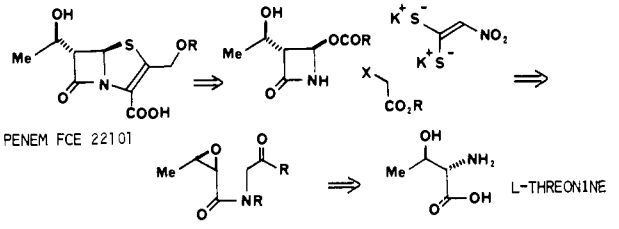
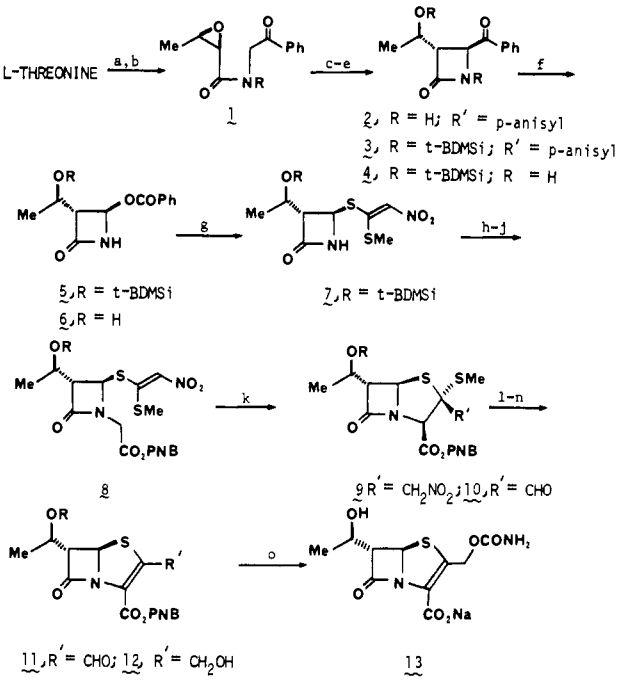
Scheme I




Scheme II[a]




[a] (a) aqueous $NaNO_2$, KBr $H_2SO_4$, 0 °C, 70%, then NaOH, and acidification, (b) *p*-$MeOC_6H_4NHCH_2COPh$, ClCOO-*i*-Bu, *N*-methylmorpholine 4-Å sieves, THF, −20 °C, then 25 °C, 70%; (c) $K_2CO_3$, DMF, 60 °C, 3–4 h, 75%; (d) *tert*-butyldimethylsilyl chloride, DMF, imidazole, 80%; (e) ceric ammonium nitrate, MeCN, −10 °C, 87%; (f) monoperphthalic acid, EtOAc, 18 h, 89%; (g) KS(KS)C=$CHNO_2$, aqueous EtOH, 0 °C, 10 min, 1 h $Me_2SO_4$, 76%; (h) $ClCOCO_2pNB$, $CH_2Cl_2$, $Et_3N$, $(i\text{-}Pr)_2NEt$, 0 °C, 75%; (i) $P(OMe)_3$, 25 °C, 90%; (j) PTS, aqueous THF, 1 h, 75%; (k) $LiN(SiMe_3)_2$, THF, −78 °C, 10 min, 56–60% (l) $LiN(Me_3Si)_2$, −78 °C; then add MeI, then ozone; 63%; (m) MCPBA, $CHCl_3$, 10 min, 0 °C, then aqueous $NaHCO_3$ 80%; (n) L-Selectride, THF, −78 °C, 61%; $Cl_3CCNO$, $CH_2Cl_2$, then $Bu_4NF$, THF, then Pd/C, $H_2$, EtOAc, aqueous $NaHCO_3$, then chromatography, LiChroprep RP-18 (Merck), 40% overall three steps.

then gave the crystalline azetidinone **5**, mp 100–102 °C, $[\alpha]_D$ −66° ($CHCl_3$). Alternatively, de-N-protection of **2** followed by a Baeyer–Villiger oxidation gave the crystalline azetidinone **6**, mp 146–147 °C, $[\alpha]_D$ +97.2 (MeOH). Reaction of **5** with the dipotassium salt of 1,1-dithio-2-nitroethene[12] followed by S-methylation led to the crystalline adduct **7**, mp 144–146 °C, dec, $[\alpha]_D$ +230.5° ($CHCl_3$). Direct reaction of **7** with methyl bromoacetate in the presence of a variety of bases led to mixtures. Hence, the acetic acid moiety was introduced in an uneventful three-step sequence[16] in good overall yield, to give **8**. The critical intramolecular Michael addition of the anion generated from **8** afforded the cyclized product **9** as a crystalline solid, mp 105–106 °C, $[\alpha]_D$ +216.9° ($CHCl_3$),[14] in which the methylthio and ester groups had an anti orientation.[14] With the bicyclic system in hand, there remained to manipulate functionality and adjust oxidation states en route to the target. Thus, the treatment of the nitronate salt derived from **9** with methyl iodide afforded the corresponding methoxy nitronate, which upon treatment with ozone gave the corresponding aldehyde **10** as a colorless oil. Sequential treatment with *m*-CPBA and then aqueous sodium bicarbonate led to spontaneous elimination and the formation of the desired penem intermediate **11** as an amorphous solid, $\lambda_{max}$ 265, 390 nm. Finally, reduction with L-Selectride (Aldrich) gave the penem **12** ($[\alpha]_D$ +33.5° ($CHCl_3$); mass spectrum, *m/e* 495 (M + 1); $\lambda_{max}$ ($CHCl_3$) 265, 324 nm), identical in all respects with authentic material prepared by a known route.[6,9] By a sequence of known steps[9] penem **12** was converted into the bioactive carbamate **13**, $[\alpha]_D$ +143° ($H_2O$), identical with an authentic sample.[9]

