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THE REARRANGEMENT OF THE TRIMETHYLSILYL GROUP IN (TRIMETHYLSILYL)PYRAZOLES

DANIEL H. O'BRIEN AND CHANG-PO HRUNG*
Department of Chemistry, Texas A&M University, College Station, Texas 77843 (U.S.A.)
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SUMMARY

A new class of compounds, the *N*-(trimethylsilyl)pyrazoles, has been prepared. Four compounds with differing substituents on the pyrazole ring show non-equivalent 3,5-substituents in their NMR spectra. These compounds undergo temperature-dependent NMR spectral changes with the 3,5-substituents becoming equivalent at high temperatures. These spectral changes are due to the rearrangement of the trimethylsilyl group between ring nitrogens. The activation energies indicate that the rearrangement is sensitive to the size of the 3,5-substituents and to the electronic influences of all three ring substituents.

INTRODUCTION

NMR evidence has recently been presented for the rearrangement of silyl groups between various electronegative atoms. Temperature-dependent spectral changes indicate the rearrangement of the trimethylsilyl group between oxygens in (trimethylsilyl)acetylacetonate[1] and between nitrogen and oxygen in trimethylsilyl-substituted anilides[2] and *N*-silylsilylimidates[3]. A more complex rearrangement of the two dialkylsilyl groups was found in the six-membered disiloxadiazines[4]. Intramolecular 1,2 shifts of trimethylsilyl groups have been observed for 1,2-bis(trimethylsilyl)indene[5]. Evidence has also been presented for the σ-rearrangement of the trimethylsilyl group in (trimethylsilyl)cyclopentadiene[6,7]. These conclusions were disputed[8]. The observed averaging of the ring protons was attributed to hydride shift rather than rearrangement of the trimethylsilyl group. However, recent evidence indicates that the rate of hydrogen migration is 10^6 slower than trimethylsilyl migration[9].

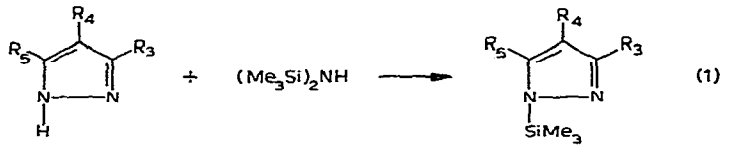
We wish to report the preparation and characterization of a new group of compounds, the *N*-(trimethylsilyl)pyrazoles. These compounds undergo temperature-dependent NMR spectral changes due to the rearrangement of the trimethylsilyl group between the ring nitrogens. The activation energies for this rearrangement indicate that it is sensitive to the electronic influence of all of the ring substituents and to the size of the 3,5-substituents.

* Based on the M.S. Thesis of C.P.H., Texas A&M University, May, 1970.

RESULTS AND DISCUSSION

Syntheses

N-(Trimethylsilyl)pyrazoles were synthesized in good yield (60 to 85%) by the reaction of pyrazole or substituted pyrazoles with hexamethyldisilazane in the presence of a small amount of ammonium sulfate[10]. Four compounds were synthesized in this manner with different substituents in the three ring positions [eqn. (1)].



(1)

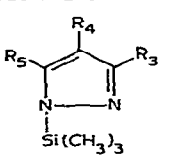
(I): R_3, R_4, R_5 = H
(II): R_3, R_5 = CH_3; R_4 = H
(III): R_3, R_4, R_5 = CH_3
(IV): R_3, R_5 = CF_3; R_4 = H

In addition to reasonable elemental analysis, NMR and IR evidence was used to prove the structures of these new compounds. The IR of each exhibited a strong band at 9.5–9.9 μ characteristic of the silicon–nitrogen stretching frequency[11]. The band for the pyrazole N–H was absent. In the NMR, the disappearance of the N–H resonance and the presence of a trimethylsilyl resonance of the correct integrated intensity indicate the formation of a silicon–nitrogen bond. All of the compounds were extremely moisture sensitive and readily hydrolyzed to give the initial pyrazole and hexamethyldisiloxane.

