Reaction of Methyl 3-Trimethylsilylpropenates with Diazoalkanes. A Facile 1,2-Trimethylsilyl Group Migration within 3-Carbomethoxy-4-trimethylsilyl-1-pyrazolines

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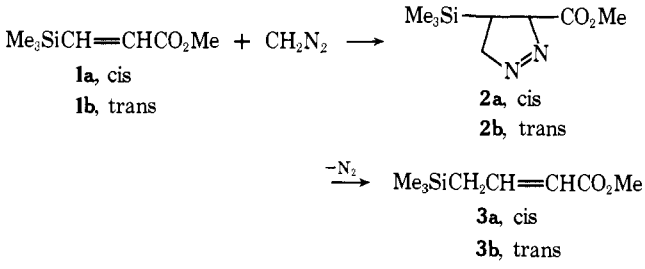
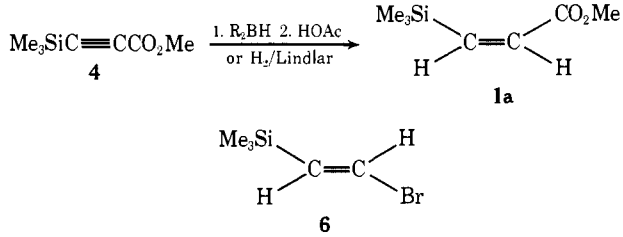
Abstract: The reaction of *cis*- and *trans*-methyl 3-trimethylsilylpropenoate with diazomethane and a series of mono- and disubstituted diazomethanes was investigated. Diazomethane stereospecifically afforded 3-carbomethoxy-4-trimethylsilyl-1-pyrazolines of retained stereochemistry which underwent trimethylsilyl group migration and nitrogen expulsion under ambient conditions to yield the corresponding methyl 4-trimethylsilyl-2-butenoates stereospecifically. Evidence is presented suggesting that the silyl group participates in nitrogen expulsion. Monosubstituted diazomethanes are believed to behave similarly, except that steric factors operate so as to produce both 4-substituted 4-trimethylsilyl-2-butenoic and 4-substituted 2-trimethylsilyl-3-butenoic esters. Disubstituted diazoalkanes led to 4-carbomethoxy 3,3-disubstituted 5-trimethylsilyl-1-pyrazolines, which underwent thermolysis to afford substituted cyclopropanes.

In an earlier communication,[1] we reported on a facile reaction between diazomethane and isomeric 3-trimethylsilyl-2-propenoic esters **1a,b** in which the homologuized esters **3a,b** were stereospecifically obtained under ambient conditions. Thus **1a** afforded only **3a,** and **1b** only **3b.** At that time, it was



suggested that the overall transformation could be understood in terms of an initial 1,3-cycloaddition of diazomethane to the α,β-unsaturated esters, followed by nitrogen extrusion concerted with silyl group migration within intermediate pyrazolines **2a,b.** We now wish to report spectroscopic evidence in support of these intermediates, together with results of a study carried out to determine the effect of diazoalkane structure on the reaction pathway.

Preparation of 1a,b. Attempts at preparation of **1a** by application of a hydroboration–protonolysis sequence[2] to methyl 3-trimethylsilylpropynoate (**4**) afforded only low and variable

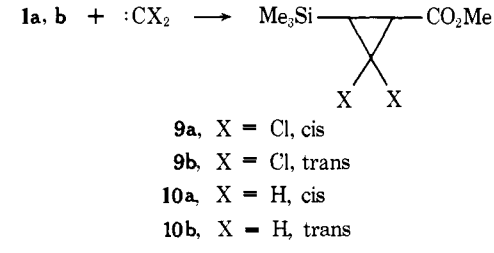


yields of **1a,** although the ester thus obtained was free of contamination by **1b.** Larger quantities of **1a** could be routinely prepared in high yield by semihydrogenation of **4** employing Lindlar catalyst, although the resulting product was invariably contaminated with small amounts (3–7%) of **1b.**

The synthesis of **1b** was not straightforward. Although methylation of acid **5** was an attractive option, its preparation from the bromide **6** by way of the Grignard reagent[3] afforded only low and variable yields (7–30%) regardless of modification. Scheme I was thus employed for the synthesis of **5.**[4] The alcohol **7,** obtained from propargyl alcohol,[5] was reduced by lithium aluminum hydride[6] to **8.** Oxidation[7] of **8** gave first the aldehyde **9** which under similar but more vigorous conditions[8] afforded **5.** Methylation of **5** then gave isomerically pure **1b,** obtained in an overall 20% yield from propargyl alcohol.

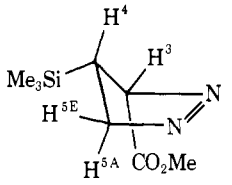
Results

Reaction of 1a and 1b with Diazolkanes. A. With Diazomethane. Addition of a slight excess of ethereal diazomethane to the pure cis ester **1a** under ambient conditions led to the production of **3a** as the only volatile product. In similar fashion, **1b** afforded only **3b.** Other runs indicated nonoptimized yields of 83% for **3a** and 75% for **3b.** Each conversion was found to be completely stereospecific within the limits of the GLC analysis employed (>99%). Superficially, these transformations are reminiscent of carbene and carbenoid insertion reactions of silicon–hydrogen, silicon–halogen, and strained silicon–carbon bonds.[10] However, both indirect and direct evidence indicates that an "insertion" process is not the cause of the observed homologation. No products of divalent carbon insertion into the Si–C bond of **1a,b** were realized using several modifications of the Simmons–Smith reaction, while reaction of each of these esters with phenyl(bromodichloromethyl)-mercury afforded only the corresponding cyclopropanes **9a,b.** In addition, the cyclopropyl esters **10a,b** were independently synthesized and shown to be stable under the conditions used for the analysis of **3a,b.** This excludes **10a,b** (not seen among the products from **1a,b**) from serving as possible thermal re-

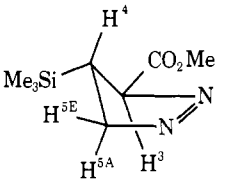


arrangement precursors for **3a,b** (vide infra). Evidence for the intermediacy of pyrazolines **2a,b** in the overall homologation process was obtained by low-temperature NMR examination of the reaction mixtures formed from **1a,b** and diazomethane. Spectral parameters so obtained are listed in Table I. The data are interpreted in terms of partly folded conformations for **2a** and **2b,** as indicated by the figures in Table I, with the large

Table I. NMR Data for *cis*-3-Carbomethoxy-4-trimethylsilyl-1-pyrazoline (**2a**) and *trans*-3-Carbomethoxy-4-trimethylsilyl-1-pyrazoline (**2b**)[a]



2a



2b

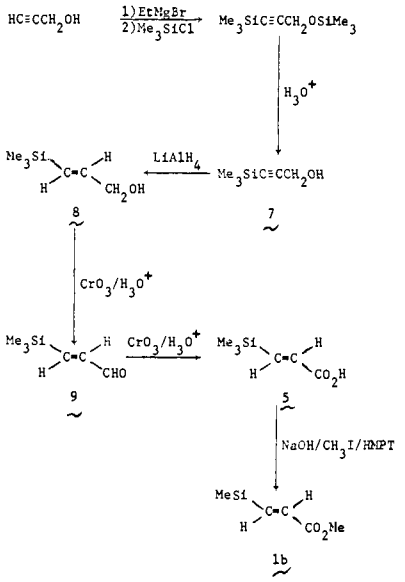
Chemical shift,[b] δ	J,[c] Hz	Chemical shift,[b] δ	J,[c] Hz
$H^3 = 5.65$	$H^3H^4 = 10.0$	$H^3 = 4.55$	$H^3H^4 = 11.5$
$H^4 = 1.1$[d]	$H^3H^{5E} = \sim 0$	$H^4 = e$	$H^3H^{5E} = 2.7$
$H^{5E} = 5.03$	$H^3H^{5A} = 2.5$	$H^{5E} = 5.12$	$H^3H^{5A} = 3.9$
$H^{5A} = 3.98$	$H^4H^{5E} = 9.0$	$H^{5A} = 3.8$[f]	$H^4H^{5E} = 9.2$
$OCH_3 = 3.69$	$H^4H^{5A} = 12.5$	$OCH_3 = 3.87$	$H^4H^{5A} = 11.7$
$SiMe_3 = 0.03$	$\lvert H^{5E}H^{5A}\rvert = 17.0$	$SiMe_3 = 0.01$	$\lvert H^{5E}H^{5A}\rvert = 17.3$

[a] Obtained in $DCCl_3$ at −44 °C. [b] Chloroform as internal standard taken as δ 7.27; AMX analysis for C-4,5 proton system. [c] ±0.5 Hz. [d] Tentative assignment; partially obscured by methyl peak from residual ether (see Experimental Section). [e] Not observable; see *d* (δ 1.2?) [f] Approximate δ; peaks partially overlain by OCH_3 absorptions.

