, C=O), 1590 (s). − ^{1}H NMR (90 MHz): δ = 0.93 (s, CMe_2), 2.52 (s, COMe), 3.05 (d, ^3J = 6.6 Hz, 5-H), 4.08 (d, ^3J = 6.6 Hz, 1-H), 7.0−7.5 (m, C_6H_5). − ^{13}C NMR (50.3 MHz): δ = 8.2 (C-6), 24.9 (CO*Me*), 37.1 (d, J = 175.9 Hz, C-5), 55.3 (d, ^1J = 185.6 Hz, C-1), 114.8 (d), 122.8 (d), 129.3 (d), 142.1 (s), 146.4 (s, C-4), 194.0 (s, CO).

$C_{14}H_{16}N_2O$ (228.3) Calcd. C 73.64 H 7.08 N 12.37
Found C 73.7 H 7.00 N 12.3

X-ray Crystal Structure Analysis of **6b**: *Crystal data:* $C_{27}H_{36}N_2OSi$, molecular mass 432.7, triclinic, space group $P\bar{1}$, a = 11.582(2), b = 11.666(3), c = 11.363(3) Å, α = 98.76(3), β = 117.89(2), γ = 101.51(2)°, Z = 2, d_{calc} = 1.13 g cm^{-3}. − *Data*

collection: Crystal size 0.50 × 0.25 × 0.25 mm, monochromatized Mo-K_α radiation, 2726 independent reflections in the range $2.0 \leq \Theta \leq 21.0°$, $\omega/2\Theta$ scan, scan width $(0.80 + 0.35 \tan\Theta)°$. – *Structure solution and refinement*[25]: Structure solution by direct methods (MULTAN), refinement by a full-matrix least-squares method. Hydrogen atom positions were localized in a ΔF map and refined with fixed isotropic temperature factors. With 2119 reflections $[I > 2\sigma(I)]$ and 424 variables, refinement converged at $R = 0.074$, $R_w = (w \cdot \Delta^2 F / \sum w \cdot F_o^2)^{1/2} = 0.073$ $\{w = 1/[\sigma^2 + (0.025 \cdot F_o)^2]\}$; shift/error ratio ≤ 1.18, residual electron density ≤ 0.30 eÅ^{-3}. Positional and thermal parameters are given in Table 5[26].

Table 5. Atomic coordinates and isotropic temperature factors [Å^2] for **6b**. Standard deviations are in parentheses

Atom	*x / a*	*y / b*	*z / c*	U_{eq}
Si	0.8858(1)	0.1827(2)	0.2304(2)	0.040(1)
O	0.9551(4)	0.4331(4)	0.1918(4)	0.061(2)
N1	0.8368(4)	0.1868(4)	0.0604(4)	0.042(2)
N2	0.8641(4)	0.0905(4)	-0.0028(4)	0.052(2)
C1	0.8160(5)	0.0670(6)	-0.1320(6)	0.064(2)
C2	0.7217(5)	0.1252(6)	-0.2292(5)	0.057(2)
C3	0.7422(6)	0.1256(7)	-0.3531(6)	0.083(3)
C4	0.5747(6)	0.0494(7)	-0.2803(7)	0.088(3)
C5	0.7536(5)	0.2491(5)	-0.1455(5)	0.051(2)
C6	0.8018(5)	0.2741(5)	-0.0119(5)	0.040(2)
C7	0.8497(5)	0.4003(5)	0.0811(5)	0.044(2)
C8	0.7687(5)	0.4921(5)	0.0356(5)	0.052(2)
C9	0.7935(6)	0.5758(6)	0.1674(7)	0.078(3)
C10	0.6178(6)	0.4320(6)	-0.0611(7)	0.077(3)
C11	0.8336(7)	0.5685(6)	-0.0313(7)	0.097(3)
C12	0.8193(5)	0.0204(5)	0.2304(5)	0.050(2)
C13	0.6764(6)	-0.0475(6)	0.1077(6)	0.066(3)
C14	0.9150(6)	-0.0548(6)	0.2311(6)	0.066(3)
C15	0.8148(6)	0.0259(6)	0.3646(6)	0.062(2)
C16	1.0762(5)	0.2372(5)	0.3413(5)	0.042(2)
C17	1.1559(6)	0.2584(6)	0.2815(6)	0.065(3)
C18	1.2988(6)	0.2914(7)	0.3581(6)	0.081(3)
C19	1.3649(6)	0.3011(6)	0.4950(7)	0.077(3)
C20	1.2902(6)	0.2812(6)	0.5579(6)	0.069(3)
C21	1.1487(5)	0.2487(6)	0.4814(5)	0.057(2)
C22	0.7967(5)	0.2754(5)	0.2907(5)	0.037(2)
C23	0.8597(5)	0.3538(5)	0.4174(5)	0.052(2)
C24	0.7870(6)	0.4122(6)	0.4636(6)	0.064(2)
C25	0.6494(5)	0.3866(6)	0.3778(6)	0.065(2)
C26	0.5855(5)	0.3111(6)	0.2511(6)	0.066(2)
C27	0.6556(5)	0.2517(5)	0.2021(5)	0.052(2)

CAS Registry Numbers

1a: 106435-62-5 / **1b**: 110907-77-2 / **1c**: 106435-61-4 / **1d**: 139130-63-5 / **1e**: 106435-59-0 / **1f**: 139130-64-6 / **1g**: 96845-68-0 / **1h**: 132298-34-1 / **4**: 3907-06-0 / **5a**: 139130-65-7 / **5c**: 139130-67-9 / **5d**: 139130-69-1 / **5e**: 139130-72-6 / **6b**: 139130-66-8 / **6c**: 139130-68-0 / **6d**: 139130-70-4 / **6e**: 139130-73-7 / **6f**: 139130-74-8 / **6g**: 139130-75-9 / **6h**: 139130-76-0 / **8d**: 139130-71-5 / **8e**: 106435-69-2 / **9**: 139130-80-6 / **10**: 26580-38-1 / **11a**: 139130-77-1 / **11b**: 139130-78-2 / **14**: 139130-79-3 / $CH_3COC(NNHPh)Cl$: 18440-58-9

☆ Dedicated to Professor *Hans-Friedrich Grützmacher* on the occasion of his 60th birthday.

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[25] The program system *Structure Determination Package* (Enraf-Nonius, Delft, The Netherlands) was used.

[26] Further crystal structure data have been deposited at Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Germany. Inquiries should be accompanied by the depository number CSD-55587, the names of the authors and the reference to this publication.

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