

Figure 1. 3-21G Molecular structures. Bond lengths in Å, angles in degrees.

energy increases monotonically upon rotation from pyramidal to planar. In the more stable form with  $M = \text{Si}$  the two Si-Si distances are very similar to those in disilane at a comparable level of theory,<sup>2</sup> with the base bond being slightly longer than the internal bond. For  $M = \text{C}$ , the Si-C bond is slightly shorter than that in methylsilane, while the Si-Si bond is much shorter than that in disilane and the analogous spiropentasilane.

Some insight into the greater resistance of the silicon species to twisting toward planarity is provided by the 6-31G\* Mulliken populations. In the pyramidal form the charge on the central atom is  $-0.748$  for  $M = \text{C}$  and  $-0.167$  for  $M = \text{Si}$ . The corresponding charges for the planar structures are  $-0.909$  and  $-0.990$ , respectively. Thus, twisting to planar results in a huge increase in the negative charge on the central silicon. Even though Mulliken populations are clearly very qualitative, we have consistently found negative charges on silicon to have a strong destabilizing effect. Similarly, note that the large negative charge on the central carbon in the pyramidal structure is likely to render this species very unstable toward electrophilic attack, and this may be related to the difficulty encountered in preparing this compound. This is much less likely to be a problem for pyramidal  $M = \text{Si}$ , in which the charge separations are much smaller. The latter may account, in part, for the observation that octamethylspiropentasilane is stable indefinitely in solution.<sup>1</sup>

A possible decomposition route for these compounds is elimination of disilene to form the cyclic methylene or silylene. To investigate the stability of the parent molecules to such a dissociation, calculations were also carried out on the singlet species shown in Figure 1. Using 6-31G\* wave functions and the  $\text{Si}_2\text{H}_4$  results published previously,<sup>5</sup> we find the silicon (carbon) compound to be more stable than the corresponding dissociation products by 64.1 (133.1) kcal/mol. Thus, both compounds are predicted to be stable with respect to this dissociation pathway. While the addition of correlation corrections is likely to stabilize the products by 10-15 kcal/mol, the qualitative conclusions drawn here are not likely to change. There are clearly several alternative decomposition pathways, including the opening of a base bond to form a diradical, ring expansion to form a five-membered cyclic silylidene or methylene, and intramolecular disproportionations. These possibilities, the corresponding reaction paths, and investigations of other metals will be the subjects of later papers.

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## Stereoselective Acyclic Enolate Formation via Conjugate Reduction: Correlation with Enone Conformational Preferences

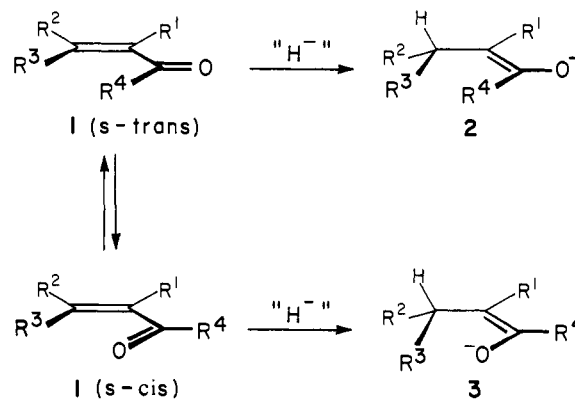
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Selective acyclic enolate formation plays a crucial role in the stereochemical outcome of several important reactions, including many aldol condensations<sup>1</sup> and certain [3,3]-sigmatropic rearrangements.<sup>2</sup> In the case of ketones, in which both the position of the enolate  $\pi$ -bond and its stereochemistry must be controlled, deprotonation of the parent carbonyl compound (either under kinetic or thermodynamic control) invariably is the method chosen to generate the desired enolate. Fair to good stereoselectivity is often observed, depending upon various structural features present. The reliance upon deprotonation as a means of acyclic ketone enolate formation does, however, impose notable limitations on the range of enolates available in relatively pure form. For example, the formation of a specific enolate regioisomer from a nearly symmetrical ketone presents a problem under either kinetic or thermodynamic conditions, as does the selective generation of a specific enolate geometrical isomer (or regioisomer for that matter) from an acyclic ketone  $\alpha$ -substituted with two similar groups in the direction of intended enolization. As a clear illustration of this latter point, there are remarkably few reports of tetra-substituted enolates that have been generated stereoselectively.<sup>3</sup> We report in this paper that the conjugate reduction of acyclic  $\alpha,\beta$ -unsaturated ketones can provide regio- and stereochemically defined enolates that are unattainable selectively by other methods.