trimethylsilyl group assuming the pseudoequatorial position in both isomers. A preference for a folded conformation has been shown for 1-pyrazoline itself,[11] as well as for numerous substituted derivatives.[12] Moreover, bulky ring substituents have been found to preferentially assume pseudoequatorial positions in these ring systems, an example being the conclusion of McGreer and Wu that both *cis*- and *trans*-3-carbomethoxy-4-ethyl-3-methyl-1-pyrazolines preferentially exist in folded conformations with the ethyl group pseudoequatorial.[13] The data of Table I support a similar interpretation for **2a** and **2b.** Thus, the large chemical shift difference between the C-5 protons (1.0 ppm in **2a** and 1.3 ppm in **2b**) infers a nonaveraged environment for these protons, with the difference in chemical shift being most reasonably attributed to the anisotropy of the azo function.[14] Thus, 5E protons, which lie in or near the plane of the C-N=N moiety, will be deshielded relative to 5A protons occupying positions substantially above or below this plane. The lower field location (by 1.10 ppm) of the pseudoequatorial C-3 proton in **2a** relative to the pseudoaxial C-3 proton in **2b** corroborates this effect. Coupling constants are also in accord with the puckered structures shown in Table I. The magnitude of the J^{34}, J^{45A}, and J^{45E} values excludes the possibility of a planar ring, since **2a** would then provide one (trans H^4-H^5), and **2b** two (trans H^3-H^4 and trans H^4-H^5), vicinal proton coupling constants predicted by the Karplus equation to be less than one-half of any of the actually observed values.[16] Similarly, the possibility that the pyrazolines are folded, but exist in conformations which position the trimethylsilyl group pseudoaxially, may be excluded by noting that the dihedral angles between these same vicinal proton pairs would then approach 90°. A near-zero coupling constant is predicted for this situation. In contrast, the observed J values are entirely consistent with the conformations indicated (Table I). The H^4-H^{5E} (or H^{3E}) dihedral angles in these conformers lie between 0 and 60°, with corresponding H^4-H^{5A} (or H^{3A}) angles between 120 and 180°; the exact angles depend on the extent of ring pucker.[17]

Parallel stereochemical information is obtainable from long-range (homoallylyic) coupling which is observed between proton sets H^3-H^{5A} in **2a** and H^3-H^{5A} plus H^3-H^{5E} in **2b.** This interaction has been interpreted in terms of σ-π overlap such

Scheme I

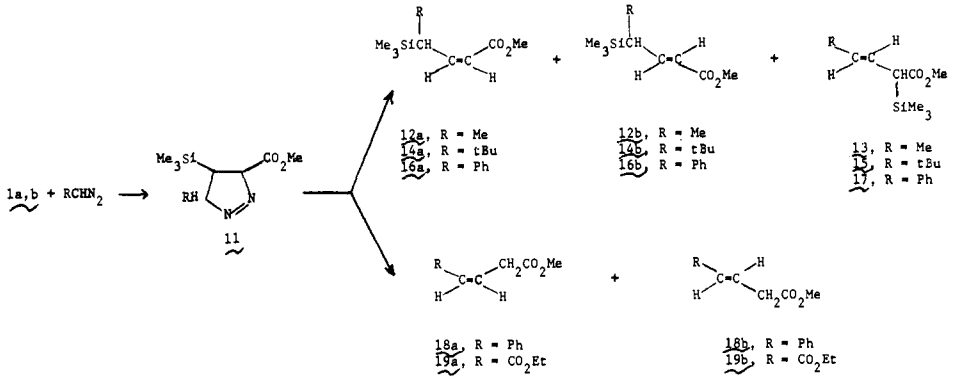


that a pair of homoallylic protons exhibit largest J when their σ bonds are each located in a plane perpendicular to that of the π system.[18] This would correspond to conformations of **2a;b** in which these σ bonds would also be perpendicular to the C^3-N=N-C^5 plane; the preferred conformers of **2a,b** are believed to exhibit a pucker angle somewhat less than that necessary for this "limiting" situation.[19] A comparison of H^3-H^5 axial-equatorial relationships within **2a,b** leads to a qualitative prediction of a small (H^3-H^{5E}) and a medium (H^3-H^{5A}) interaction in **2a,** but a medium (H^3-H^{5E}) plus a strong (H^3-H^{5A}) interaction in **2b.** Again, the observed data are in agreement with this analysis (Table I).

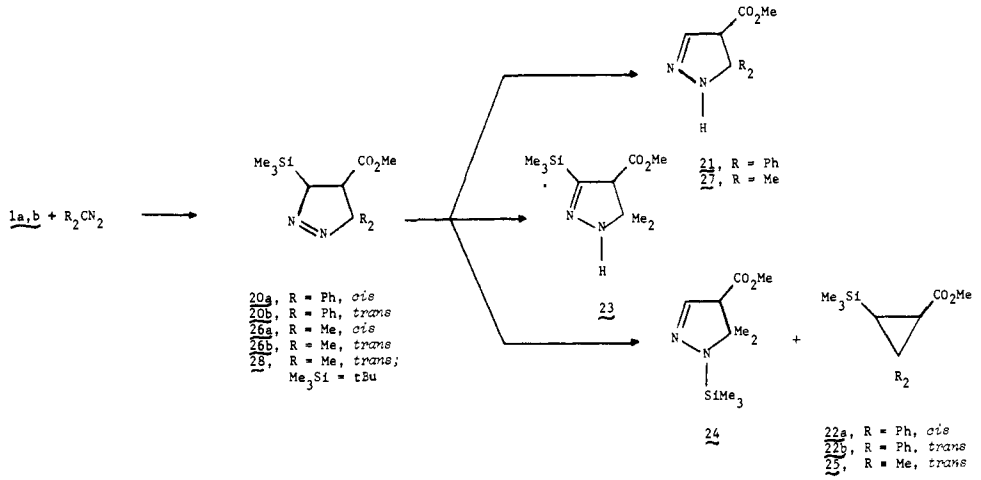
The internal consistency of the spectral data for **2a,b** with the proposed structures indicates that the pyrazolines are generated with retained stereochemistry from the esters **1a,b** (see Discussion section). Evidence that additional stable intermediates or products do not intervene in the sequences **1** → **2** → **3** was provided by a series of NMR spectra taken of reaction mixtures containing **2a** and **2b** over the temperature range −44 to 25 °C. At low temperatures, only absorptions attributable to **2a** (from **1a**) and **2b** (from **1b**), and to excess **1** plus residual ether solvent, were present. Thus, the pyrazolines are generated stereospecifically within the limits of the NMR analysis. Above 0 °C, the absorptions due to **2a,b** diminished with the simultaneous appearance of only absorptions due to **3a,b,** respectively. It was a point of concern that small amounts of **3b,** possibly formed from **1a,** were not being detected (even by GLC) because of preferential (**3b** over **3a**) further reaction with diazomethane still present during product formation.[20] That this was unlikely was shown by the absence of **3b** in a run in which the **1a**:diazomethane ratio was 55:1.

B. With Monosubstituted Diazomethanes. The reactions of **1a,b** with monosubstituted diazomethanes are assumed to proceed through 1-pyrazoline intermediates by analogy to their behavior with diazomethane. Moreover, the structures of homologuized products are consistent with the assumption of such intermediates. As indicated by Scheme II and the data of Table II, the eventual course of reaction is heavily influenced by the nature of the diazo carbon substituent. Whereas diazomethane afforded only homologuized products which correspond to a C-4 to C-5 trimethylsilyl group migration within the intermediate pyrazoline, replacement of hydrogen by methyl (diazomethane → diazoethane) results also in products which must arise through a C-4 to C-3 silyl group shift. Thus **13** is formed from **1a,b** in addition to the expected **12a** and **12b,** respectively. The formation of **12b** from **1b** occurs stereospe-

Scheme II



Scheme III



cifically, as does possibly **12a** from **1a,** although the available data allow an interpretation of slightly lower stereospecificity for the latter case.

The reaction of *tert*-butyldiazomethane with either **1a** or **1b** affords only **15,** the product of C-4 to C-3 silyl group migration. This represents a complete reversal of the regiospecificity displayed by **2a,b** for this transformation.

Analysis of product mixtures arising from phenyldiazomethane and **1a** or **1b** was complicated by the hydrolytic lability of the initially produced olefinic materials. For example, **1b** afforded, according to GLC analysis, a mixture of **16b** and the desilylated (and isomerized) **18b.** Although **16b** could be isolated by GLC and spectrally characterized, efforts at excluding moisture from the reaction system failed to completely inhibit disilylation. Similarly, **1a** gave rise to a product mixture which NMR analysis indicated may have contained some **16a,** but **18b** was also present, and only **18b** remained after several days. In this case, we were unable to isolate and characterize **16a.** GLC analysis after only **18b** remained indicated that the reaction mixture contained 0.5 equiv of hexamethyldisiloxane, indicating that hydrolytic desilylation of a precursor organosilicon species was occurring. Similar, but more pronounced, hydrolytic instability was displayed by the initial rearrangement products obtained from **1a,b** and ethyl diazoacetate, as only desilylated olefins **19a** and **19b** were detectable by GLC or NMR analysis of the crude reaction mixtures.[21,22]

C. With Disubstituted Diazomethanes. Addition of diphenyldiazomethane to **1a** resulted in a 71% yield of *cis*-4-carbomethoxy-3,3-diphenyl-5-trimethylsilyl-1-pyrazoline (**20a**), while identical treatment of **1b** afforded 69% of the isomeric **20b.** Assignment of structure for **20a,b** followed from analytical and spectral data consistent with that for other 1-pyrazolines,[23] together with the assumption of stereospecificity for the cycloaddition process. That cycloaddition had occurred

Table II. Product Composition Data (Relative Yields[a]) for the Reaction of Methyl 3-Trimethylsilyl-2-propenoates with Some Diazoalkanes

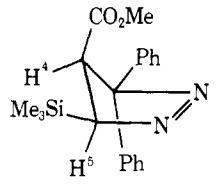
Ester	Diazoalkane	Products (%)
1a	CH_2N_2	**2a** (>99)
1b		**2b** (>99)
1a	CH_3CHN_2	**12a** (58) **12b** (2)[b] **13** (40)
1b		**12b** (68) **13** (32)
1a	*t*-$BuCHN_2$	**15** (>97)
1b		**15** (>97)
1a	$PhCHN_2$	**18b** (>97)
1b		**18b** (>97)
1a	EtO_2CCHN_2	**19a** (18) **19b** (82)
1b		**19a** (18) **19b** (82)

