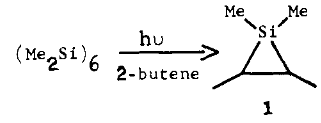
as for carbon, as the immediate products of addition of silylenes are much less stable than cyclopropanes, and only isolable with great effort.[4,11]

We describe here in preliminary fashion the determination of the stereospecificity of silylene addition to *cis*- and *trans*-2-butene.

We chose as silylene precursor dodecamethylcyclohexasilane, a molecule known to produce dimethylsilylene on irradiation.[5] As substrate we selected the isomeric 2-butenes both for their inherent simplicity and to maintain contact with classical carbene chemistry.[6] We hoped not to isolate the anticipated silirane **1**, but rather to study **1** indirectly through the product of methanolysis, **2**. Irradiation of dodecamethylcyclohexasilane through quartz with a 450-W Hanovia medium-pressure mercury arc followed by addition of excess methanol led to **2** in 20–24% yield.[7] Authentic **2** was made by the reaction of 2-butylmagnesium bromide with dimethyldimethoxysilane. In the ^{1}H NMR spectrum of **2**, H_c appeared as a broad multiplet at δ 0.66 ppm and the diastereotopic H_b and H_a as a pair of broad multiplets at δ 1.55 and 1.18 ppm.



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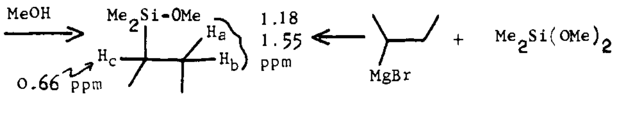

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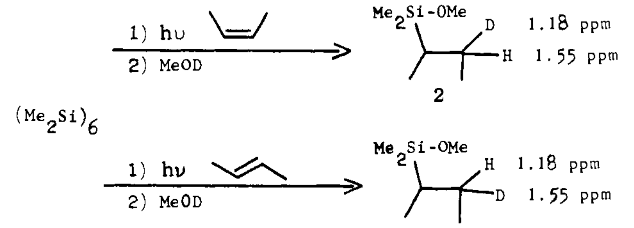
When the ring opening of **1** was carried out with CH_3OD, *cis*-2-butene led to a monodeuterio-**2** in which a broad multiplet remained at δ 1.55 ppm, but which lacked the multiplet at δ 1.18 ppm. With *trans*-2-butene as substrate the situation was the opposite: the signal at 1.18 ppm remained and that at 1.55 ppm had vanished. However, these broad multiplets were most difficult to analyze quantitatively, and we turned instead to an examination of the ^{2}H NMR spectra. In these spectra the multiplets "missing" in the ^{1}H NMR spectra appeared as singlets. Thus *cis*-2-butene led to **2** in which a single peak at δ 1.18 ppm appeared, and *trans*-2-butene to **2** possessing a signal at δ 1.55 ppm. No evidence for the peak corresponding to the product of methanolysis of **2** from *cis*-2-butene could be found in the material from *trans*-2-butene, but there was a small amount (~5%) of the compound from trans olefin in the product from *cis*-2-butene. However, recovered *cis*-2-butene could be shown to contain 2–3% *trans*-2-butene after photolysis and thus the figure of 5% represents a generous upper limit to the nonstereospecificity of the reaction.



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As a bonus, this work demonstrates that the opening of siliranes by methanol is also stereospecific. It is already known that silacyclopropenes open in what might be called cis fashion,[8] but the corresponding information was not available for siliranes, although Seyferth and co-workers had observed that a single compound appeared to be formed by methanolysis of a silirane.[4]

It must be noted that this work does not establish the *kind* of stereospecificity in either the addition reaction or opening. In principle, both the addition to give the silirane and the subsequent opening could be either cis or trans. Although the details of the ring opening remain to be established, it does not seem reasonable to postulate a trans addition of the silylene to the olefin. Silylenes are singlet ground states,[2,5,9,10] and a sensible expectation is that we are seeing the silicon counterpart of the known cis addition of singlet carbenes.[6]

Acknowledgment. Ms. Mary Baum of this department and Dr. M. Kelly of JEOL Analytical Instruments Division were most helpful in the determination of the ^{2}H NMR spectra. Conversations with Professor P. P. Gaspar on silylene chemistry and with Professor K. Mislow on stereochemistry have been very instructive.

