

experiment while as expected MM2 produces values less than experiment but agreeing almost as well. All calculations for $^{1-3}$ are at least 0.8 kcal/mol different from experiment, but as always, caution should be exercised in comparing enthalpies of activation calculated for rotation in the gas phase and free energies of activation measured in solution.

The entropies of activation necessary to reconcile the MM2 calculated values and the DNMR experimental values range from -8 to -17 eu, rather greater in size than is normally considered likely for an internal rotation, but we have determined⁵ a value of -7.2 eu for the compound **4**. This value is significantly in the correct sense, and it is unfortunate that the quality of the changes in the low-temperature carbon-13 spectra of **1-3** do not allow the determination of entropies of activation for these molecules. To reconcile the MM2OS calculated enthalpies and the experimental free energies would require unprecedented *positive* entropies of activation for these bridged compounds.

Neither set of force field parameters predicts that the *tert*-butyl compound **4** has a greater rotational barrier than the bridged compounds. A consideration of entropies of activation may also help to remove this discrepancy. In the *tert*-butyl compound **4**, the entropy¹⁴ of the more congested transition state can be quite different from that of the unconstrained ground state. For the bridged compounds **1-3**, constraints are present in both the ground and transition states, so there is less scope for entropy change.¹⁴ The more negative entropy of activation for the *tert*-butyl compound that results would lead to the higher free energy of activation, which is experimentally observed.

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Supplementary Material Available: Relevant NMR spectral details and spectral changes with temperature (2 pages). Ordering information is given on any current masthead page.

(14) The important entropy term is that associated with rotation of individual methyl groups. There are five of these for the *tert*-butyl compound and only two for the bridged compounds.

Isolation and Characterization of Iron Methylene (FeCH₂) via FTIR Matrix Isolation

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Since the early work of Fischer,¹ a number of simple alkylidene and methylene complexes have been reported.² The isolation and characterization of these complexes is of importance since they are now recognized as major intermediates in catalytic processes such as olefin metathesis³ and alkane activation.⁴ We report here the matrix isolation and characterization of the simple unligated species FeCH₂.

Iron atoms were codeposited with a mixture of argon and diazomethane onto a rhodium-plated copper mirror at 14 K. The infrared spectra, measured with an IBM IR98 Fourier Transform spectrometer, showed new peaks at 2995.0, 2941.6, 1122.4, 700.3, and 623.6 cm⁻¹ (Figure 1). These absorptions retained the same

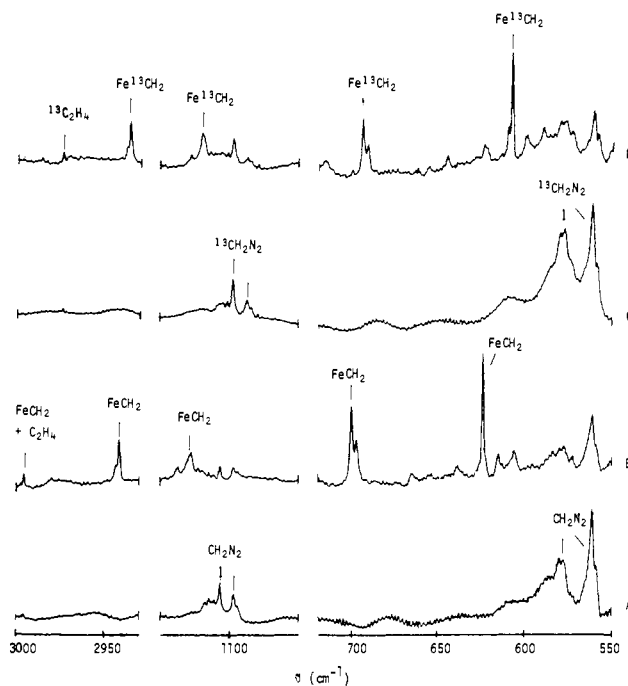


Figure 1. FTIR spectra of matrix-isolated diazomethane and diazomethane iron in solid argon. Molar ratios: (A) CH₂N₂:Ar = 9.8:1000; (B) Fe:CH₂N₂:Ar = 9.5:9.8:1000; (C) ¹³CH₂N₂:Ar = 11.6:1000; (D) Fe:¹³CH₂N₂:Ar = 7.7:11.6:1000. The strongest peak at 623.6 cm⁻¹ in B has an absorbance of 0.092.

Table I. Iron-Carbon Stretching Frequencies (cm⁻¹) for Some Selected Matrix-Isolated Organoiron Compounds

Fe=CH ₂	623.6	present study
HFe-CH ₃	522	ref 5
HFe-CHCH ₂	507	ref 7
H ₃ CFe-CHCH ₂	538	ref 8

relative intensities at different iron and diazomethane concentrations and remained in the spectrum even under the most dilute conditions (Fe:CH₂N₂:Ar = 0.07:1.0:100).

Preliminary isotopic studies using carbon-13 enriched diazomethane showed that the peak at 623.6 cm⁻¹ is shifted by 15.9 cm⁻¹. The same band showed an iron-54 isotopic shift of 2.3 cm⁻¹. Thus both isotopic studies indicated that the 623.6-cm⁻¹ peak is due to an iron-carbon stretching mode and that the species contains only one iron atom and one carbon atom. By comparing the measured iron-carbon stretching frequency of this species to those known for iron-carbon single bonds (Table I), one concludes that this Fe-C bond must involve some double-bond character. Other bands related to this species were observed at 2995.0, 2941.6, 1122.4, and 700.3 cm⁻¹ and were assigned to the asymmetric and symmetric stretching, bending, and rocking or wagging modes of a CH₂ group. Thus the species responsible for these absorptions as well as the Fe=C stretching frequency has been identified as iron methylene, Fe=CH₂. Additional studies on the reactions of iron and ¹³CH₂N₂, CD₂N₂, and CHDN₂ are in progress.