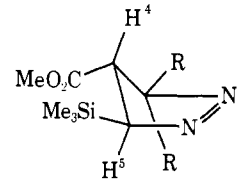
[a] See Experimental Section for absolute yields. [b] After correction for 7% **1b** in starting **1a.**

in a direction opposite to that exhibited by diazomethane was indicated by the comparatively low field (relative to **2a,b**) chemical shifts of the C-4 protons,[24] and confirmed by subsequent chemistry. No tendency for **20a,b** to isomerize to ester-conjugated 2-pyrazolines was observed, whereas such isomerization is typical of 1-pyrazolines bearing a C-3 proton adjacent to an ester function.[25,26] In contrast to **2a,b, 20a** was stable under ambient conditions, and could be recovered from hot hexane. However, heating **20a** in protic solvents led to disilylation and the formation of **21,** while long thermolysis in refluxing hexane afforded a 2:3 ratio of *cis*- and *trans*-methyl-2,2-diphenyl-3-trimethylsilylcyclopropane carboxylate (**22a,b**). The pyrazoline **20b,** obtained from **1b,** proved to be more thermally stable than **20a,** but eliminated nitrogen in refluxing octane to give a 1:4 ratio of **22a** and **22b.**

Substitution of 2-diazopropane for diphenyldiazomethane

Table III. NMR Data for Various 4-Carbomethoxy 3,3-Disubstituted 5-Trimethylsilyl-1-pyrazolines[a]





20b, R = Ph
26b, R = Me
28, R = Me; Me_3Si = *t*-Bu

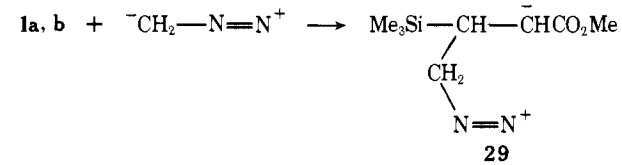
	20a, δ	20b, δ	26b, δ	28, δ[b]
R	7.1–7.6 (m)	7.0–8.3 (m)	0.90 (s),[c] 1.27 (s)	1.02 (s), 1.56 (s)
H^4	3.94 (d, *J* = 8 Hz)	3.65 (d, *J* = 7 Hz)	2.20 (d, *J* = 8.7 Hz)	2.17 (d, *J* = 9 Hz)
H^5	4.18 (d, *J* = 8 Hz)	5.24 (d, *J* = 7 Hz)	4.45 (d, *J* = 8.5 Hz)	4.53 (d, *J* = 9 Hz)
OCH_3	3.15 (s)	3.29 (s)	3.48 (s)	3.67 (s)
$SiMe_3$	0.34 (s)	−0.04 (s)	0.00 (s)	1.02 (s) (*t*-Bu)

[a] Obtained in $DCCl_3$; CH_3CN internal standard taken as δ 2.00; chemical shifts measured to midpoint of doublets. [b] Data from ref 26. [c] Absorption overlapped by that of methyl group from ethyl ether in sample.

in the cycloaddition reaction resulted in the same "reversed" regiochemistry, but the isolated products possessed rearranged structure. Thus, **1a** afforded a 75% yield of **23,** shown by NMR analysis of the crude reaction mixture to have arisen before subsequent manipulation. Different results were obtained with **1b,** as GLC analysis of the reaction mixture showed the presence of the 2-pyrazoline (**24**) and the trans-substituted cyclopropane **25** in approximately a 1:1 ratio. However, an NMR spectrum of the crude reaction mixture showed no peaks attributable to **24** or **25,** but did display absorptions consistent with the 1-pyrazoline **26b.** Chemical shift and coupling constant values for **26b** (Table III) compare favorably with those reported for the analogous *trans*-4-carbomethoxy-3,3-dimethyl-5-*tert*-butyl-1-pyrazoline (**28**).[26] Thermolysis of **26b** under the GLC conditions is thus implicated as the origin of **24** and **25.** The dimethyl compound **26b** displayed water sensitivity behavior parallel to that of its diphenyl analogue **20a** in that the use of moist 2-diazopropane in the cycloaddition reaction led to a high yield of the desilylated 4-carbomethoxy-5,5-dimethyl-2-pyroazoline (**27**). As expected for a compound containing a silicon–nitrogen bond, **24** was also found to be highly sensitive to water, and gave **27** upon hydrolysis.

Discussion

The generation of pyrazolines **2a,b** in the reaction between **1a,b** and diazomethane lies within the context of known 1,3-cycloaddition behavior of diazoalkanes and α,β-unsaturated esters.[27-29] The regioselectivity normally exhibited in these reactions[30] is reflected in the structures of the pyrazolines **2a,b** in that the carbon terminus of the diazomethane bonds to the β carbon of the α,β-unsaturated system. Moreover, the stereospecificity of the present cycloadditions (**1a** → **2a** and **1b** → **2b**) is also consistent with the well-established stereospecificity (retention of dipolarophile geometry) of 1,3-dipolar cycloaddition reactions. This is strong evidence against the intermediacy of a dipolar structure (**29**) which would result



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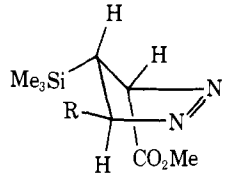
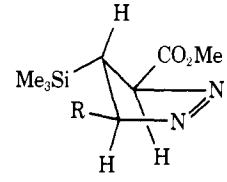
from conjugate addition of the diazomethane dipole to **1a,b.** Provided that bond rotation was fast relative to other processes, rotation within **29** would lead to a mixture of stereoisomers regardless of whether ring closure to pyrazolines **2a,b** or direct rearrangement to **3a,b** occurred.

This same stereospecificity should apply to the formation of the 5-monosubstituted 1-pyrazolines (**11**) assumed to be precursors of **12–19.** Moreover, the structures of the latter products are consistent with a regiochemistry for **11** which is parallel to that of **2,** a point also supported by the marked difference in chemical behavior of **2** and **11** vs. **20** and **26.** Based on steric control of the orientation of the "two planes" complex leading to cycloadduct,[31] the structures of **11a,b** are



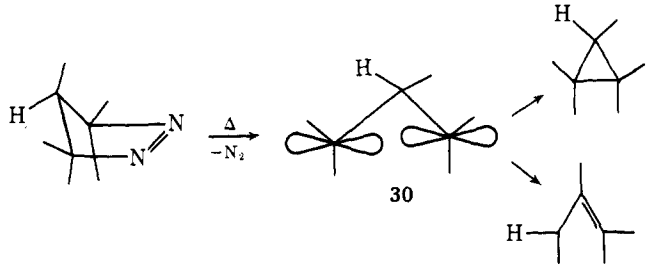
11a



11b

predicted to have 5-substituents trans to the C-4 trimethylsilyl group. These substituents would be located equatorially in folded conformations analogous to those of **2a,b.**

The process by which, in general, olefinic products arise from 1-pyrazolines is of significant interest. A number of alkyl-substituted pyrazolines have been extensively investigated in connection with the trimethylene problem.[32] Crawford and co-workers have reported that in these systems, thermolysis directly affords a nitrogen-free intermediate (**30**).[33-35] This



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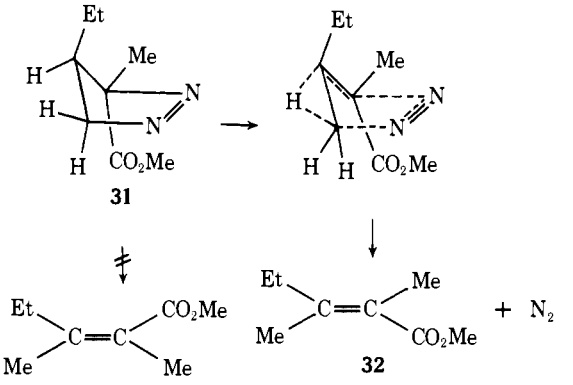
subsequently partitions between cyclopropanes of mixed stereochemistry and small amounts[36] of olefinic products which arise from hydrogen migration to one of the carbon termini of **30.** In contrast, work carried out by McGreer and collaborators on pyrazolines bearing an electron-withdrawing group (e.g., carbomethoxy) at C-3 indicates that, for these species, migration of a C-4 hydrogen is concerted with nitrogen extrusion.[39] These pyrazolines are then predicted to undergo thermolysis preferentially from that conformer which places

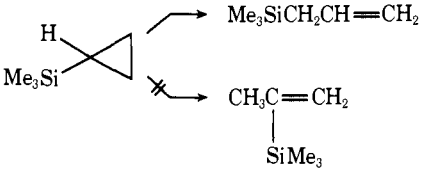
a C-4 hydrogen in the pseudoequatorial position, thus orienting it in an anti relationship to the breaking C–N bond. Hydrogen migration within this context results in the (observed) stereospecific generation of olefinic products (e.g., **31** → **32**).[40]



Crawford has shown that this concerted, "backside" migration process does not predict results obtained in purely alkyl-substituted pyrazolines,[37,41] confirming that the presence of the carbomethoxy function fundamentally alters the behavior of the pyrazoline system in this regard.

The behavior of pyrazolines **2** and **11** (→ **12, 13, 15**) parallels that of systems investigated by McGreer in that olefins are generated stereospecifically, but differs in a number of important aspects. First, the trimethylsilyl group migrates to the exclusion of C-4 hydrogen. For **2a,b,** product analysis has shown that migration occurs exclusively to C-5 in a highly stereospecific manner. These observations are consistent with (1) a transition state in which the silyl group participates (by backside approach) in the breaking of the C^5–N bond or (2) a process in which 1,2-silyl group migration occurs within a nitrogen-free intermediate (**30,** H = $SiMe_3$) which displays C^1–C^3 residual bonding during its lifetime. Completely parallel considerations apply to the behavior of **11a,b** expected in the light of observed product stereochemistry. Thus, **11a** (R = CH_3) will afford **12a** and **11b** (R = CH_3) will afford **12b** via a trimethylsilyl group shift to the rear of the C^5–N bond. Moreover, **13** will arise from a silyl group shift to the backside of C^3–N bond within *either* **11a** or **11b.**[42] Similar arguments should be applicable to all other systems studied which would lead to **11a,b** as intermediates (R = *t*-Bu, Ph, CO_2Et). An examination of the percent C-3 migration product obtained from the reaction of **1a,b** with CH_2N_2 (0, 0), CH_3CHN_2 (40, 32), and *t*-$BuCHN_2$ (100, 100) indicates that steric factors control the migration mode of the bulky trimethylsilyl group.