A summary of the NMR data for compounds (I)–(IV) is presented in Table 1.

TABLE 1

NMR SPECTRAL DATA FOR (TRIMETHYLSILYL)PYRAZOLES



Compound	B.p. (°C)	Chemical shifts (δ)[a]			Peak separation 3,5-substituents[b] (Hz)
		R_3	R_4	R_5	
(I)	152–153	7.68 d	6.22 m	7.56 d	11.6
(II)	185–186	2.10 b	5.70 b	2.16 d	6.0
(III)	204–205	2.01 s	1.76 s	2.06 b	5.0
(IV)	135–136	[c] b	6.72 b	[c] m	447.4

[a] Chemical shifts reported in ppm downfield from TMS (internal); multiplicity of peaks: s, singlet; d, doublet; m, multiplet; b, broad peak with unresolved fine structure. [b] Peak separation at 100 MHz. [c] Fluorine-19 chemical shifts not determined.

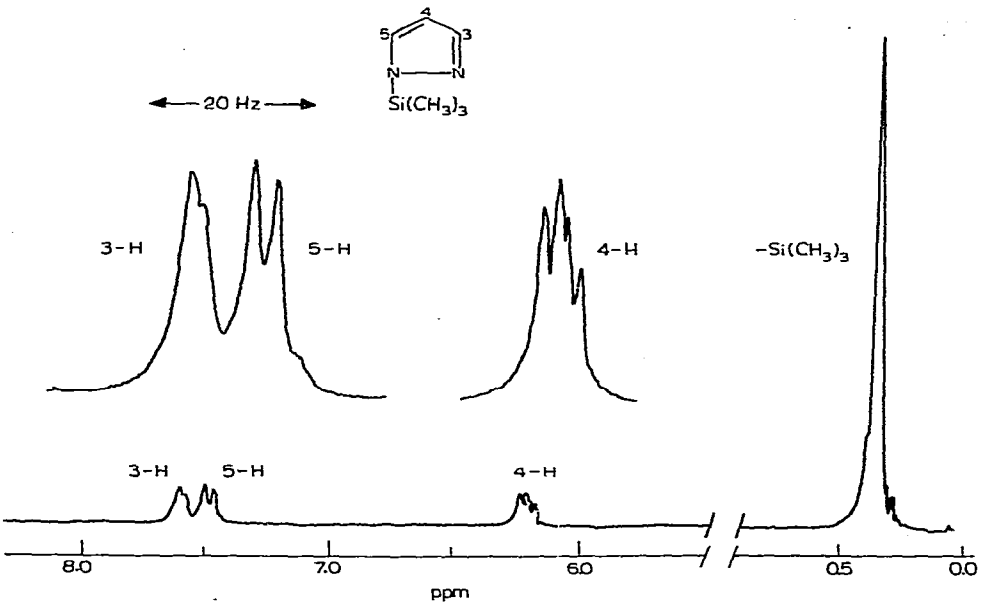


Fig. 1. Room temperature spectrum of (trimethylsilyl)pyrazole (I) at 60 MHz (neat liquid).

For (I)–(III), the proton spectra show the non-equivalence of the 3,5-substituents at room temperature. Compound (I) has two doublets for the 3,5-hydrogens and a doublet of doublets for the 4-hydrogen (Fig. 1). Coupling between the 3,4-hydrogens and the 4,5-hydrogens is slightly different (J_{34} 1.2 Hz, J_{45} 2.2 Hz). The upfield resonance (δ 7.56 ppm) is *tentatively* assigned to the 5-hydrogen based on the expectation that this coupling will be larger, reflecting the greater double bond character of the C_4–C_5 bond. Compound (II) shows two resonances for the 3,5-methyl groups. One is a broadened singlet with unresolvable coupling to the 4-hydrogen while the other is a doublet. Compound (III) also shows two resonances for the 3,5-methyl groups.