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(7) Compound **2** was identified by elemental analysis and an examination of nuclear magnetic resonance, infrared, and mass spectra. Kumada et al. found the adducts of methylphenylsilylene and olefins to be unstable under conditions approximating ours.[3g] A referee has inquired as to the possibility of observation of silirane **1** by ^{1}H NMR. We have tried, but the debris formed from photochemical decomposition of $(Me_2Si)_6$ sufficiently complicates the spectrum so that a clear picture of **1** does not emerge.

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Stabilities of Stereoisomeric Imine Anions

Sir:

The stereospecific generations and alkylations of allyl and heteroallyl anions are of considerable synthetic value, because the anions shown in Figure 1 are more stable in the syn configuration shown than in the anti.[1-24] Isoelectronic neutral systems, such as enols and enol ethers[25] and carboxylic acids, esters, and imidates, also adopt the syn geometries about the oxygen.[26]

Several explanations of these or related phenomena have been proposed. (1) Hoffmann and Olofson suggested that polyenes and charged species prefer those conformations which have maximum π HOMO stabilization; that is, systems having homoaromatic $[4n + 2]\pi$-electron systems are preferred to those lacking homocyclic conjugation.[3] These authors also pointed out that a methyl group could act as a pseudo-π orbital.[3] Such 6π-electron *homoaromaticity* could account for the greater stability of the syn isomers of all 11 species shown

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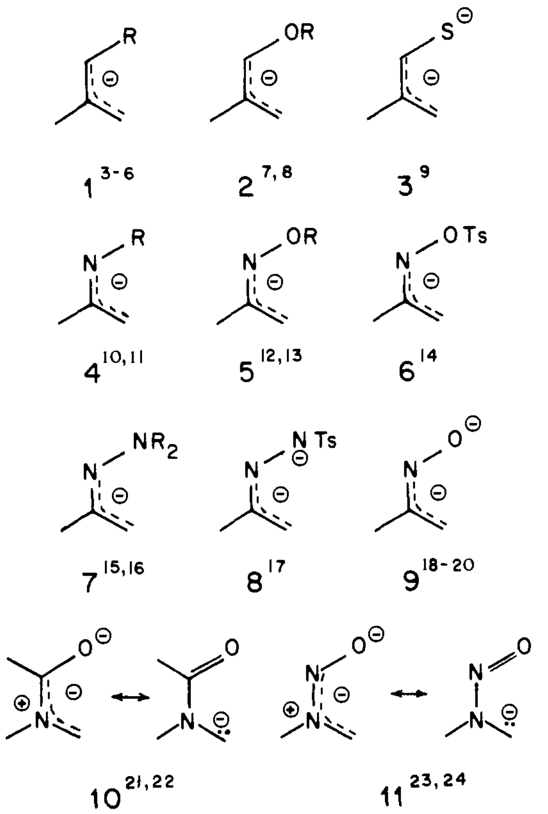


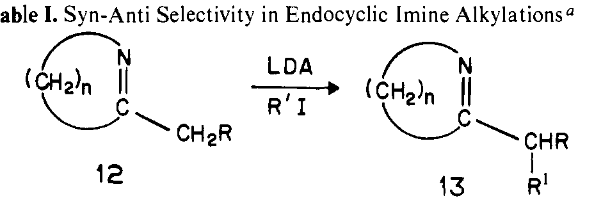
Figure 1. Species which prefer the syn configuration (shown) in solution.

