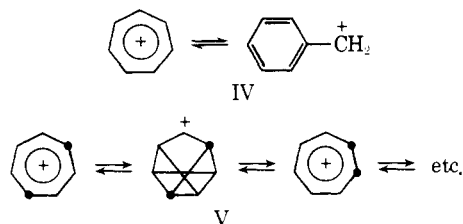


voltages.<sup>11</sup> A recent report<sup>12</sup> dealing with the mass spectra of tropylium salts has indicated that the appearance potentials of the  $C_7H_7^+$  ions derived from tropylium iodide, bromide, and tetrafluoroborate are identical (6.74 eV), close to the spectroscopic ionization potential of the cycloheptatrienyl radical (6.24 eV), and very close to the electron impact value for the cycloheptatrienyl radical (6.60 eV). This suggests that prior to vaporization, the tropylium ion undergoes a "one-electron reduction" to the radical followed by ionization to the  $C_7H_7^+$  ion, presumably the tropylium ion. Hence, either the tropylium ion or the cycloheptatrienyl radical or both is undergoing skeletal reorganization prior to the formation of  $C_6H_5^+$  ions, perhaps *via* a series of benzyl ion-tropylium ion isomerizations (IV) or *via* a series of valence tautomeric shifts (V). The



observed data imply that the near total loss of positional identity of the carbon atoms in toluene may not occur solely, if at all, in the process leading to the formation of  $C_7H_7^+$  ions, but rather after its formation. Further studies on II including other ions in the spectrum will be discussed later.

**Acknowledgment** is made to the Indiana State University Research Fund Committee for their support of this work and to Mr. J. Boal of the Mellon Institute for running the spectra.

(11) D. H. Williams and R. G. Cooks, *Chem. Commun.*, 663 (1968); S. Meyerson, *Appl. Spectrosc.*, **22**, 30 (1968); W. A. Bryce and E. W. C. Clarke, *Advan. Mass Spectrom.*, **1**, 392 (1959).

(12) G. Hvistendahl, K. Undheim, and P. Gyorosi, *Org. Mass Spectrom.*, **7**, 903 (1973).

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### On the Stereoselectivity and Regiospecificity of Spiroannulations with 1-Lithiocyclopropyl Phenyl Sulfide

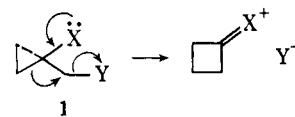
Sir:

The directed ring expansion of cyclopropylcarbinyl systems to cyclobutyl systems has shown much promise in synthetic organic chemistry.<sup>1-3</sup> In this communication we wish to show for **1** ( $X = PhS$ ) that (1) the re-

(1) C. R. Johnson, *Accounts Chem. Res.*, **6**, 341 (1973); H. H. Wasserman, R. E. Cochoy, and M. S. Baird, *J. Amer. Chem. Soc.*, **91**, 2376 (1969); H. H. Wasserman, H. W. Adikes, and O. E. de Ochoa, *ibid.*, **93**, 5586 (1971); J. R. Salaun and J. M. Conia, *Tetrahedron Lett.*, 2849 (1972); J. P. Barnier, B. Garnier, C. Girard, J. M. Denis, J. Salaun, and J. M. Conia, *ibid.*, 1747 (1973); E. Wenkert, R. A. Mueller, E. J. Reardon, S. S. Sathe, D. J. Scharf, and G. Tosi, *J. Amer. Chem. Soc.*, **92**, 7428 (1970); W. F. Erman, R. S. Treptow, P. Bakuzis, and E. Wenkert, *ibid.*, **93**, 657 (1971).

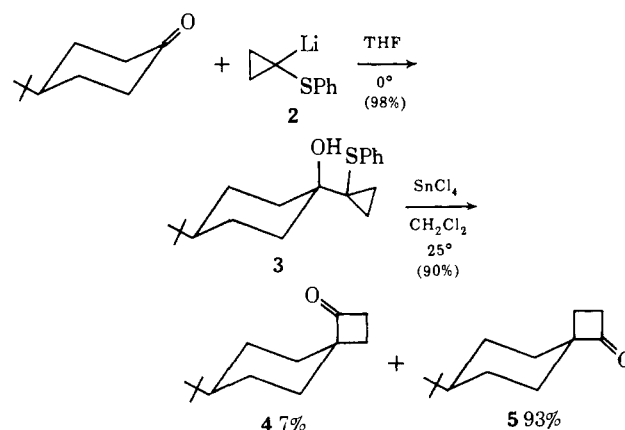
(2) (a) B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **93**, 3773 (1971); (b) M. J. Bogdanowicz and B. M. Trost, *Tetrahedron Lett.*, 887 (1972); (c) B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **95**, 289 (1973); (d) B. M. Trost and M. J. Bogdanowicz, *ibid.*, **95**, 5311, 5321 (1973).