The ^{19}F NMR spectrum of compound (IV) shows two separate peaks for the 3,5-trifluoromethyl groups. The trimethylsilyl resonances for (I)–(III) are sharp singlets. However, for (IV) the trimethylsilyl resonance is a quartet [$J(CF_3$–$SiCH_3)$ 0.76 Hz]. This quartet is caused by the long-range coupling of the silicon methyls to *one* of the trifluoromethyl groups through six bonds. This long-range coupling further substantiates the non-equivalence of the 3,5-substituents of the (trimethylsilyl)pyrazoles at room temperature.

Thermal rearrangement of the (trimethylsilyl)pyrazoles

The peak separation between the 3,5-substituents of each compound was found to be a function of temperature. As the temperature is increased, the peak separation decreases, the peaks coalesce and gradually sharpen. These changes were found to be completely reversible, the original spectrum being obtained when the temperature is lowered. Variable temperature NMR spectra for (II) and (III) are presented in Figs. 2 and 3. This change is particularly apparent for (III) which has a methyl group in the 4-position differing only slightly in chemical shift from the 3,5-

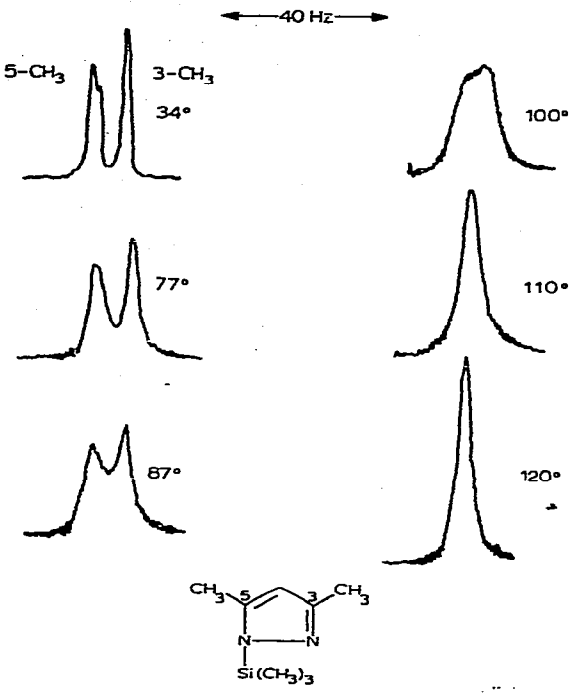
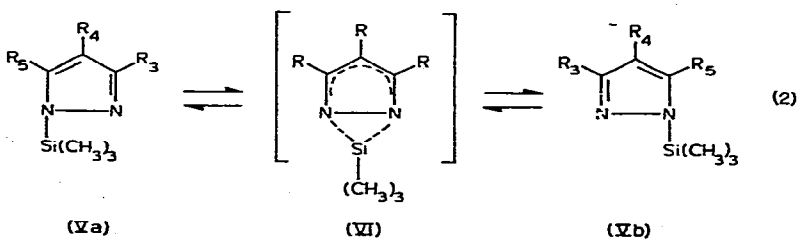


Fig. 2. Variable temperature spectra of 3,5-methyls of (II) at 60 MHz (neat liquid).

methyls (Fig. 3). It can be seen clearly that the resonance due to the 4-methyl undergoes no change during the coalescence of the 3,5-resonances. Therefore, the 4-methyl resonance is not influenced by the rate process which causes the 3,5-substituents to coalesce.