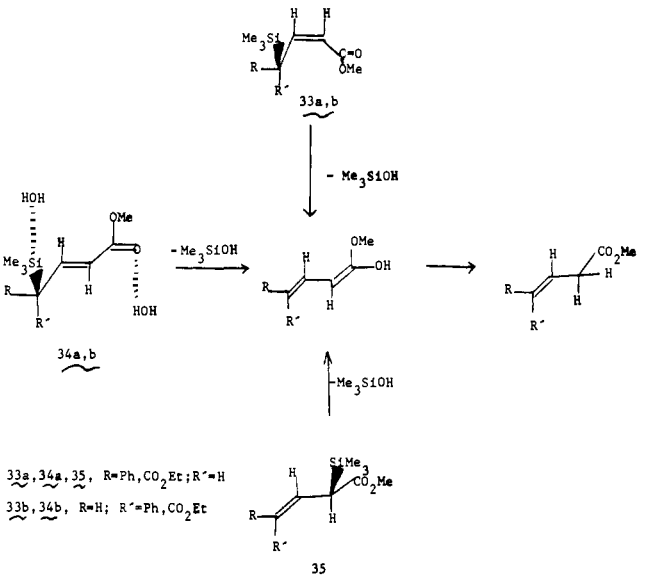
If a process which required an anti relationship of the migrating group and the breaking C–N bond was operating for the 4-silylpyrazolines, highly favored silyl group (over hydrogen) migration might be expected based on the orientation of this group in the preferred conformers of, for example, **2a,b.** However, no analogy to this behavior is found in 4-alkyl- or 4-aryl-substituted pyrazolines which also bear a hydrogen at C-4, even though in a number of these compounds, the substituent group is positioned equatorially in the preferred conformer.[13,43,44] Instead, olefinic products are obtained which arise from exclusive C-4 hydrogen migration from the (less stable) ring-flip conformer in which this hydrogen is equatorial.[45] Stereoelectronic considerations aside, the trimethylsilyl group may be inherently more prone to migration than hydrogen in these systems. Examples of thermally induced silyl group migrations from carbon to vicinal carbon are rare, but have been observed in cyclopropylsilanes.[46] Product studies have shown that silicon migrates in high preference to any geminal hydrogen in such cases to form allylsilanes, and in one report, the rate of trimethylsilyl group migration within a *preformed* 1,3 diradical was estimated to be greater than 10^6 times the rate of hydrogen migration.[46a]



A rough lower estimate for the rate constant associated with the decomposition of 1-pyrazolines obtained from **1a,b** and diazomethane, diazoethane, and *tert*-butyldiazomethane was obtained from the observation that nitrogen evolution in each case was essentially complete after 0.5 h at 25 °C. For comparison purposes, rate data reported for 3-carbomethoxy-3-methyl-1-pyrazoline[39] were extrapolated to 25 °C. *The 4-trimethylsilyl-substituted pyrazolines expel nitrogen at a rate which is ca. 10^7 faster than this value.* This large rate enhancement suggests that nitrogen loss is concerted with silyl group migration, and that the trimethylsilyl group participates much more effectively than does hydrogen in this regard. The observation that no cyclopropyl products are observed in the present transformations, but are always formed from nonsilicon analogues, is a further indication of highly preferred silyl group migration in these systems.

Little stereochemical information was obtainable from the reaction of **1a,b** with phenyldiazomethane and ethyl diazoacetate because of the hydrolytic lability of the initially formed homologuized organosilanes. Sensitivity to desilylation in these compounds is attributed to conjugative stabilization of the enol form of **18, 19** by the phenyl and carboethoxy functions. The observed trans olefins (**18b, 19b**) can arise from either *cis*- or *trans*-4-trimethylsilyl enoates oriented in the most favorable stereoelectronic conformations for disilylation as shown in Scheme IV (**33a, 34a**). Desilylation of 2-trimeth-

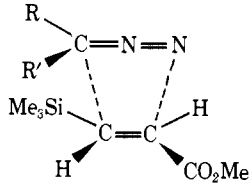
Scheme IV



ylsilyl enoates (**35**) gives identical results. The observed cis olefin **19a** could arise from **33b** or **34b,** but the identical **19a: 19b** ratios obtained from both **1a** and **1b** suggest that equilibration may have occurred after desilylation under the harsher conditions used for the reaction of ethyl diazoacetate with **1a,b** (65 °C, 48 h vs. 25 °C, 2 h for $PhCHN_2$ and 25 °C, 0.5 h for $RCHN_2$).[47]

The reversal in regiochemistry exhibited by the cycloaddition products of **1a,b** with diphenyl- and diazomethane vs. that observed from even bulky (e.g., *tert*-butyl) monosubstituted

diazomethanes is consistent with steric considerations within the "two-planes" picture (**36**) of the 1,3-cycloaddition process.[31] Significant van der Waals strain can result in the "normal" addition mode if both R and R′ are larger than hydrogen, although one such bulky group can be accommodated. For example, *trans*-methyl 3-*tert*-butylpropenoate (**3b**, Me_3Si = *t*-Bu) adds diazoethane to give the "normal" cycloadduct with the carbomethoxy function at C-3 of the resulting 1-pyrazoline, but 2-diazopropane affords only the "abnormal" 4-carbomethoxy-3,3-dimethyl-5-*tert*-butyl-1-pyrazoline.[26]



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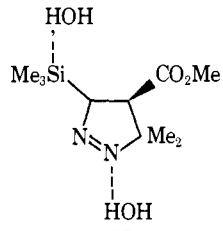
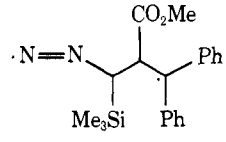
The instability of **20a** and **20b** under protic conditions is viewed as arising from disilylation as indicated in **37** (→ **21**, **27**). Only the tautomer (**23**) of the initially formed **26a** was observed, in contrast to **26b**, for which spectral evidence could be obtained. Tautomerism of 1-pyrazolines to 2-pyrazolines under the conditions of cycloaddition is commonplace when a strongly electron-withdrawing 3 substituent is present,[28,48] but this is the first instance of a silyl group possibly acting in this capacity.[49] The observation that **26a** undergoes tautomerism under the reaction conditions, but **26b** does not, is consistent with a more accessible α-silyl proton in the former because of the adjacent, cis (to H-5) carbomethoxy group in the latter.[31a] Similarly, tautomerism of both **20a** and **20b** may be sterically inhibited by the cis phenyl group at C-3 (see Table III conformations).



37

The thermolysis of **20a,b** was examined in order to compare their behavior to that of **2a,b** and **11**. Cyclopropane products (**22a,b**) of mixed stereochemistry were obtained. No information is available which would allow a choice between concerted or stepwise expulsion of nitrogen within these pyrazolines. However, the cis/trans product ratios are inconsistent with predominant backside displacement of N_2 within an intermediate such as **38**,[50,51] as a high degree of inversion of configuration would then be predicted, regardless of the extent of rotation within **38**.



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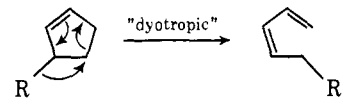
The appearance of **24** among the thermolysis products of **26b** is of some interest. This seems best rationalized as the product of thermally induced 1,3-sigmatropic migration of the trimethylsilyl group. A parallel rearrangement has been postulated to occur from 3,4,5-tricarboethoxy-3-trimethylsilyl-1-pyrazoline[52] and similarly substituted pyrazoles,[53] but no data evidencing the intermediacy of the C-silylated compound of the rearrangement were presented in these reports.[54] That the structurally similar **20a** and **20b** did not exhibit migration to a significant extent on thermolysis may be due to different conditions or may reflect a steric inhibition to migration due to the nonbonded trimethylsilyl-phenyl group interactions which would result in the products.

In concluding, we note that the transformations of, e.g., **2a,b** → **3a,b** bear a similarity to intramolecular, two σ-bond rearrangement processes which Reetz has defined as "dyotropic".[55] A pertinent example of the latter incorporating both a cyclic structure and a participating π bond is shown (**39**).[55] Extension of this concept suggests the terms "triotropic" for the general class of transformations involving simultaneous reorganization of three σ bonds and "triotropic cycloreversion" for the present rearrangements (**40**).[56] The latter are recognized as thermally allowed reactions proceeding via an aromatic transition state (**41**).[62]



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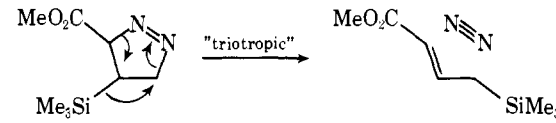

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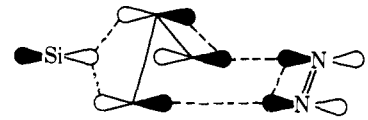

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Experimental Section

IR spectra (neat, values in μm) were obtained with Beckman IR-8 and IR-12 spectrometers. NMR spectra (solvent, internal standard) were recorded using Varian A-60A or JEOL PFT-100 spectrometers (chemical shift values are assigned from the center of a multiplet). Unless otherwise stated, distillations were carried out using short-path apparatus, and reactions run under inert gas atmospheres. Suitable shielding was employed during distillation of diazo compounds. Diazomethane was prepared from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide[63] ("Diazald", Aldrich Chemical Co., Milwaukee, Wis.) and standardized by benzoic acid derivatization followed by ester determination (GLC) using standard solutions of methyl benzoate. Ethereal diazomethane was stored over KOH pellets before use. This and other volatile diazo compounds were purified by distillation from KOH pellets under vacuum into a dry ice cooled receiver.

