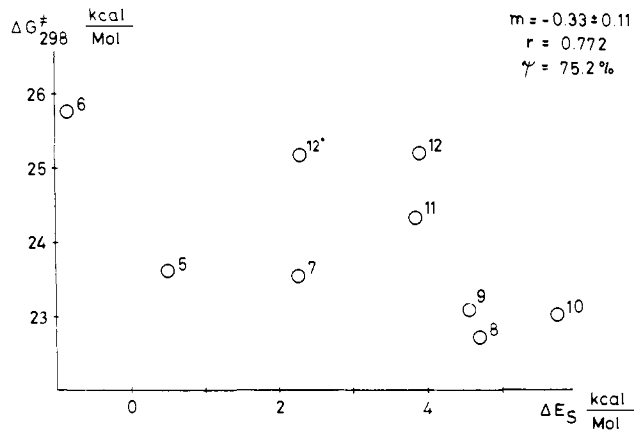

Figure 2. Solvolysis rates in ethanol as a function of strain energy differences.

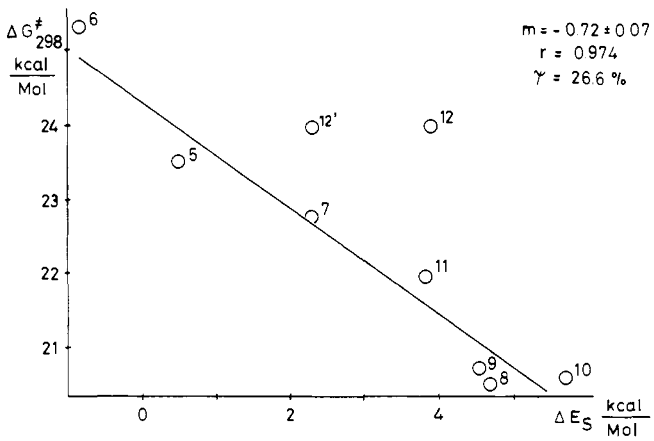

Figure 3. Solvolysis rates in trifluoroethanol as a function of strain energy differences.

To calculate strain energy differences for solvolysis reactions of cycloalkyl tosylates we have simulated the sp^3 ground state as methylcycloalkane and the sp^2-like transition state as cycloalkanone, assuming the strain energy difference ΔE_s between the methylcycloalkanes (weighted average) and the ketone conformer with the lowest energy to mimic the relevant steric changes. Use of the methyl instead of the tosyloxy group may be expected to lead to exaggeration of ΔE_s, but the necessary solvation of the leaving group and the cation can, on the other hand, increase the steric requirements for the ground state more than for the transition state.

We first measured solvolysis rates in 80% ethanol (25 °C) and tried to correlate ΔE_s with the log k values, assuming the reactivity differences to be due more to activation enthalpy than to entropy changes ($\Delta\Delta H^* > \Delta\Delta S^* T$). The observed poor correlation (Figure 2) led us to investigate rates in the weakly nucleophilic trifluoroethanol[5] (TFE, 97%, 25 °C) which can help to suppress differential solvent assisted pathways[6] and thus to unify the solvolysis mechanism of the different tosylates. The log k values for TFE do in fact represent a linear function of ΔE_s (Figure 3); moreover, the observed sensitivity ($m = 0.72$) indicates that an increase in strain differences ΔE_s yields almost the same numerical decrease in solvolysis activation energy.

The results fully support the *I*-strain concept and imply that an sp^2-like transition state occurs for all investigated compounds at a similar point on the reaction coordinate and without differential hindrance of solvation. Analysis of the separate energy contributions by the force field (see supplementary material) furthermore substantiates the original idea[1] of large Pitzer strain changes, since 55–75% of ΔE_s are obtained from torsional and 1,4 van der Waals interactions; bond angle changes contribute 10–30% to ΔE_s. Transanular repulsions, however, are calculated to change by not more than 3% between the sp^3 and sp^2 states even of medium rings.

The solvolysis rate of cyclododecyl tosylate deviates substantially from the linear correlation (Figures 1 and 2). This exception can be due to a breakdown of the assumption of a single common sp^2 intermediate formation from all conformers of one cycloalkyl tosylate. The Curtin–Hammett principle[1b] requires for the present case that equilibration between the sp^2-like intermediates or transition states is much faster than their formation. This does not necessarily hold for cyclododecane where conformational change is known to be much slower[4d] than in medium rings or in cyclopentane. Indeed the cyclododecane point comes closer to the regression line (from 12 to 12′) if ΔE_s is calculated between methyl and oxo substitution in the "corner" and "noncorner" ring position separately, again with weighting according to the different conformer stabilities. For the methyl compound the force-field calculation yields 38% corner and 62% noncorner substitution, in fair accordance with the experiment[4d] (33 and 67%, respectively, at 25 °C).

Supplementary Material Available: ORTEP representations of the relevant conformers, torsional angles, and distribution of steric energy differences (10 pages). Ordering information is given on any current masthead page.

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On the Stereochemistry of the Addition of Dimethylsilylene to *cis*- and *trans*-2-Butene[1]

Sir:

Silylenes, the second-row counterpart of carbenes, have been something of a poor relation in the family of divalent species. It has only been recently, through the efforts of the research groups of Barton, Gaspar, and Seyferth in this country, Kumada and Sakurai in Japan, and others,[2] that it has become clear that most, if not yet all, reactions of divalent carbon have their counterparts in silylene chemistry. Our knowledge of even the better known reactions of silylenes is still in a rather primitive state. For instance, despite the demonstration that siliranes can be formed from olefins and various silylene precursors,[2,3] the stereochemistry of addition is not known. Such a determination is, of course, not nearly so simple for silicon

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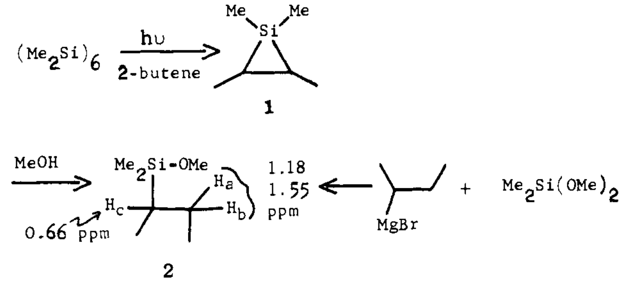
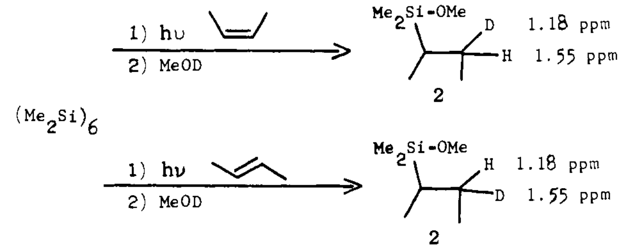
as for carbon, as the immediate products of addition of silylenes are much less stable than cyclopropanes, and only isolable with great effort.[4,11]

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 ^1H 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.



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 ^2H NMR spectra. In these spectra the multiplets "missing" in the ^1H 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.



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 ^2H 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 ^1H 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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