The rationale for investigating the well-known conjugate reduction reaction<sup>4</sup> as a means of stereoselective enolate formation was based on the supposition that known ground-state conformational preferences of enones,<sup>5</sup> which are quite pronounced in some cases, might be reflected in the resultant enolate ratios. Specifically, we reasoned that an enone (such as **1**) that exists almost exclusively as the *s*-trans conformer would give rise mainly to the enolate **2** and, conversely, that a predominantly *s*-cis enone would give the enolate **3**. The preferred ground-state enone



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**Table I.** Comparison of Enone Conformational Preferences with Product Enolate Ratios

	enone 1				approx enone ratio <sup>a</sup>	enolate ratio <sup>a,b</sup>	yield <sup>c</sup>
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>			
a	<i>i</i> -Pr	H	H	<i>n</i> -Hex	>20:1	170:1 <sup>d</sup>	69%
b	Ph	H	H	<i>n</i> -Hex	>20:1	100:1 <sup>d</sup>	96%
c	<i>n</i> -Pr	H	H	<i>i</i> -Pr	>20:1	50:1 <sup>d</sup>	83%
d	H	<i>n</i> -Bu	H	<i>n</i> -Hex	3:1	2:1 <sup>e</sup>	71%
e	H	<i>n</i> -Bu	H	<i>t</i> -Bu	<1:100	<1:300 <sup>e</sup>	85%
f	H	H	<i>n</i> -Bu	<i>n</i> -Hex	1:20	1:30 <sup>e</sup>	68%
g	H	H	<i>n</i> -Bu	<i>i</i> -Pr	<1:100	1:300 <sup>e</sup>	82%
h	Me	Me	Me	<i>n</i> -Hex	1:3	1:4 <sup>e</sup>	91%

<sup>a</sup>*s*-*trans*:*cis* 2:3, estimated from published calculations and experimentally determined ratios.<sup>5</sup> <sup>b</sup>Determined by silylation and capillary GC of the resulting crude mixture. <sup>c</sup>Internal standard GC yield. The remainder generally consists of 10–25% of the simple saturated ketone. <sup>d</sup>Reduction with L-Selectride. <sup>e</sup>Reduction with Li/NH<sub>3</sub>.

conformer is known to be controlled by the specific substitution pattern on the double bond (R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>) and in the α'-position (R<sup>4</sup>).<sup>5</sup> In general, an alkyl substituent in the α-position (R<sup>1</sup> = alkyl, R<sup>3</sup> = H) causes the *s*-*trans* conformer to be favored, while one in the *cis* β-position (R<sup>3</sup> = alkyl) shifts the ratio in favor of *s*-*cis*. A *trans* β-substituent has little effect upon the ratio, but increased branching in the α'-position (R<sup>4</sup>) results in an increased preference for the *s*-*cis* enone regardless of other substituents. We felt it might be possible to use these conformational generalizations to predict which of the two enolate stereoisomers should predominate for any specific substitution pattern. Mindful of the fact that conformer reactivities and interconversion rates, embodied in the Curtin–Hammett Principle, could well render this simple hypothesis invalid, we have tested eight representative acyclic enones and found that the model is indeed a useful one.

The first example was chosen such that the *s*-*trans* conformer would be strongly preferred in the ground state.<sup>6</sup> Reduction of **1a** (Table I) with L-Selectride<sup>6a</sup> (Aldrich) (THF, -78 °C, 15 min) followed by silylation (Me<sub>3</sub>SiCl/Et<sub>3</sub>N,<sup>7</sup> -78 → -10 °C) gave a mixture of silyl ethers, corresponding to **2a** and **3a**, in a ratio of 170:1 (69% yield) as determined by capillary GC analysis of the crude reaction mixture.<sup>8</sup> As expected, increasing the steric bulk at R<sup>4</sup> and decreasing it at R<sup>1</sup> results in a reduction in stereoselectivity (see **1e**), from 170:1 to 50:1. The corresponding α-phenyl enone (**1b**) gave a similar result (100:1, 96% yield). Determination of the stereochemistry of the major isomer in these examples and others was readily made by 250-MHz proton difference NOE analysis.