Methyl 3-Trimethylsilylpropynoate (4). 3-Trimethylsilylpropynoic acid[64] (10 g, 70 mmol) in 100 mL of ether was treated with 80 mmol of diazomethane in 250 mL of ether. Distillation gave 9.5 g (87%) of **4**:[1] bp 71–75 °C (14 mm); IR 3.36 m, 4.58 m, 5.84 s, 6.96 m, 8.2 vs, 11.38 s, 11.89 vs, 13.29 m, 14.25 m.

***cis*-Methyl 3-Trimethylsilylpropenoate (1a). A. From Hydroboration–Protonolysis of 4.** A THF solution of 55 mmol of disiamylborane was added to 7.8 g (50 mmol) of **4** in 100 mL of THF under N_2.[65] After stirring at 0–5 °C for 1 h, then 25 °C for 0.5 h, 14 mL of glacial acetic acid was added, and the mixture heated at 65–70 °C for 2 h. Sodium hydroxide solution (6 N, 45 mL) was then added below 10 °C, followed by 13 mL of 30% H_2O_2 at 35–40 °C. Workup followed by spinning band fractionation afforded 1 g (13%) of **1a**,[1] bp 80–84 °C (80 mm), which GLC (10 ft 15% FFAP, 130 °C) indicated contained 7% **4** and 6% 4-methyl-2-butanol. IR (**1a**): 3.26 w, 3.31 m, 3.35 s, 3.40 m, 3.47 w, 5.76 s, 6.24 w, 6.94 s, 7.29 s, 8.02 s, 8.25 s, 8.53 s, 9.99 m, 11.00 m, 11.9 s, 13.08 s, 13.95 w, 14.48 m, 15.23 m.

An alternate reduction was carried out as follows. To 30.1 mmol of dicyclohexylborane[66] at 0 °C was added 3 g (19.2 mmol) of **4** in 15 mL of THF. After 1 h at 0 °C (dicyclohexylborane dissolved), and 0.5 h at 20 °C, 3 mL of glacial acetic acid was added and the mixture stirred for 10 min. Ether was added, and the solution was extracted with 10% $NaHCO_3$, dried, and fractionated (Widmar column). A mixture of **1a** and unreacted **4** was obtained; the major and purest

fraction had bp 73–80 °C (50 mm), and was 80% **1a**. Total yield of **1a** was 0.77 g (26%).

B. From Semihydrogenation of 4. An atmospheric pressure hydrogenation apparatus was fitted with a side-arm reaction flask containing 4 g of Lindlar catalyst poisoned by lead acetate[67] and 82 mL of THF. The apparatus was evacuated and hydrogen admitted over water to a pressure slightly over 1 atm. After 5 min of stirring, 10 g (64 mmol) of **4** was injected and the reaction monitored periodically by GLC; absorption of 64 mmol of H_2 required 4.5 h. The catalyst was removed by filtration and the filtrate distilled to give 8.3 g (82%) of **1a**, bp 81–85 °C (60 mm), which GLC showed also contained 7% methyl-3-trimethylsilylpropanoate,[68] 3% **1b**, and 4% unreacted **4**. The propanoic ester had IR 3.36 m, 3.42 w, 5.74 s, 6.97 w, 7.38 w, 8.01 m, 8.28 m, 12.00 s. Anal. Calcd for $C_7H_{16}O_2Si$: C, 52.45; H, 10.06. Found: C, 52.32; H, 10.39.

The removal of **4** from samples of **1a** was carried out as follows.[69] A stirred mixture of 10.6 g of **1a** containing 7% (4.7 mmol) of **4** in 15 mL of methanol was treated dropwise with a solution of 0.85 g (5.0 mmol) of silver nitrate in 3 mL of water and 9 mL of methanol. The solution became warm and a cloudy suspension formed. After 10 min more, a solution of 1.7 g of KCN in 3 mL of water was added. After the precipitate had dissolved, workup gave 8.8 g (83%) of **1a** free of **4**. The **1a**:**1b** ratio was unchanged.

***trans*-3-Trimethylsilylpropenoic Acid (5). A. The Grignard Route.** A THF solution of β-trimethylsilylvinylmagnesium bromide (150 mL, 0.38 M) was added dropwise under N_2 to a mechanically stirred slurry of powdered dry ice in THF. After warming to 25 °C, it was poured into dilute hydrochloric acid and the organic phase extracted with aqueous potassium carbonate. Acidification and workup then afforded 0.6 g (7%) of **5**, bp 83–90 °C (3 mm) [lit.[3] bp 113 °C (13 mm)]. By using a large excess of dry ice and external cooling (−78 °C) of the reaction flask, a yield of 30% was obtained in one run. The organic phase, above, was distilled to give 0.9 g of a liquid, bp 80–90 °C (0.5 mm), which contained at least four components. The major of these were collected by GLC and identified as follows. *trans,trans*-1,4-Bis(trimethylsilyl)-1,3-butadiene:[70] NMR (CCl_4, $HCCl_3$) δ 6.7, 6.4, 6.1, 5.8 (4 H, AA′BB′ pattern), 0.14 (18 H, s); IR 3.31 m, 3.36 s, 3.42 m, 6.44 m, 7.11 w, 7.68 w, 8.02 s, 8.61 m, 9.95 s, 11.9 vs, 13.08 m, 14.35 s. *trans,trans*-1,5-Bis(trimethylsilyl)-1,4-pentadien-3-one: NMR (CCl_4, $HCCl_3$) δ 7.07, 7.57 (4 H, AB pattern, J = 19 Hz), 0.01 (18 H, s); IR 3.32 w, 3.38 s, 3.44 w, 6.08 s, 6.33 m, 7.12 w, 7.61 w, 7.22 w, 8.06 s, 8.27 s, 8.38 m, 8.73 m, 9.29 w, 10.08 s, 10.89 w, 12.0 vs, 13.32 m, 13.85 w, 14.49 m. Anal. Calcd for $C_{11}H_{22}OSi_2$: C, 58.34; H, 9.79. Found: C, 58.42; H, 9.41.[71]

B. According to Scheme I. The following compounds were obtained in the indicated yields by literature procedures: **7** (75%) [bp 61–66 °C (10 mm) [lit.[5] bp 65° (10 mm)]; NMR δ 4.19 (2 H, s), 3.18 (1 H, s), 0.10 (9 H, s); IR 3.0 s, 3.35 s, 4.6 s, 7.1 m, 7.4 m, 8.0 s, 9.6 s, 10.2 m, 12.0 s, 13.3 m, 14.4 w]; **8**[6] (87%) using no sodium methoxide and at 25 °C, bp 63–64 °C (10 mm), 95% pure by GLC, identified by IR comparison;[72] **9**[7] (60%), bp 50–54 °C (35 mm), 98% pure by GLC, identified by NMR comparison;[73] IR 3.35 m, 3.42 w, 3.55 w, 3.68 w, 5.91 s, 6.33 w, 8.00 m, 9.25 m, 10.10 m, 11.95 s, 13.00 w, 13.74 w, 14.40 w.

To a solution of 3.32 g (25.6 mmol) of **9** in 20 mL of acetone was added 1.95 g (19.5 mmol) of CrO_3 in 1.65 mL of H_2SO_4 and 6.35 mL of water. The mixture was stirred for 6 h at 60 °C and 2 additional days at 25 °C. Workup gave 2.11 g (57%) of **5**, bp 65–70 °C (0.4 mm).

***trans*-Methyl 3-Trimethylsilylpropenoate (1b).**[74] A 25% aqueous solution of 1.44 g (36.0 mmol) of sodium hydroxide was added to 3.44 g (23.9 mmol) of **5** in 40 mL of hexamethylphosphortriamide, and the solution stirred for 1 h at 25 °C. Methyl iodide (13 g, 96 mmol) was then added, the mixture stirred overnight, and subjected to acid workup. Distillation gave 13 g (87%) of **1b**,[1] bp 68–74 °C (20 mm), which GLC (15 ft 15% TCEP, 170 °C) showed was free of **1a**. IR 3.27 w, 3.35 s, 3.42 m, 3.49 w, 5.72 s, 6.25 m, 6.96 s, 7.66 s, 8.16 s, 8.59 s, 10.06 s, 12.0 s, 13.24 m, 13.78 w, 14.42 m, 15.3 m.

Reaction of 1a,b with Diazoalkanes. A. With Diazomethane. An ethereal solution of diazomethane (15 mL of 2.3 N solution, 3.5 mmol) was added to 0.5 g (3.2 mmol) of **1a** in 3 mL of ether at 25 °C under N_2. GLC analysis (10 ft 15% FFAP, 140 °C, bromobenzene internal standard) after 20 h indicated an 83% yield of **3a**:[1] IR 3.28 w, 3.37 s, 3.43 m, 5.83 s, 6.14 s, 6.94 m, 7.17 w, 8.01 s, 8.37 s, 8.48 s, 8.72 s, 9.75 m, 10.08 w, 10.29 w, 11.12 w, 11.8 s, 12.21 s, 13.52 w, 14.0 w, 14.4 w, 15.39 m. In another run, 18.2 mg (0.115 mmol) of GLC-collected **1a** was treated with 575 μL (0.115 mmol) of 0.20 N diazomethane. GLC showed **3a** as the only product, free of **1b** or cyclopropane isomers **10a,b**. No **1b** was observed to form when 0.115 mmol of **1a** was treated with 0.002 mmol of diazomethane.

