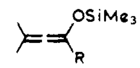
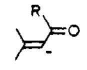
Utilization of **8** as a synthetic equivalent of **9** has so far been limited to protonation (hydrolysis) and halogenation, but other more useful electrophiles are being studied.



8

≡



9

A typical experimental procedure for the preparation of allenol silyl ethers is as follows (run 6). To a stirred solution of 0.37 mL (3.2 mmol) of 1-hexyne in 5 mL of dry THF at 0 °C was added 2.8 mL (3.2 mmol, 1.15 M) of MeLi (1:1 LiBr complex in ether). After 15 min, the solution was cooled to −78 °C and 0.47 mL (3.0 mmol) of ethyl trimethylsilyl ketone was added dropwise. A white precipitate formed. After 15 min, 0.25 mL (4.0 mmol) of MeI was added and the flask was warmed to 0 °C and stirred for 30 min. The contents were then partitioned between cold aqueous 7% $NaHCO_3$ and ether-pentane (1:1) and washed with saturated NaCl. After drying (Na_2SO_4, then K_2CO_3) and concentration of the organic layer, distillation of the residue (Kugelrohr, 24 mm, bath temperature 89-91 °C) gave 0.50 g (74%) of 3-trimethylsilyloxy-5-methyl-3,4-nonadiene as a clear, mobile liquid: NMR ($CDCl_3$) δ 0.12 (s, 9 H), 0.80-1.12 (m, 6 H), 1.20-1.68 (m, 4 H), 1.74 (s, 3 H), 1.92-2.36 (m, 4 H); IR (salt plate) 2960, 1962, 1628, 1467, 1260, 1201, 1178, 855 cm^{-1}; MS calcd for $C_{13}H_{26}OSi$ 226.1753, found 226.1738.

Acknowledgment. The authors thank the National Science Foundation for a research grant in support of this work and Cristina Montes for the preparation of several silyl ketones.

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(3) (a) The derivatization of siloxybenzyllithium formed by Brook rearrangement of the silyl carbinol has been reported: Wright, A., West, R. *J. Am. Chem. Soc.* **1974**, *96*, 3214. Reaction occurs at oxygen or carbon depending on electrophile. (b) Kuwajima, I., Kato, M. (*Chem. Commun.* **1979**, 708) have recently shown that vinyltrimethylsilylcarbinols, prepared by vinyl Grignard addition to silyl ketones, serve as precursors for siloxyallyllithium reagents.

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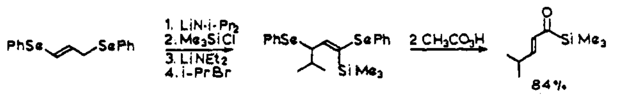
(6) Only a small number of vinyl silyl ketones have been reported.[1,7] The enone used in runs 12-15 was prepared as shown. A number of related enones have been prepared by similar procedures (M. C. Clark, unpublished results).



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(8) Earlier work[3a] has shown that the equilibrium i ⇌ ii lies on the right for R = H and on the left for R = Ph.

i ii

(9) Note that a second alkyl substituent at the *center* of the allyl system is tolerated (run 12).

(10) The half-life of the reaction is 30 min at 0 °C in 1:1 ether-THF.

(11) One side reaction that we have observed is a [1,4] sigmatropic O to C silicon shift in the siloxyallyl anion to give β-silyl enolate. Similar rearrangements have been reported for related systems: Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063. Evans, D. A., Takacs, J. M., Hurst, K. M. *J. Am. Chem. Soc.* **1979**, *101*, 371.

(12) Merault, G., Bourgeois, P., Donogues, J., Duffaut, N. (*J. Organomet. Chem.* **1974**, *76*, 17) have prepared several allenol silyl ethers by reductive silylation of acetylenic ketones.

(13) For a recent review of enol silane chemistry, including many applications in organic synthesis, see Rasmussen, J. K. *Synthesis* **1977**, 91.

(14) Fellow of Alfred P. Sloan Foundation, 1975-1979.

(15) Deceased Oct 4, 1979.