in Figure 1.[27] Epiotis and co-workers have developed the general concept of steric attraction to explain the preferred conformations of some disubstituted ethylenes and related species.[28a] (2) Epiotis et al. also analyzed *σ-orbital interactions* (σ-σ* and n-σ*), which can produce a syn or anti preference in molecules lacking cyclic homoconjugation.[28] Similar considerations have been very successful in rationalizing preferred conformations of acyclic molecules with polar bonds.[28,29] (3) Classically, preferred conformations of molecules with polar bonds and lone pairs often have been rationalized as resulting from a minimization of *dipole-dipole* (*electrostatic*) *interactions.*[30] Bank explained the greater stability of *syn*- than of *anti*-alkenyl anions in this way,[2] but such effects have received only occasional consideration for the other systems in Figure 1.[10,31] (4) For the systems in Figure 1 which have a substituent, Z, with lone pairs, chelation of a covalently bound metal (usually Li) to Z often has been proposed to explain the syn preference.

However, we recently observed complete syn selectivity in the alkylation of lithiated ketimines[10] and aldimines.[11] In anions **4** (R = alkyl), the preference for the syn over anti configuration was estimated to exceed 4.5 kcal/mol.[11] Such a large stereochemical preference could not be attributed to homoaromaticity or chelation effects, and brought into question as well the importance of these interactions in the other anions shown in Figure 1. To establish the gas-phase stabilities of **4** and related systems, we have undertaken a theoretical study of these anions and some of the corresponding lithiated species. We report here additional experimental results and the first of these calculations.

First, we have extended our alkylation studies to include four endocyclic ketimines, **12a–d.** In contrast to their exocyclic counterparts,[10] these give exclusively the product resulting from alkylation at the anti carbon, as summarized in Table I. This remarkable total reversal of stereochemical stabilities can be accounted for by the theoretical calculations which follow.

Table I. Syn-Anti Selectivity in Endocyclic Imine Alkylations[a]



	substituents	**13**, % yield
a	$n = 3$, R = CH_2CH_3, R′ = CH_2CH_3	≥ 98
b	$n = 4$, R = H, R′ = CH_3	≥ 95
c	$n = 4$, R = CH_3, R′ = CH_3	≥ 95
d	$n = 5$, R = $CH_2CH_2CH_3$, R′ = $CH_2CH_2CH_3$	≥ 95

[a] Standard conditions: (1) anion formation at 0 °C in THF using 1 equiv of lithium diisopropylamide (LDA); (2) cooling to −78 °C; (3) addition of alkyl halide and, after 1 h, warming to 0 °C before workup. The only detectable product in any reaction was **13**, as identified from ^1H and ^{13}C spectra. The limits of detection of syn were carefully proved in formation of **13a** by synthesizing the product of syn alkylation independently and examining the sensitivity of ^{13}C to its presence; 2% of syn product was just detectable after 40 000 scans on a Varian FT-80.

Table II. Energies of Syn and Anti Imines, Anions, and Models

compd	syn, au	*E*(anti) − *E*(syn), kcal/mol
acetaldehyde imine (I)	−132.870 28	−0.8
vinylamine (II)	−132.875 15	
acetaldehyde imine anion (III)	−132.222 01	4.7
N-methyl acetaldehyde imine anion (IV)[a]	−171.193 28	6.2
acetone imine anion[a]	−171.204 37	4.5
acetaldehyde imine radical	−132.268 69	−0.5
acetaldehyde imine cation	−131.933 80	−9.2
acetyl fluoride imine[b]	−231.613 26	−4.7
acetyl fluoride imine anion[b]	−230.986 76	−0.4
π-lithio acetaldehyde imine (V)	−139.724 07	−16.1
σ(*N*)-lithio acetaldehyde imine (VI)[c]	−139.744 15	0.5
acetaldehyde enol	−152.670 74	2.1
F-protonated vinyl fluoride	−176.891 20	−0.9

[a] Standard methyl group, but all other geometrical parameters were optimized. [b] Species with NH syn to F is more stable. [c] The species with NH syn to C_3 is more stable.