Treatment of 3.2 mmol of **1b** as above afforded 75% of **3b**[1] free of **1a** or **10a,b**. IR (**1b**): 3.30 s, 3.37 w, 5.82 s, 6.09 s, 6.94 m, 7.07 w, 7.55 s, 7.91 s, 7.98 s, 8.31 s, 9.84 s, 9.55 s, 10.18 m, 10.84 m, 11.8 s, 13.05 w, 13.68 m, 13.84 m, 14.33 m, 15.13 m. In another run, the reaction of 8.9 mmol of **1b** and 13.8 mmol of diazomethane was monitored by GLC. The following percentage of **1b** was converted after the elapsed time indicated (min): 15 (1), 80 (13), 90 (26), 95 (30).

NMR observation of intermediate pyrazolines **2a,b** was effected as follows. To an ethereal solution of 18.2 mg (0.115 mmol) of GLC-collected **1a** or **1b** at −42 °C (acetonitrile–dry ice bath) in an NMR tube was added by syringe 400 μL (0.08 mmol) of 0.2 N ethereal diazomethane precooled to −78 °C. The mixture was allowed to warm to −23 °C and held at this temperature (CCl_4–dry ice bath) until the yellow color of diazomethane disappeared (2.5 h). Volatiles were removed at −23 °C (1 mm), the NMR tube immersed in a −42 °C bath, and precooled (−42 °C) $CDCl_3$ slowly added. NMR spectra were taken at intervals of 10 °C starting at −24 °C. Below 0 °C, only absorptions due to **2a,b** plus residual **1a,b** and ether were present; above this temperature, absorptions due to **3a,b** grew at the expense of those of **2a,b**.

B. With Diazoethane. Diazoethane[75] (5.7 mmol, 18.3 mL of a 0.31 N ethereal solution, redistilled over KOH pellets into a receiver at −78 °C) was added to 1.0 g (6.3 mmol) of **1a** in 5 mL of ether. After 20 min at 25 °C, the yellow color of diazomethane was discharged. Analysis by GLC (20 ft, 20% SE-30, 150 °C) indicated the following (% yield): *cis*-methyl 2-trimethylsilyl-2-pentenoate (**12a**) (34), *trans*-methyl 4-trimethylsilyl-2-pentenoate (**12b**) (5), and *trans*-methyl 2-trimethylsilyl-3-pentenoate (**13**) (25). **12a:** NMR ($CDCl_3$, PhH) δ 6.12 (1 H, t, J = 11.5 Hz, CH=C), 5.66 (1 H, d, J = 11.5 Hz, C=CHCO$_2$, 3.69 (3 H, s, OCH$_3$), 3.37 (1 H, m, SiCH), 1.14 (3 H, d, J = 6.9 Hz, CH$_3$), 0.02 (9 H, s, SiMe$_3$); IR 3.28 w, 3.37 m, 3.41 w, 3.46 w, 5.84 m, 6.17 m, 6.96 m, 7.09 w, 7.27 w, 7.71 w, 8.02 m, 8.36 s, 8.63 s, 9.66 w, 10.01 w, 10.22 w, 10.79 m, 12.0 s, 12.2 s, 13.29 w, 13.54 w, 14.48 w, 15.51 m. Anal. Calcd for $C_9H_{18}O_2Si$: C, 58.01; H, 9.74. Found: C, 57.96; H, 9.64. **12b:** NMR ($CDCl_3$, PhH) δ 7.17 (1 H, dd, J = 7.6, 15.6 Hz, CH=C), 5.66 (1 H, d, J = 15.5 Hz, C=CHCO$_2$), 3.73 (3 H, s, OCH$_3$), 1.91 (1 H, m, SiCH), 1.15 (3 H, d, J = 6.8 Hz, CH$_3$), 0.04 (9 H, s, SiMe$_3$); IR 3.37 s, 3.41 w, 3.46 w, 5.84 s, 6.14 s, 6.97 m, 7.26 w, 7.5 m, 7.73 s, 8.00 s, 8.37 s, 8.53 s, 8.80 s, 8.89 s, 9.07 m, 9.36 w, 9.56 w, 9.9 w, 10.13 w, 10.28 m, 10.84 w, 11.27 m, 11.9 s, 13.30 w, 13.63 w, 13.92 w, 14.47 w, 15.40 v4 m. Anal. Found: C, 57.97; H, 9.63. **13:** NMR ($CDCl_3$, PhH) δ 5.68 (1 H, dd, J = 9.8, 15.2 Hz, C=CH), 5.37 (1 H, m, J = 5.8, 14.9 Hz, MeCH=C), 3.66 (3 H, s, OCH$_3$), 2.86 (1 H, d, J = 9.3 Hz, CHCO$_2$), 1.71 (3 H, d, J = 5.9 Hz, CH$_3$), 0.08 (9 H, s, SiMe$_3$); IR 3.28 w, 3.36 m, 3.47 w, 5.82 s, 6.97 m, 7.24 w, 7.46 m, 8.00 s, 8.23 m, 8.41 m, 8.68 s, 8.85 m, 9.32 m, 9.75 w, 10.0 w, 10.30 m, 10.67 w, 11.14 w, 11.84 s, 13.3 w, 14.0 w, 14.4 w, 15.5 w. Anal. Found: C, 58.18; H, 9.62.

Identical treatment of 3.15 mmol of **1b** with 2.85 mmol of diazoethane resulted in decolorization within minutes and afforded 54% **12b** and 25% **13**.

C. With *tert*-Butyldiazomethane. A solution of 1.0 g (6.3 mmol) of **1a** and 10 mL of ether was treated with 15 mL of a 0.40 N (6.1 mmol) ethereal solution of *tert*-butyldiazomethane[76] at 25 °C. The evolved gas was monitored, and was equal to the theoretical amount of N_2 after 20 min. GLC indicated a 66% yield of *trans*-methyl 2-trimethylsilyl-5,5-dimethyl-3-hexenoate (**15**). NMR ($CDCl_3$, PhH) δ 5.62 (1 H, dd, J = 9.3, 16 Hz, C=CH), 5.33 (1 H, d, J = 16 Hz, *t*-BuCH=C), 3.67 (3 H, s, OCH$_3$), 2.86 (1 H, d, J = 10 Hz, CHCO$_2$), 1.05 (9 H, s, *t*-Bu), 0.10 (9 H, s, SiMe$_3$); IR 3.37 s, 3.44 w, 3.48 w, 5.78 s, 6.01 w, 6.83 w, 6.97 w, 7.30 w, 7.45 w, 7.95 s, 8.34 m, 7.96 s, 9.32 m, 10.22 m, 11.70 s, 13.15 w, 14.10 w. Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59. Found: C, 63.08; H, 10.48.

Identical treatment of **1b** on the same scale led to an equivalent amount of nitrogen in 20 min and a 90% yield of **15**.

D. With Phenyldiazomethane. Especial efforts were made to ensure anhydrous conditions. Glassware was boiled in distilled water for 1 h, rinsed, dried, and flamed out under dry (magnesium perchlorate) nitrogen. Phenyldiazomethane[77] was dried successively over sodium sulfate and KOH pellets and distilled [70 °C (2.5 mm)]. This material was dissolved in ether and 5 mL of the resulting 1.3 N solution (6.3 mmol) added at once to 1.0 g (6.3 mmol) of **1a** in 5 mL of ether. Gas

evolution was monitored by collection over di-*n*-butyl phthalate; after 2 h, evolution had essentially ceased, giving 112 mL of N_2. After solvent removal, GLC indicated a complex mixture of products (at least six peaks on 10 ft, 20% SE-30, 200 °C), the major of which was identified as *trans*-methyl 4-phenyl-3-butenoate (**18b**). NMR ($CDCl_3$, Me_4Si) δ 7.31 (5 H, m, Ph) 6.51 (1 H, d, J = 16.1 Hz, PhCH), 6.26 (1 H, m, J = 6.1, 15.9 Hz, C=CH), 3.71 (3 H, s, OCH_3), 3.25 (2 H, d, J = 6.1 Hz, CH_2); IR 3.28 w, 3.37 w, 5.78 s, 6.70 w, 6.97 m, 7.11 w, 7.39 w, 7.72 m, 7.99 s, 8.34 s, 8.61 s, 10.35 s, 13.4 m, 14.45 m. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.88; H, 6.76.

An NMR spectrum ($CDCl_3$, CH_3CN) of the crude reaction mixture showed, among others, peaks attributable to **18b** plus absorptions which would correspond to *cis*-methyl 4-phenyl-4-trimethylsilyl-2-butenoate (**16a**) at δ 6.93 (t, J = 12 Hz, CH=CCO_2), 6.00 (d, J = 11.6 Hz, C=$CHCO_2$), 5.13 (d, J = 12.0 Hz, SiCH). Upon standing, GLC indicated that **18b** grew at the expense of other peaks present in the chromatogram, and after 3 days, constituted the only product peak (89% yield). Quantitative analysis of the reaction mixture at lower temperature (80 °C) then indicated the presence of 0.5 equiv of hexamethyldisiloxane.

Treatment of 0.53 g (3.3 mmol) of **1b** with 3.3 mmol of phenyldiazomethane led to evolution of 86 mL (90%) of gas in 2 h. GLC showed two peaks, one of which was **18b** (81% yield after standing 3 days) and the other (approximately 50% initially) a hydrolytically unstable compound which slowly disappeared. Again, 0.5 equiv of hexamethyldisiloxane was present after all of the latter had desilylated. This unstable material was spectrally characterized as *trans*-methyl 4-phenyl-4-trimethylsilyl-2-butenoate (**16b**), but elemental analysis could not be obtained. NMR ($CDCl_3$, CH_3CN) δ 7.1–7.6 (6 H, m, PhCCH), 5.85 (1 H, t, J = 15.6 Hz), 3.79 (3 H, s, OCH_3), 3.26 (1 H, d, J = 10.0 Hz, SiCH), 0.10 (9 H, s, $SiMe_3$); IR 3.28 w, 3.36 w, 5.72 s, 6.13 s, 6.27 m, 6.70 w, 6.98 m, 8.01 s, 8.12 s, 8.60 s, 9.45 s, 10.34 m, 11.84 s, 13.26 m, 13.41 m, 14.36 m.