In contrast to these three enones, **1f** exists mainly in the *s*-*cis* ground-state conformation. Although L-Selectride gave predominantly 1,2-reduction of **1f**, dissolving metal reduction and silylation (excess Li/NH<sub>3</sub>, -78 °C; isoprene; replace NH<sub>3</sub> with THF at -10 °C; Me<sub>3</sub>SiCl, Et<sub>3</sub>N) gave a 1:30 mixture of **2f** and **3f** (68% yield), again in accord with the simple conformational hypothesis.<sup>9</sup> Once again, increasing steric bulk of R<sup>4</sup> shifts the conformational equilibrium toward *s*-*cis*, so that the reduction of

(6) For 3-methyl-3-buten-2-one the *s*-*trans*:*s*-*cis* ratio is reportedly 13:1.<sup>5</sup> This ratio is expected to be even greater when the R<sup>1</sup> group is larger than the R<sup>3</sup> group (isopropyl vs. *n*-hexyl).<sup>5</sup>

(7) Previously centrifuged to remove triethylamine hydrochloride.

(8) All silyl ethers exhibited satisfactory 250-MHz proton NMR spectra and high-resolution mass spectra (of individual isomers by GC/HRMS). Authentic samples of extremely minor isomers were prepared by allowing enolate mixtures to equilibrate before silylation. Where applicable, authentic product mixtures were prepared by standard methods.

(9) The mechanisms of conjugate reduction by L-Selectride and Li/NH<sub>3</sub> obviously are different; however, in both cases the product enolate geometry is established when electron density is increased in the enone π\* orbital either by electron transfer or hydride attack at the β-position. In either reaction the bond order between C-2 and C-3 (the incipient enolate π-bond) increases as the reaction progresses, which eventually “locks” the geometry of the resulting double bond. L-Selectride is the more convenient of the two reagents, and it gives a slightly better enolate ratio than does Li/NH<sub>3</sub>, at least in the case of **1e** (50:1 vs. 10:1). This minor discrepancy may reflect the different reduction mechanisms involved, but it does not detract from the overall predictive value of our conformational hypothesis (e.g., compare **1d** to **1f**).

**1g** is considerably more selective (1:300) than it is for **1f**. It should be noted that the predominant enolates in these cases (**3**), which are thermodynamically more stable than their geometric isomers, cannot be generated nearly as selectively by more conventional methods.<sup>1</sup> As further confirmation of the predictive power of the stereochemical hypothesis, reduction of **1e**, for which the *s*-*cis* conformer heavily predominates, produces exclusively (<1:300) the enolate **3**.

Several other results also proved to be consistent with the simple model. Two enones in the table show little conformational preference: **1d** because of a lack of “controlling” substituents (R<sup>1</sup>, R<sup>3</sup>, or bulky R<sup>4</sup>) and **1h** because of a competition between controlling substituents (R<sup>1</sup> and R<sup>3</sup>). The reduction of these enones thus is expected to be relatively nonselective, and the slight *s*-*trans* preference of **1d** results in only a 2:1 enolate ratio. Furthermore, **1h** gives a 1:4 enolate ratio that reflects the fact that the R<sup>3</sup> substituent predominates—but only slightly—over an identical R<sup>1</sup> substituent in determining the conformer populations.

A knowledge of enone ground-state conformational preferences thus does allow one to predict which enolate geometrical isomer will predominate in these reactions. On the basis of the representative examples described in this paper, a wide range of enolates that are highly substituted or otherwise difficult to generate selectively are now readily available.

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**Supplementary Material Available:** General procedures for the preparation of starting enones, representative conjugation reduction procedures, and spectra for product silyl enol ethers (10 pages). Ordering information is given on any current masthead page.

## Picosecond Dynamics of the Excited *trans*-Stilbene/Fumaronitrile Charge-Transfer Complex

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The coupling of the molecular motions of solvent and reactant molecules in photochemical reactions has been of considerable interest.<sup>1</sup> We report the use of picosecond absorption spectroscopy to examine the “microdynamics”<sup>2</sup> of the excited *trans*-stilbene/fumaronitrile charge-transfer complex.<sup>3–5</sup> In particular, we can measure the absolute rates of ion pair separation.

The experimental procedure for obtaining absorption spectra of transient intermediates with a time resolution of 25 ps has been previously described in detail.<sup>6</sup> Irradiation was performed with 355-nm pulses at room temperature on 0.05 M *trans*-stilbene/0.3 M fumaronitrile (TS/F) solutions. The irradiated solutions were rapidly stirred and frequently changed to prevent the buildup of photoproducts.

Excitation of the charge-transfer band of the TS/F complex in several different solvents generates a transient within the laser pulse which is assigned to the radical cation of *trans*-stilbene (TS<sup>•+</sup>(A), λ<sub>max</sub> = 478 nm)<sup>7</sup> (Figure 1). Although the λ<sub>max</sub> of

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