For a variety of model systems, complete geometry optimizations for a variety of model systems were carried out with ab initio SCF-MO calculations using the split-valence 4-31G basis set.[32] Anion calculations are in general somewhat problematical,[33] but 4-31G calculations give reasonable structural data and relative energies for anions.[34,35]

Figure 2 shows the fully optimized geometries and relative energies of *syn*- and *anti*-acetaldehyde imine and vinylamine and of relevant anions.[36-38] The energies discussed here are tabulated in Table II. In the anions, III, the bond lengths approach those of vinylamine, although the charges (N-1, −0.89; C_2, +0.14; C-3, −0.55, in *syn*-III) are indicative of appreciable allyl anion character.[39] The NCC angles in III are considerably larger than those in I and are comparable with those in allyl anion ($\angle$CCC = 132°) and propene ($\angle$CCC = 125°), respectively.[35] The syn anion is found to be 4.7 kcal/mol more stable than the anti. This difference is slightly less in acetone imine anion, and increases to 6.2 kcal/mol in the *N*-methyl derivative, IV.

The very large preferred CCN angle (133°) in both *syn*-III and *syn*-IV suggests the reason for the favored anti imine anion formation from **12**. Constraint of the CCN angle in *syn*-III to 120° and reoptimization of all other geometrical parameters at the 4-31G level resulted in a 6.8-kcal/mol calculated increase in energy. In the anions derived from **12a–d**, the ring

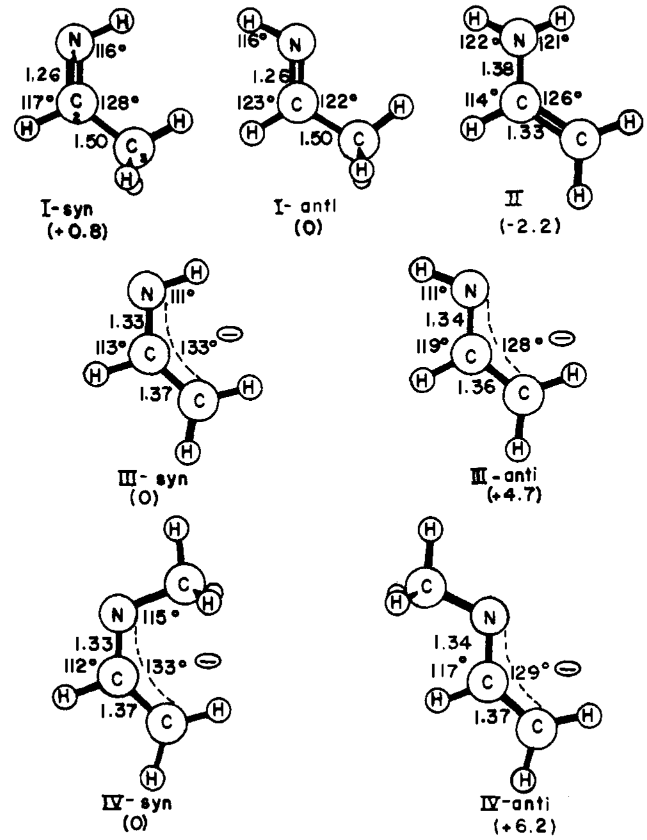


Figure 2. 4-31G//4-31G geometries of *syn-* and *anti*-acetaldehyde imine (I), vinylamine (II), *syn-* and *anti*-acetaldehyde imine anions (III), and *N*-methyl acetaldehyde imine (IV). Relative energies are shown in parentheses.

constrains this angle to 120°, or less, so that syn anions would have appreciable angle strain compared with the unfettered anti anions. Thus the cyclic anti anions are more stable.

These calculations and those for models **5, 7, 9, 10,** and **11** indicate that acyclic syn imine anions are usually 2–10 kcal/mol more stable than the corresponding anti imine anions. III has no π orbital on H and so homoaromatic interactions are impossible here. They may be insignificant in the other species shown in Figure 1, as well. Only σ-orbital effects or dipolar (electrostatic) effects remain as viable general effects to account for the stabilities of the syn configurations of these anions.