These thermal phenomena are best explained by the intramolecular rearrangement of the trimethylsilyl group between ring nitrogens [eqn. (2)]. Although only limited evidence is available for dilute solutions because of the difficulty in finding a suitable solvent, similar coalescence temperatures and activation energies *above* coalescence were found for neat liquids and dilute solutions. This indicates that the process is intramolecular and is best described as shown in eqn. (2). It should be noted, however, that the same spectral changes would result if migration occurred from N_1 to N_2 via carbons 3, 4 and 5, *provided* the amount of *C*-bonded trimethylsilyl isomers remained small. The rearrangement shown by eqn. (2) can be regarded as an



(2)

(Va) (VI) (Vb)

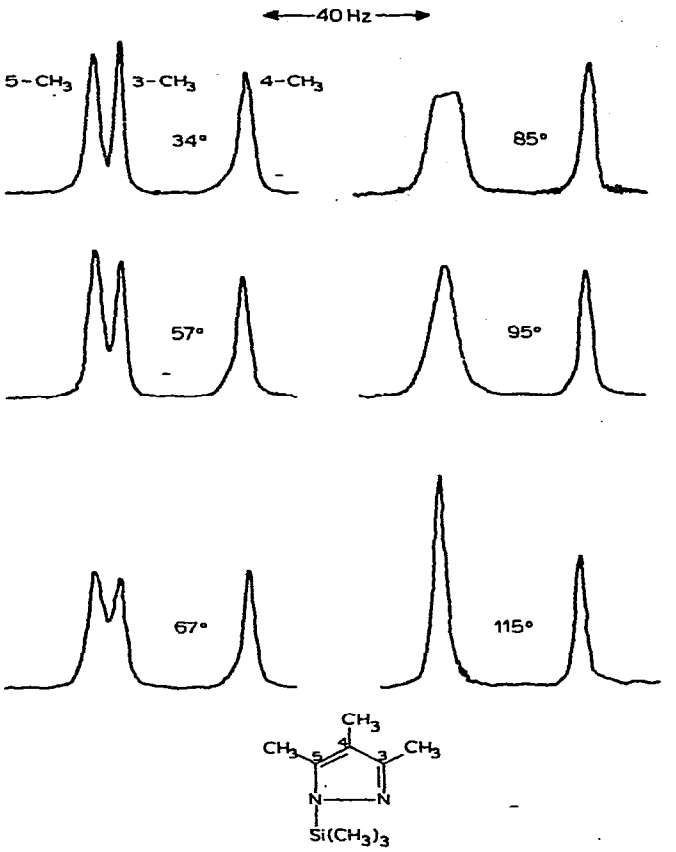


Fig. 3. Variable temperature spectra of 3, 4, 5-methyls of (III) at 60 MHz (neat liquid).

intramolecular substitution at silicon. It has a similarity to the facile anionic rearrangements of trimethylsilyl groups in (trimethylsilyl)hydrazines reported by West[12].

The activation energies for (I)–(IV) calculated from linewidth measurements are collected in Table 2. The observed decrease in going from the unsubstituted (tri-

TABLE 2

ACTIVATION ENERGIES FOR (TRIMETHYLSILYL)PYRAZOLES

Compound	E_a (kcal/mole)	T_c[a] (°C)	Temp.[b] range (°C)
(I)	~32[c]	165	
(II)	28±2	105	106–130
(III)	24±2	90	91–130
(IV)		>170	

[a] Coalesence temperatures. [b] Temperature range used for E_a calculation. [c] Estimated (see Experimental).

methylsilyl)pyrazole (I) to the (trimethylsilyl)pyrazole with three ring methyls (III) can be qualitatively interpreted as a combination of steric influences of the 3,5-substituents and electronic influences of the 3,4,5-substituents. The decrease in activation energy in going from (I) to (II) may be largely due to steric repulsions between the 3,5-methyl groups and the bulky trimethylsilyl group. Molecular models show that there is considerable crowding between these groups when the trimethylsilyl is fixed to one or the other nitrogen [(Va) or (Vb)]. This steric strain would be relieved in the pentacoordinate transition state (VI) leading to a lowering of the activation energy.

However, a decrease in the activation energy is found when the 4-hydrogen is replaced by a methyl group in going from compound (II) to (III). Since the four position is well removed from the bulky trimethylsilyl, this decrease must be due to an increase in the electron density in the ring. This electronic effect is best explained as due to increased electron density at the free nitrogen. If electron donation by the methyl caused any significant increase in the strength of the silicon–nitrogen bond, opposite activation energy trends would be observed.