Diiron was also found to react with diazomethane in solid argon to yield (N₂)₂Fe₂CH₂. This diiron compound probably has a bridging methylene although additional isotopic work will be required to fully elucidate its structure. The presence of nitrogen can be inferred from the strong nitrogen-nitrogen stretching frequency which appears at 1812 cm⁻¹.

When hydrogen was added to the Fe/CH₂N₂ system in argon, CH₃FeH was produced⁵ along with methane. At higher diazomethane concentrations, absorptions due to ethylene were observed (Figure 1). The dimerization of methylene appears to be favored

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by higher iron concentration, in accord with the observations of Brady and Pettit who studied the reactions of diazomethane over metal surfaces (Fischer-Tropsch catalysts).⁶ The diazomethane reaction with atomic and diatomic iron will be discussed in detail in a future publication.

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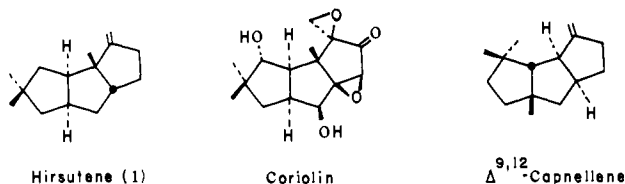
Tandem Radical Approach to Linear Condensed Cyclopentanoids. Total Synthesis of (±)-Hirsutene

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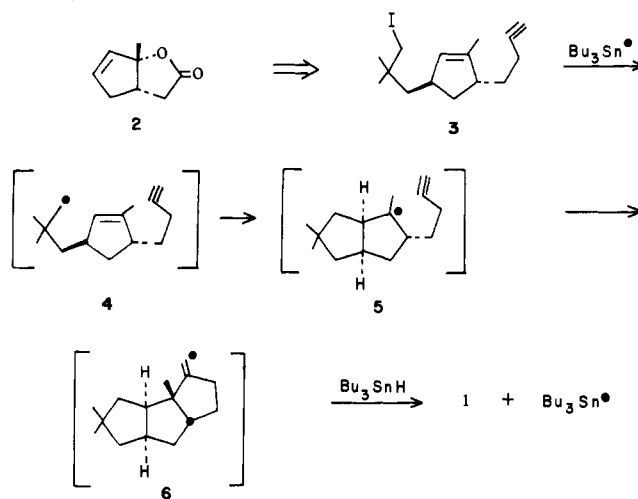
Hirsutene (**1**),^{2a} the parent member of the hirsutane family,



has proven to be an important target for illustration of synthetic strategies directed toward linear condensed cyclopentanoids.² Frequently, new annulation procedures have been devised to sequentially construct each ring in the tricyclic system.^{3,4} A tandem construction of rings can present an inherently more efficient approach to linear condensed cyclopentanoids provided that the stereochemistry can be controlled, that the cyclization precursors are readily available, and that the approach is sufficiently general to permit construction of the more functionalized coriolsins and the isomerically related capnellenes.^{3a,b} We now report a total synthesis of (±)-hirsutene via a tandem radical cyclization which realizes the first two of these goals.

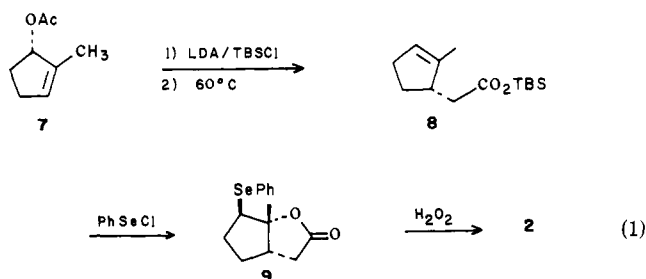
Synthesis of condensed cyclohexanoid systems by cation-initiated polyolefinic cyclizations has proven extremely fruitful.⁵ We

Scheme I



felt that a related approach to condensed cyclopentanoids might be devised employing radical-initiated polyolefinic cyclizations.^{6,7} In view of the extensive studies on the cyclization of hex-5-enyl radicals,⁶ it is quite surprising that this reaction has received almost no use in condensed cyclopentanoid synthesis. The tandem radical approach to hirsutene is outlined in Scheme I. Treatment of iodide **3** with tri-*n*-butyltin hydride should generate transient radical **4**. In turn, **4** should suffer two successive hex-5-enyl-like radical cyclizations (**4** → **5** → **6**) and finally a hydrogen atom abstraction. This would produce hirsutene (**1**) from **3** in a single step via the standard radical chain mechanism. Of concern is the second cyclization (**5** → **6**) which involves conversion of a 3° radical to a significantly less stable vinyl radical.⁸ It was envisioned that **3** would be readily available from simple vinyl lactone **2** by $\text{S}_{\text{N}}2'$ -anti addition and subsequent chain elongation. Note that since both hexenyl radical cyclizations must proceed in a cis fashion,^{3a} the $\text{S}_{\text{N}}2'$ -anti opening of **2** effectively ensures the cis-anti-cis stereochemistry present in hirsutene.

Equation 1 illustrates the facile synthesis of vinyl lactone **2**.



2-Methylcyclopentenone^{9a} was reduced (NaBH_4 , CeCl_3)^{9b} and

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(4) Noteworthy exceptions include the approaches of Wender, Little, and Houk (unpublished) which employ simultaneous multiple ring construction.^{2b,k}