Various model calculations we have performed indicate that the syn preference arises from the greater electrostatic repulsion between the nitrogen lone pair and the partial minus charge at C-3 in the anti species.[43] That is, C-3 of III has significant negative charge ($q_\pi = -0.54$, $q_\sigma = -0.01$) since it is one terminus of an allyl anion system. To minimize electrostatic repulsion of this π charge at C-3 with the negative charge in the vicinity of the N-1 σ lone pair, and simultaneously to maximize attraction for the hydrogen ($q = +0.17$) on N-1, the syn conformation is adopted. Evidence for this somewhat reactionary contention comes from several lines of evidence.

(1) In the presence of a negative charge placed 2 Å above C-3 of III, the preference for the syn species increases to 8.2 kcal/mol.[39,42] For I, the 0.8-kcal/mol preference for the anti species becomes a 4.0-kcal/mol preference for the syn species when a negative charge is placed 3 Å above C-3. These calculations do not change one-electron interactions in any way, but crudely model the repulsion of the π charge at C-3 for the NH fragment. These results show that electrostatic repulsion between the electrons at C-3 and the lone-pair electrons at N-1 are of the right order of magnitude to explain differences in energy between syn and anti isomers.[43]

(2) 4-31G//4-31G calculations on the *syn-* and *anti*-acetaldehyde imine radical and cation indicate 0.5- and 9.2-kcal/mol preferences, respectively, for the anti species. These results are in accord with electrostatic domination of the preferred conformation, but are opposite to expectation based on σ-orbital interactions. The σ^*_{CH} orbital remains approximately constant in energy for the anion, radical, and cation. The σ^*_{CC} orbital energy decreases along this series, since the bond length increases. The change from minus to plus charge on C-3 also lowers the σ^*_{CC} orbital energy. Since anti n–σ^*_{CC} overlap is better than syn overlap, this σ orbital effect should actually favor the syn species most in the cation. Both of the ionic species prefer the conformation which gives less n–σ^* charge-transfer stabilization.

For comparison with the above stabilities, the crotyl ($CH_3CH{=}CHCH_2{}^*$) anion prefers the cis configuration by 1.5 kcal/mol, whereas the crotyl radical and cation favor the trans by 1.0 and 3.5 kcal/mol, respectively, according to 4-31G calculations.[6] These preferences have been explained by invoking homoaromaticity in the cis anion and homoantiaromaticity in the cis cation,[6] but our parallel results for species in which no homoaromatic interactions are possible suggest that the stabilities of the crotyl species may be dominated by electrostatic effects as well.

(3) The stabilities of the imine of acetyl fluoride and the corresponding anion (Table II) can be rationalized neatly on the basis of n_N–σ^*_{CF} interactions. Finally, in the isoelectronic series, $CH_2{=}CHNH^-$, $CH_2{=}CHOH$, $CH_2{=}CHFH^+$, where n–σ^* interactions should uniformly favor the syn species, $E(\text{anti}) - E(\text{syn})$ is 4.7, 2.1, and -0.9 kcal/mol, consistent with the C-3 π charge trend: -0.54, -0.15, and $+0.16$, respectively.

These results show that electrostatic interactions, which are equivalent to interactions between local bond and lone-pair dipoles, are crucial in determining the preferred configurations of ionic species and polar molecules.[44,45] Calculations in progress are designed to establish definitively the physical phenomenon responsible for the preferred conformations of polar molecules in solution and the role of metal coordination.

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(42) These calculations were performed with a program kindly furnished to us by Professor K. Morokuma. See Kitaura, K.; Morokuma, K. *Int. J. Quantum Chem.* **1976**, *10*, 325.

(43) Calculations using the point charge approximation and Mulliken charges lead to the same conclusion.

(44) The stabilities of *cis*-1,2-difluoroethylene and related haloalkenes are examples which cannot be explained on the basis of electrostatic effects.[28,40,45]

(45) Skancke, A.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 4063.