For compound (IV), only slight changes in peak position and slight peak broadening were noted up to 150°. For this reason it was not possible to measure the activation energy. The peak separation of the non-equivalent trifluoromethyl groups is considerably larger than that for the other three compounds (447 Hz) and a considerably higher coalescence temperature is expected. However, the strong electron-withdrawing power of the trifluoromethyl groups probably decreases the basicity of the free nitrogen compared to compounds (I)–(III), and one would predict that (IV) would have the highest activation energy.

The simplicity of the new system described in the present work offers a new approach for the study of factors influencing bonding at silicon. Work is now underway to prepare silylpyrazoles with other substituents in the four position and to prepare *N*-pyrazole derivatives of other group IV elements.

EXPERIMENTAL

Materials

Pyrazole, 3,5-dimethylpyrazole, hexafluoroacetylacetone and hexamethyldisilazane were commercially available and were used without further purification. Diphenyl ether was dried over sodium and vacuum distilled before use. 3-Methyl-2,4-pentanedione was synthesized from the reaction of acetylacetone with iodomethane[13]. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

3,4,5-*Trimethylpyrazole*

A solution of 27.5 g (0.55 mole) of hydrazine hydrate in 150 ml of absolute ethanol was added dropwise to a solution of 56.8 g (0.50 mole) of 3-methyl-2,4-pentanedione in 200 ml of absolute ethanol containing two drops of glacial acetic acid. The reaction mixture was refluxed for 18 h. After distillation of the solvent, a white solid formed. Recrystallization of the solid from hexane gave 39.0 g (0.36 mole, 71 % yield) of white crystals of 3,4,5-trimethylpyrazole (m.p. 136–137°).

3,5-Bis(trifluoromethyl)pyrazole

This pyrazole was prepared in the same manner as 3,4,5-trimethylpyrazole using 52.0 g (0.25 mole) of hexafluoroacetylacetone and 15.0 g (0.30 mole) of hydrazine hydrate. Recrystallization from hexane gave 34.0 g of white crystals of 3,5-bis(trifluoromethyl)pyrazole (65% yield, m.p. 68–70°).

N-(Trimethylsilyl)pyrazole, (I)

Hexamethyldisilazane (80 ml, 62.0 g, 0.38 mole) was injected through a rubber septum into a flask containing pyrazole (51.0 g, 0.74 mole) and a few crystals of ammonium sulfate. The reaction mixture was refluxed for 12 h. Fractional distillation under an atmosphere of dry nitrogen gave (I) (nc), a clear liquid (66.0 g, 0.47 mole, 64% yield, b.p. 152–153°). (Found: C, 51.46; H, 8.76; N, 19.86; Si, 20.02. $C_6H_{12}N_2Si$ calcd.: C, 51.38; H, 8.62; N, 19.96; Si, 20.03%.)

3,5-Dimethyl-N-(trimethylsilyl)pyrazole, (II)

Compound (II) was prepared in a manner similar to that for (I) using 32.2 g (0.34 mole) of 3,5-dimethylpyrazole and 36 ml (28.1 g, 0.17 mole) of hexamethyldisilazane to give (II) (nc) (35.3 g, 0.21 mole, 61% yield, b.p. 185–186°). (Found: C, 57.16; H, 9.85; N, 16.83; Si, 16.39. $C_8H_{16}N_2Si$ calcd.: C, 57.10; H, 9.57; N, 16.64; Si, 16.69%.)

3,4,5-Trimethyl-N-(trimethylsilyl)pyrazole, (III)

Compound (III) was prepared in a manner similar to that for (I) using 15.6 g (0.14 mole) of 3,4,5-trimethylpyrazole and 28 ml (20.0 g, 0.12 mole) of hexamethyldisilazane to give (III) (nc) (18.5 g, 0.10 mole, 70% yield, b.p. 204–205°). (Found: C, 59.47; H, 10.12; N, 15.58; Si, 15.10. $C_9H_{18}N_2Si$ calcd.: C, 59.28; H, 9.95; N, 15.36; Si, 15.41%.)