The presently described synthesis constitutes a tactically and conceptually new approach for the construction of the optically active azetidinones and penems. It has the attractive features of utilizing readily available, inexpensive starting materials, and it involves a novel ring-forming step under mild conditions in comparison to the original Woodward[2] or other recently reported methods.[4-8]

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**Supplementary Material Available:** NMR, IR, and mass spectra of **1–3**, **5–8**, and **10–12** and stereoviews of **6** and **9** (38 pages). Ordering information is given on any current masthead page.

(16) For the conversion of related oxalimide esters to acetates, see ref 4-6.

## Molecular and Electronic Structures of Metallaspiropentanes

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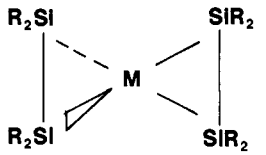
Recent efforts in this laboratory have concentrated on synthesizing metallaspiropentane compounds (I) with M = C, Si, Ge,




Sn, Ni, and Zn. To date, the molecule with M = Si and R = methyl has been successfully prepared,[1] while attempts to synthesize the corresponding carbon compound have not reached fruition. This paper presents initial ab initio calculations on the species with M = C and Si and with R = H.

Geometries for all species were calculated with the 3-21G[2] basis set at the closed-shell Hartree–Fock level of computation. Subsequently, single-point 6-31G*[3] calculations were carried out at the 3-21G geometries. All calculations were performed using an IBM version of GAUSSIAN80.[4]

The 3-21G molecular structures of the two parent species are displayed in Figure 1. for both species the most stable structure is the twisted (distorted pyramidal) form, with the planar structure being higher in energy by 66.2 and 32.3 kcal/mol for M = Si and C, respectively, at the 6-31G* level. For both molecules, the

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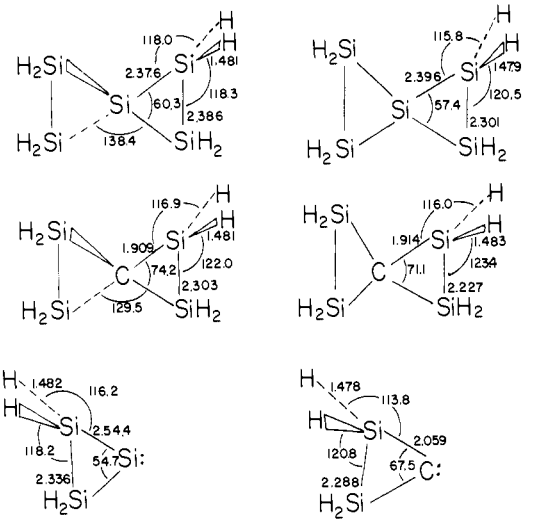

**Figure 1.** 3-21G Molecular structures. Bond lengths in Å, angles in degrees.

energy increases monotonically upon rotation from pyramidal to planar. In the more stable form with M = Si the two Si–Si distances are very similar to those in disilane at a comparable level of theory,[2] with the base bond being slightly longer than the internal bond. For M = 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 = C and −0.167 for M = 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 = 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.[1]

A possible decomposition route for these compounds is elmination 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 $Si_2H_4$ results published previously,[5] 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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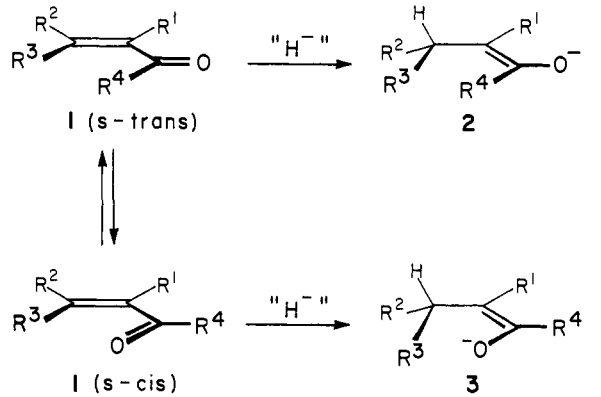
Selective acyclic enolate formation plays a crucial role in the stereochemical outcome of several important reactions, including many aldol condensations[1] and certain [3,3]-sigmatropic rearrangements.[2] In the case of ketones, in which both the position of the enolate π-bond and its stereochemistry 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 α-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.[3] We report in this paper that the conjugate reduction of acyclic α,β-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[4] as a means of stereoselective enolate formation was based on the supposition that known ground-state conformational preferences of enones,[5] 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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