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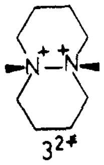
Estimation of Strength of the "Three-Electron σ Bond" of a Hexaalkylhydrazine Monocation Radical

Sir:

One-electron reduction of tricyclic hexaalkylhydrazine dications $\mathbf{1}^{2+}$ [1] and $\mathbf{2}^{2+}$ [2] has been shown to give very long-lived red radical cations which appear to be best described as having "three-electron σ bonds", i.e., with one electron in an orbital which is largely σ* N–N in character. We report here that the less constrained dication $\mathbf{3}^{2+}$ [3] gives a similar but much shorter lived species, whose lifetime allows estimation of the strength of the three electron bond for this molecule.

1^{2+}

2^{2+}



3^{2+}

Solvated electrons were produced by pulse radiolysis[4] of N_2-saturated water containing 0.1 M *tert*-butyl alcohol, to scavenge the hydroxyl radicals produced, and 1–2 × 10^{-4} M dication. Decay of optical absorption of e_{aq}^- was monitored[1] at 600 nm and was accompanied by growth of monocation radical $\mathbf{1}^{+\cdot}$–$\mathbf{3}^{+\cdot}$ absorption. All three dications react rapidly with e_{aq}^- (see Table I), although the rate constant for $\mathbf{1}^{2+}$ reduction is significantly lower than that for the other two. A larger geometry change upon accepting an electron is suggested for system **1** by the 14.7-G nitrogen splitting constant of $\mathbf{1}^{+\cdot}$ (indicating nearly planar nitrogens) than for **2**, because a(N) of $\mathbf{2}^{+\cdot}$ is 34.4 G (indicating nearly tetrahedral nitrogens).[1,2] Interestingly, these dications are not reduced by isopropyl alcohol radical ($\cdot CMe_2OH$, generated by pulse radiolysis of N_2O-saturated water containing 10^{-1} M isopropyl alcohol), despite the fact that the electron transfer is quite exothermic.[5] A substantial steric effect on the rate of electron transfer appears to be involved. All three radical cations have very similar absorption spectra (see Table I). Those observed for $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ agree well with data obtained by conventional methods, although a significantly higher ϵ value was observed for $\mathbf{1}^{+\cdot}$ in this work. We presume that partial decomposition had occurred in the samples of $\mathbf{1}^+$ previously prepared.[1]

Although $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ are known to be long lived, the optical absorptions of these species were found to disappear partially in a rapid process. This is indicated by the optical spectra before and after this rapid decay which are identical except for intensity. The decay process essentially followed second-order kinetics. These facts would indicate that the radical cations produced react with another transient produced by the pulse which we suggest to be the $\cdot CH_2CMe_2OH$ radical. This latter species is formed by the reaction of OH· radicals and H· atoms with *tert*-butyl alcohol and in a yield exceeding that of the radical cation only by 20–25%. The only partial decay of the radical cation absorption is explained by the fact that the $\cdot CH_2CMe_2OH$ + $\mathbf{1}^{+\cdot}$ ($\mathbf{2}^{+\cdot}$ or $\mathbf{3}^{+\cdot}$) reaction (k_2 ~2–3 × 10^9 M^{-1} s^{-1}) has to compete with the bimolecular decay of two $\cdot CH_2CMe_2OH$ radicals ($2k_2$ = 1.3 × 10^9 M^{-1} s^{-1}).

Because $\mathbf{2}^{+\cdot}$ cannot be reacting by addition to the weak three electron σ bond as this would require a nitrogen inversion which is far too costly in energy to be consistent with the rapid

Table I. Rate Constants for Reaction of Hexaalkylhydrazine Dications with e_{aq}^-, and Absorption Maxima of the Products

starting compound	k_2, M^{-1} s^{-1}, for e_{aq}^- + dication	cation radical, λ_{max}, nm (ϵ, M^{-1} cm^{-1})
1^{2+}	1.4 × 10^{10}	480 (2600)
2^{2+}	5.0 × 10^{10}	470 (4500)
3^{2+}	4.9 × 10^{10}	470 (4600)

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