3,5-Bis(trifluoromethyl)-N-(trimethylsilyl)pyrazole, (IV)

Compound (IV) was prepared in a manner similar to that for (I) using 20.4 g (0.10 mole) of 3,5-bis(trifluoromethyl)pyrazole and 22 ml (17.1 g, 0.13 mole) of hexamethyldisilazane to give (IV) (nc) (23.5 g, 0.08 mole, 85% yield, b.p. 135–136°). (Found: C, 34.49; H, 3.47; F, 41.20; N, 10.43; Si, 9.93. $C_8H_{10}F_6N_2Si$ calcd.: C, 34.79; H, 3.65; F, 41.26; N, 10.13; Si, 10.17%.)

NMR measurements

Varian Associates Models A-60 and HA-100 NMR spectrometers equipped with variable temperature probes were used for all proton spectra. Proton chemical shifts are reported in ppm downfield from tetramethylsilane (internal). ^{19}F spectra were obtained using a Varian Associates Model HA-100 spectrometer equipped with a V-4311 radio frequency unit operating at 94.1 MHz. A Hewlett–Packard Model 200 CD audio oscillator was used for spin decoupling. Temperature was measured using an ethylene glycol sample and a shift-temperature correlation chart.

Samples for variable temperature measurements were distilled directly into NMR tubes under vacuum and the sample tubes sealed since the compounds were extremely sensitive to hydrolysis by atmospheric moisture. If significant amounts of hydrolysis occurred, the ring resonances of the starting pyrazole interferred with the variable temperature coalescence process resulting in poor activation energy values.

Activation energy determinations

Under ideal experimental conditions, it is desirable to obtain NMR rate data both below and above coalescence. Such data allow greater precision because of the wide temperature range available. It is also desirable to study dilute solutions in order to be able to follow the rate process as a function of concentration and to be able to decouple the resonances involved in the rate process. In the present work, choice of a suitable solvent was particularly difficult because of the high coalescence temperatures and the sensitivity to protonic solvents. Several solvents were tried and the most suitable appeared to be diphenyl ether. However, below coalescence, specific solvent effects were noted. In the slow exchange region, the chemical shift difference of the non-equivalent 3,5-positions was found to be a function of concentration (Table 3). Such specific interaction of aromatic solvents on chemical shifts is quite

TABLE 3

SOLVENT EFFECT OF DIPHENYL ETHER

Concentration[a]	Peak separation, 3,5-substituents[b]		
	(I)	(II)	(III)
Neat	11.6	6.0	5.0
1/1	35.0		13.2
1/7	36.8	13.3	16.5
1/60	41.0	16.5	

[a] Mole/mole, based on integration. [b] Measured at 35°, in Hz at 100 MHz.

common[14]. As a result of these solvent effects, the activation energies calculated from line width measurements below coalescence for decoupled spectra of compounds (I)–(III) in dilute solutions of diphenyl ether were inordinately low (3–6 kcal/mole). This can best be rationalized as due to a slow decrease in the solvent-induced chemical shift difference over a broad temperature range. For the neat liquids below coalesence, the 3,5-resonances overlapped one another and spin decoupling was not possible. In this region of the rate process, more precise activation energy determinations must await computer-calculated line shape analysis.

For the neat liquids of (II) and (III), no temperature-dependence of the chemical shifts of the non-equivalent sites was observed. Also, above coalesence, the activation energies determined for compounds (II) and (III) for *both* the neat liquids and dilute solutions in diphenyl ether were similar (Table 2)[15]. For this reason and because the coalesence temperatures neat and in dilute solutions were the same, the process is best described as intramolecular.

For compounds (I) and (IV), the activation energies above coalescence were not determined because of the high temperatures necessary. The activation energy of (I) was estimated from the activation energy of (II) [or (III)] and the chemical shift differences at the slow exchange limit. For this reason, this value should be considered only approximate.

ACKNOWLEDGEMENT

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