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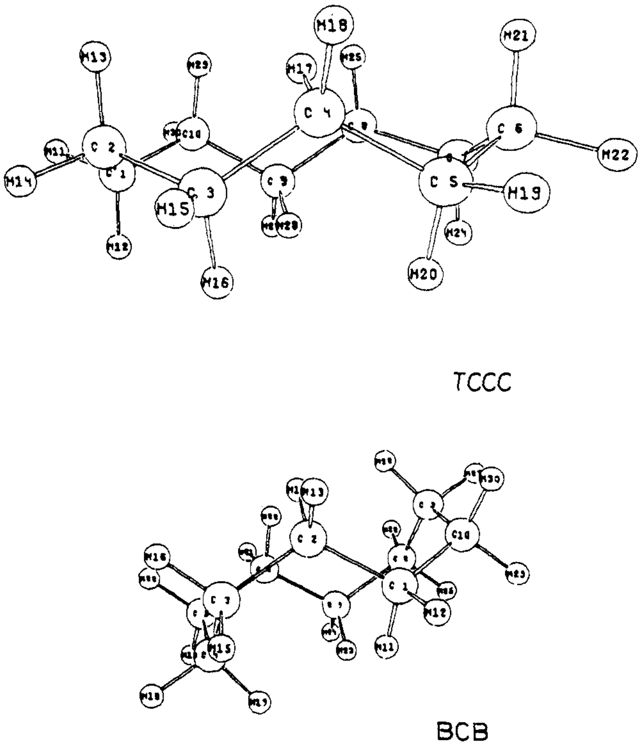
Received November 1, 1979

Molecular Mechanics Calculations of Reactivity Differences between Alicyclic Compounds

Sir:

The *I*-strain explanation of Brown for the differences in nucleophilic substitution, ketone reduction, cyanohydrin equilibria, etc., between alicyclic compounds represents one of the earliest attempts to relate steric energy changes accompanying $sp^3 \rightleftharpoons sp^2$ interconversions to chemical reactivity.[1a] Thus Brown suggested that relief of torsional angle or Pitzer strain and of transanular repulsions eases the formation of an sp^2 center in medium-ring compounds, opposite to strain-free cycloalkanes. Molecular mechanics force fields[2] allow calculations not only on ground states but in principle also on transition states and thus in particular on steric hindrance in reactivity. Other than in related earlier force-field approaches to reaction rates,[3] a rigorous test of the *I*-strain hypothesis requires strain energy calculations of a large number of conformations for each ring compound. This is illustrated with methylcyclodecane (Figure 1), where minimizations using the Allinger force field[2] yield the following conformer distribution. TCCC: Me in position 2, 16%; in position 3, 30%; in position 4, 14%. BCB: Me in position 2, 15%; in position 3, 22%; in position 4, 3%. Low-temperature ^{13}C NMR measurements have so far offered limited information supporting conformational equilibria of medium-ring compounds.[4]



TCCC

BCB

Figure 1. Cyclodecane conformations: TCCC, twist chair chair chair; BCB, boat chair boat.

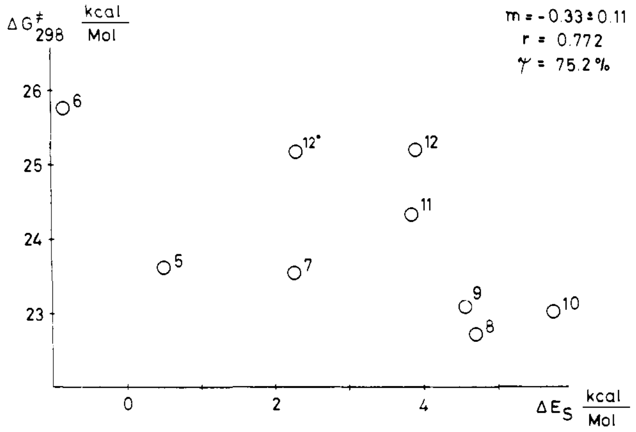


Figure 2. Solvolysis rates in ethanol as a function of strain energy differences.

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).

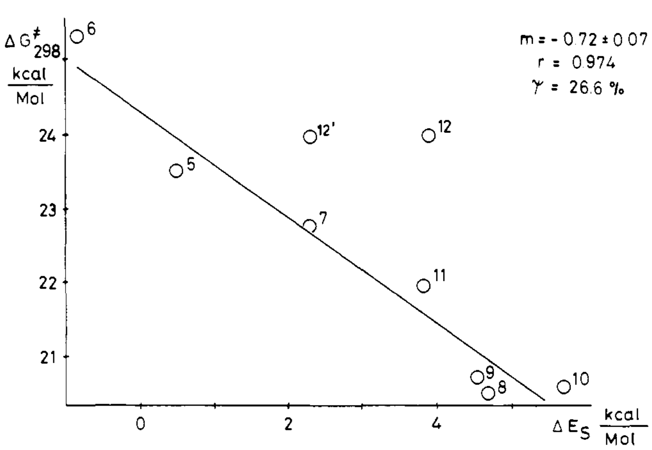


Figure 3. Solvolysis rates in trifluoroethanol as a function of strain energy differences.

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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Received September 14, 1979

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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