E. With Ethyl Diazoacetate. Special attention was paid to maintain anhydrous conditions. Ethyl diazoacetate[78] (0.72 g, 6.3 mmol) was added at 65 °C to a solution of 1.0 g (6.3 mmol) of **1a** in 5 mL of THF (freshly distilled from $LiAlH_4$). The evolved gas amounted to 82% of the theoretical after 43 h at 65 °C; no **1a** remained at this time. GLC (8 ft, 20% polyphenyl ether, 160 °C) indicated a 58% yield of either *trans*-methyl 4-carboethoxy-2-butenoate or *trans*-ethyl 4-carbomethoxy-2-butenoate (**19b**) and a 13% yield of either of the corresponding cis isomers (one of which is **19a**). The major product had NMR ($CDCl_3$, CH_3CN) δ 6.99 (1 H, m, J = 7.5 Hz, C=CHCCO_2), 5.94 (1 H, d, J = 17.3 Hz, C=$CHCO_2$), 4.17 (2 H, q, J = 7 Hz, CH_2O), 3.69 (3 H, s, OCH_3) 3.25 (2 H, d, J = 7.4 Hz, CH_2), 1.26 (3 H, t, J = 7 Hz, CH_3); IR 3.33 m, 3.36 m, 6.81 s, 6.03 m, 6.97 m, 7.30 w, 7.78 s, 8.35 s, 8.65 s, 9.3 w, 9.66 m, 10.15 m, 10.68 w, 11.7 w, 11.8 w. Anal. Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 55.55; H, 7.21. The minor product had NMR (CCl_4, $CHCl_3$) δ 6.5 (1 H, m, C=CHCCO_2), 5.82 (1 H, d, J = 13 Hz, C=$CHCO_2$), 4.17 (2 H, q, J = 7 Hz, CH_2O), 3.74 (CH_2, overlapped with OCH_3), 3.69 (s, OCH_3), 1.36 (3 H, t, J = 7 Hz, CH_3); IR 3.32 m, 3.35 m, 5.83 s, 6.05 m, 6.95 m, 7.30 m, 7.54 s, 8.6 s, 9.76 m, 10.22 w, 11.26 w, 12.2 m, 13.3 w. Anal. Found: C, 55.63; H, 7.00.

Identical treatment of **1b** on the same scale afforded 4.6 mmol (73%) of N_2 in 48 h. A 41% yield of **19b** (or isomer) and a 9% yield of **19a** (or isomer) was obtained, together with 0.5 equiv of hexamethyldisiloxane.

F. With Diphenyldiazomethane. A mixture of 1.0 g (6.3 mmol) of **1a** and 1.2 g (0.29 mmol) of diphenyldiazomethane[79] in dry hexane was stored at 0 °C for 10 days. The white crystals which formed were washed with hexane to give 1.56 g (71%) of pure *cis*-4-carbomethoxy-3,3-diphenyl-5-trimethylsilyl-1-pyrazoline (**20a**): mp 81–83 °C; NMR (Table III); IR 3.28 w, 3.37 m, 5.80 m, 6.27 w, 6.47 w (-N=N-),[26,80] 6.72 m, 6.98 m, 7.40 s, 8.02 m, 8.6 s, 9.32 m, 9.80 w, 10.00 w, 10.22 m, 10.45 w, 11.01 m, 12.0 s, 13.40 s, 14.48 s. Anal. Calcd for $C_{20}H_{24}N_2O_2Si$: C, 68.14; H, 6.86; N, 7.95. Found: C, 67.90; H, 6.92; N, 8.03.

The pyrazoline **20a** could be recrystallized from hot hexane to give, with some loss, material identical with that above. Recrystallization from methanol–water led to the desilylated 4-carbomethoxy-5,5-diphenyl-2-pyrazoline (**21**): mp 110–112 °C; NMR (CCl_4, Me_2SO) δ 6.9–7.7 (10 H, m, Ph_2), 6.63 (1 H, s,[81] C=CH), 4.55 (1 H, s,[81] $CHCO_2$), 7.25 (3 H, s, OCH_3), N-H not observed; IR 2.99 s (N-H),[23] 3.26 m, 5.88 s, 6.34 (C=N),[23] 6.73 w, 7.12 s, 8.10 s, 9.18 w, 9.81 s, 10.19 m, 10.79 w, 10.91 w, 11.10 w, 11.37 w, 11.71 m, 12.38 w, 13.32 s, 14.43 s, 15.02 m. Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.83; H, 5.75; N, 9.99. Found: C, 73.09; H, 5.99; N, 9.98.

Thermolysis of **20a** in refluxing hexane overnight afforded three products in approximately a 1:10:6 ratio (order of elution, 5 ft, 15% FFAP, 200 °C). The last two compounds were isolated and identified as respectively *trans*- and *cis*-methyl 2,2-diphenyl-3-trimethylsilylcyclopropanecarboxylate (**22b, 22a**). **22b:** NMR ($CDCl_3$, CH_2Cl_2) δ 7.4–7.9 (10 H, m, Ph_2), 3.61 (3 H, s, OCH_3), 2.86 (1 H, d, J = 8 Hz, $CHCO_2$), 1.73 (1 H, d, J = 8.5 Hz, CHSi), −0.13 (9 H, s, $SiMe_3$); IR 3.24 m, 3.27 m, 3.36 s, 3.42 m, 5.82 s, 6.24 w, 6.69 m, 6.96 s, 7.18 m, 7.64 m, 7.92 s, 8.01 s, 8.30 s, 8.59 s, 9.27 m, 9.37 m, 9.58 w, 9.80 s, 10.83 m, 11.29 s, 11.9 s, 12.88 m, 13.36 s, 14.33 s. Anal. Calcd for $C_{20}H_{24}O_2Si$: C, 74.03; H, 7.42. Found: C, 74.06; H, 7.45. **22a:** NMR ($CDCl_3$, CH_2Cl_2) δ 7.2–7.7 (10 H, m, Ph_2), 3.75 (3 H, s, OCH_3), 2.49 (1 H, d, J = 10.5 Hz, $CHCO_2$), 1.06 (1 H, d, J = 10.5 Hz, CHSi), −0.04 (9 H, s, $SiMe_3$); IR 3.25 m, 3.28 m, 3.37 s, 3.43 m, 5.80 s, 6.25 w, 6.70 m, 6.97 s, 7.20 m, 7.72 m, 8.04 s, 8.40 s, 8.55 s, 8.80 m, 9.37 w, 10.60 w, 10.79 w, 11.50 m, 11.97 s, 13.40 m, 14.24 s, 14.40 s. Anal. Found: C, 74.53; H, 7.32. Duplicate analyses did not improve the carbon value. The stereochemistry of **22a,b** was predicated on the basis of vicinal coupling constants.[15]

The reaction of **1b** and diphenyldiazomethane on the same scale as with **1a** was carried out at reflux in 10 mL of dry hexane for 2.5 h. Recrystallization from hexane led to 1.5 g (69%) of *trans*-4-carbomethoxy-3,3-diphenyl-5-trimethylsilyl-1-pyrazoline (**20b**): mp 89–91 °C; NMR (Table III); IR 3.24 m, 3.40 m, 3.36 m, 3.43 m, 3.50 w, 5.82 m, 6.24 w, 6.46 w, 6.72 m, 6.67 m, 7.43 m, 8.19 s, 8.53 s, 8.96 m, 9.26 m, 9.70 w, 10.16 m, 10.51 m, 10.96 m, 11.9 s, 12.40 s, 13.34 s, 14.43 s, 15.32 w. Anal. Found: C, 68.13; H, 6.95. Overnight reflux of **20b** in hexane led to recovered starting materials; thermolysis in refluxing octane overnight gave a **22b:22a** ratio of 83:17.

G. With 2-Diazopropane. All glassware was boiled in distilled water for 1 h, rinsed with distilled water, and dried before use. A 2.5-mL portion of 1.3 N ethereal 2-diazopropane[82] (redistilled from KOH pellets, 3.2 mmol) and 0.5 g (3.2 mmol) of **1a** in 5 mL of ether was stirred at 25 °C for 1 h under N_2 and solvent removed. GLC analysis (20 ft, 20% SE-30, 230 °C) indicated a 75% yield of 4-carbomethoxy-5,5-dimethyl-3-trimethylsilyl-2-pyrazoline (**23**): NMR ($CDCl_3$, $CHCl_3$) δ 5.53 (1 H, s, NH), 3.69 (3 H, s, OCH_3), 3.45 (1 H, s, $CHCO_2$), 1.32 (3 H, s, CH_3), 1.14 (3 H, s, CH_3), 0.16 (9 H, s, $SiMe_3$); IR 2.98 m (N-H), 3.36 m, 5.82 m, 6.51 w,[83] 6.99 m, 7.30 m, 7.52 m, 8.02 s, 8.4 m, 8.69 m, 9.7 m, 11.56 m, 11.98 s, 13.24 m. Anal. Calcd for $C_{10}H_{20}N_2O_2Si$: C, 52.59; H, 8.83. Found: C, 52.80; H, 8.58.

In another run, an NMR spectrum taken of the crude reaction mixture after solvent removal showed that **23** was present prior to GLC analysis.

Treatment of **1b** identical with that above for 10 min (to disappearance of red color of 2-diazopropane) followed by GLC analysis indicated a yield of 49% 4-carbomethoxy-5,5-dimethyl-1-trimethylsilyl-2-pyrazoline (**24**) and 42% *trans*-methyl 2,2-dimethyl-3-trimethylsilylcyclopropanecarboxylate (**25**).[86] NMR (**24**) ($CDCl_3$, $CHCl_3$) δ 6.38 (1 H, d, J = 1.5 Hz, N=CH), 3.64 (3 H, s, OCH_3), 3.55 (1 H, d, J = 1.7 Hz, $CHCO_2$), 1.38 (3 H, s, CH_3), 1.09 (3 H, s, CH_3), 0.17 (9 H, s, $SiMe_3$); IR 3.37 s, 3.43 m, 5.78 s, 6.39 w, 6.85 m, 6.98 m, 7.22 w, 7.32 m, 7.49 m, 8.00 s, 8.19 s, 8.42 s, 9.2 m, 9.75 s, 9.96 s, 10.48 w, 10.78 w, 11.9 s, 12.40 s, 13.28 s, 14.55 m, 15.68 m. Anal. Calcd for $C_{10}H_{20}N_2O_2Si$: C, 52.59; H, 8.83. Found: C, 52.42; H, 8.58.

NMR (**25**) ($CDCl_3$, PhH) δ 3.67 (3 H, s, OCH_3), 1.50 (1 H, d, J = 7.3 Hz, $CHCO_2$), 1.27 (3 H, s, CH_3), 1.19 (3 H, s, CH_3), 0.45 (1 H, d, J = 7.3 Hz, CHSi), 0.07 (9 H, s, $SiMe_3$); IR 3.36 s, 5.81 s, 6.98 m, 7.15 m, 7.61 m, 7.82 m, 8.02 s, 8.36 s, 8.61 s, 9.00 m, 9.14 m, 9.41 m, 10.75 w, 11.14 m, 11.59 s, 11.99 s, 13.15 m, 14.5 w. Anal. Calcd for $C_{10}H_{20}O_2Si$: C, 59.95; H, 10.06. Found: C, 60.01; H, 10.04.

In another run, an NMR spectrum of the crude reaction mixture after solvent removal only showed absorptions consistent with *trans*-4-carbomethoxy-3,3-dimethyl-5-trimethylsilyl-1-pyrazoline (**26b**) (Table III).

In yet another run, 2-diazopropane was employed which was distilled, but not from KOH. There was obtained an 84% yield of 4-carbomethoxy-5,5-dimethyl-2-pyrazoline (**27**): NMR ($CDCl_3$, PhH) δ 6.77 (1 H, s, N=CH), 4.85 (1 H, broad s, NH), 3.76 (3 H, s, OCH_3), 3.58 (1 H, s, $CHCO_2$), 1.50 (3 H, s, CH_3), 1.15 (3 H, s, CH_3); IR 2.98 m (N-H), 3.34 s, 5.80 s, 6.27 w, 6.95 s, 7.22 m, 7.31 s, 7.56 s, 7.89 s, 8.37 s, 9.33 w, 9.8 m, 10.37 w, 10.67 w, 10.83 m, 12.0 m, 12.5

m, 13.5 s. Anal. Calcd for $C_7H_{12}N_2O_2$: C, 53.83; H, 7.74; N, 17.98. Found: C, 53.80; H, 7.72; N, 17.68. This same material (**27**) was obtained by treating pure **24** with water.

Reaction of 1a,b with Phenyl(bromodichloromethyl)mercury.[87] A mixture of phenyl(bromodichloromethyl)mercury (1.4 g, 3.2 mmol), 0.50 g (3.2 mmol) of **1a,** and 15 mL of dry benzene was heated at 80 °C under N_2 for 13 h. GLC analysis indicated 34% **1a** remaining and a 37% yield of *cis*-methyl 2,2-dichloro-3-trimethylsilylcyclopropanecarboxylate (**9a**): NMR (CCl_4, $CHCl_3$) δ 3.72 (3 H, s, OCH_3), 2.61 (1 H, d, J = 12.5 Hz, $CHCO_2$), 1.16 (1 H, d, J = 12.5 Hz, CHSi), 0.22 (9 H, s, $SiMe_3$); IR 3.36 s, 3.42 m, 5.78 s, 6.96 s, 7.29 s, 8.00 s, 8.36 s, 8.51 s, 9.3 w, 9.80 m, 10.54 m, 11.04 m, 11.8 s, 13.0 m, 13.66 m, 14.4 m, 15.56 m. Anal. Calcd for $C_8H_{14}O_2Cl_2Si$: C, 39.83; H, 5.87. Found: C, 39.86; H, 5.55.

Similar treatment of **1b** with 1.5 equiv of the mercurial afforded 35% unreacted **1b** and a 35% yield of trans isomer **9b.** NMR (CCl_4, $CHCl_3$) δ 3.86 (3 H, s, OCH_3) 2.50 (1 H, d, J = 9.5 Hz, $CHCO_2$), 1.65 (1 H, d, J = 9.5 Hz, CHSi), 0.47 (9 H, s, $SiMe_3$); IR 3.36 m, 3.42 w, 5.77 s, 6.95 m, 7.28 s, 7.99 s, 8.31 s, 8.39 s, 8.52 s, 9.31 w, 9.65 m, 10.55 m, 11.53 s, 11.9 s, 12.99 m, 13.18 m, 13.69 m, 14.35 m. Anal. Found: C, 39.96; H, 5.86.

***cis*- and *trans*-Methyl 2-Trimethylsilylcyclopropanecarboxylate (10a,b).** A 3:7 mixture of *cis*- and *trans*-ethyl 2-trimethylsilylcyclopropanecarboxylates was prepared from the reaction of ethyl diazoacetate and trimethylvinylsilane according to the literature procedure.[88] This material was allowed to stand overnight in acidified (hydrogen chloride) methanol followed by 1 h at reflux. The product consisted of a 3:7 mixture of *cis*- and *trans*-methyl 2-trimethylsilylcyclopropanecarboxylates (**10a,b**), as indicated by GLC analysis (order of elution, 10 ft 15% β,β'-oxypropionitrilephenylacetonitrile, 100 °C). NMR (**10a**) ($CDCl_3$, $CHCl_3$) δ 3.77 (3 H, s, OCH_3), 1.8–2.1 (1 H, m, $CHCO_2$), 1.1–1.6 (2 H, m, CH_2), 0.3–0.7 (m, CHSi), 0.35 (s, $SiMe_3$), last two absorptions overlapped; IR 3.30 m, 3.36 s, 3.42 m, 5.78 s, 6.94 s, 7.20 s, 7.8 m, 8.01 s, 8.34 s, 8.50 s, 9.86 m, 9.1 m, 9.47 w, 9.78 w, 9.94 m, 10.98 m, 11.25 m, 11.62 s, 11.94 s, 12.96 m, 13.23 m, 14.5 m, 15.55 m. Anal. Calcd for $C_8H_{16}O_2Si$: C, 55.77; H, 9.36. Found: C, 55.68; H, 9.27.

The trans isomer **10b** had NMR ($CDCl_3$, $CHCl_3$) δ 3.75 (3 H, s, OCH_3), 0.4–1.9 (4 H, m, all cyclopropyl H), 0.27 (9 H, s, $SiMe_3$); IR 3.30 m, 3.35 s, 3.42 m, 5.78 s, 6.94 s, 7.22 s, 7.99 s, 8.33 s, 8.53 s, 9.04 m, 9.80 m, 10.36 w, 11.02 s, 11.9 s, 12.98 m, 13.35 s, 14.43 m, 14.8 w, 15.32 m. Anal. Found: C, 55.78; H, 9.17.

Various modifications[89] of the Simmons–Smith reaction using **1a,b** and methylene iodide failed to give **10a,b.**

Rate Comparisons. The rate data for thermolysis of 3-carbomethoxy-3-methyl-1-pyrazoline (reported for the temperature range 109–126 °C in tetralin) were corrected to reflect the formation of olefinic products, and a plot of log k vs. $1/T$ constructed and extrapolated to 25 °C. The value of k thus obtained (10^{-10} s^{-1}) was compared with the value for *trans*-3-carbomethoxy-4-trimethylsilyl-1-pyrazoline ($k = 10^{-3}$ s^{-1}) obtained by following the disappearance of **1b** (95% conversion after 30 min) and noting that nitrogen evolution had ceased by this time. This represents a lower value for the rate of **2b** decomposition, as the prior cycloaddition step may be rate determining. The reaction of **1a,b** with *tert*-butyldiazomethane gave the theoretical amount of N_2 within 20 min after mixing.

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Catalyzed Oxidation Reactions. 4. Picolinic Acid Catalysis of Chromic Acid Oxidations[1,2]

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Abstract: Picolinic acid and several closely related acids are effective catalysts in the chromic acid oxidation of primary and secondary alcohols; the oxidation of other substrates is accelerated only moderately. The reaction is first order in chromium(VI), alcohol, and picolinic acid; it is second order in hydrogen ions at low acidity and approaches acidity independence at high perchloric acid concentrations. A primary deuterium kinetic isotope effect is observed at high but not at low acidities. At low acidity the reaction has a considerably lower activation energy and more negative activation entropy than at higher acidities. The reactive intermediate in the proposed mechanism is a negatively charged termolecular complex formed from chromic acid, picolinic acid, and alcohol. The rate-limiting step of the reaction changes with the acidity of the solution. At higher acidities the intermediate termolecular complex is formed reversibly and the overall reaction rate is determined by the rate of its decomposition into reaction products; at low acidities the formation of the complex is irreversible and hence rate limiting. Picolinic acids with a substituent in the 6 position show a greatly reduced catalytic activity. This observation is interpreted as suggesting a square pyramidal or octahedral structure for the reactive chromium(VI) intermediate. The temperature dependence of the deuterium isotope effect has been determined and the significance of the observed large values for $E_a^D - E_a^H$ and A^D/A^H is discussed.

Oxalic acid[3] and α-hydroxy acids[4] accelerate the oxidation–reduction reaction between alcohols and chromic acid by factors up to 10^4. The rapid reaction taking place under these conditions is a cooxidation process in which both the alcohol and the organic acid are oxidized. We proposed that the rate-limiting step of the cooxidation reaction involves a single-step