(3) B. M. Trost, D. Keeley, and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **95**, 3068 (1973).



actions involve carbonium ions and are nonstereoselective, (2) the reactions are nonetheless highly stereoselective, (3) migrations to cyclohexyl carbon involve formation of an axial bond, and (4) electronic not steric factors control the regiospecificity in the case of spiroannulations with enones. These results have special significance in light of their synthetic consequences<sup>1-3</sup> and their comparison to the behavior of cyclopropylcarbinyl systems not possessing such directing groups.<sup>4</sup>

Reaction of the organolithium **2** with 4-*tert*-butylcyclohexanone produces an adduct as a 99:1 mixture of two isomers.<sup>5,6</sup> By analogy to organometallic additions to this ketone,<sup>7</sup> the major product was assigned the stereochemistry depicted in **3**. Treatment with 1 equiv of anhydrous stannic chloride followed by hydrolysis produces primarily cyclobutanone **5**.<sup>2</sup> Obtention of the



product requiring retention of configuration at the migration terminus strongly suggests a carbonium ion intermediate rather than a migration concerted with loss of the leaving group. Consideration of the stability of the intermediates allows a rationalization of the delightfully high stereoselectivity seen. Cyclopropylcarbinyl cations assume the bisected geometry (**6**) as the preferred conformation. Migration by path "b" (equatorial migration) swings the phenylthio unit over the top of the cyclohexane ring and thus creates substantial steric crowding. Migration by path "a" (axial migration) swings this unit into a relatively uncrowded region away from the cyclohexane ring. The differential steric crowding favors path "a" which leads to the major observed product. Preferred axial migration contrasts to other intramolecular rearrangements in which the equatorial pathway predominates.<sup>2,8</sup>

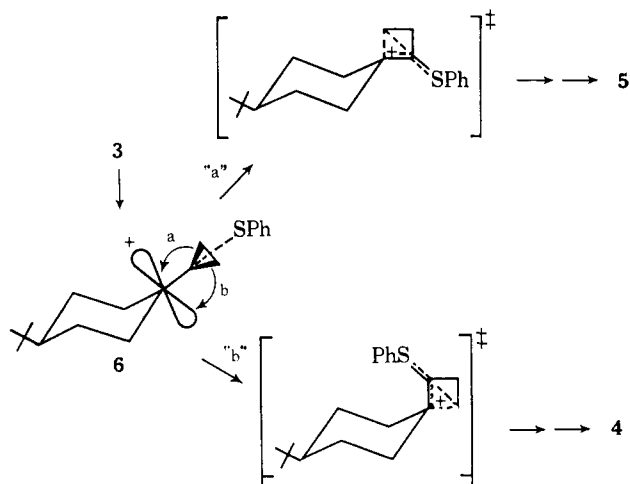
(4) (a) K. Rajeswari and T. S. Sorenson, *J. Amer. Chem. Soc.*, **95**, 1239 (1973); (b) M. Julia and Y. Noël, *Bull. Soc. Chim. Fr.*, 3749 (1968).

(5) All new compounds had spectral properties and analytical data in complete accord with the assigned structure.

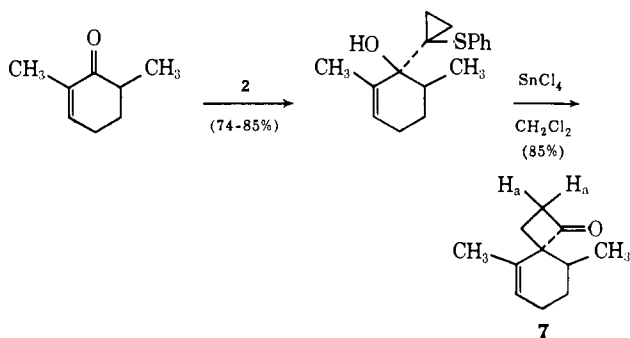
(6) This analysis was performed by liquid-liquid chromatography on a Corasil II column, flow rate of 2.8 ml/min, hexane solvent.

(7) (a) W. W. Houlihan, *J. Org. Chem.*, **27**, 3860 (1962); (b) H. Felkin and C. Frajerman, *Tetrahedron Lett.*, 1045 (1970); (c) H. O. House and W. L. Respess, *J. Org. Chem.*, **30**, 301 (1965); (d) J. Moulines and R. Lalonde, *Bull. Soc. Chim. Fr.*, 1075 (1971); (e) C. R. Johnson, C. W. Schroeck, and J. R. Shanklin, *J. Amer. Chem. Soc.*, **95**, 7424 (1973), report equatorial to axial attack of 4:1 for phenylthiomethyl lithium with 4-*tert*-butylcyclohexanone.

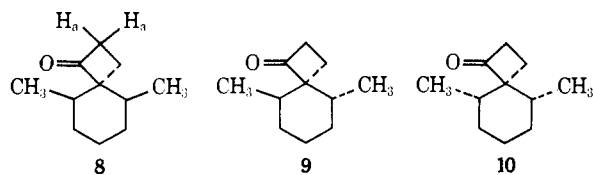
(8) For example, see G. Andrews and D. A. Evans, *Tetrahedron Lett.*, 5121 (1972); D. A. Evans and G. C. Andrews, *J. Amer. Chem. Soc.*, **94**, 3672 (1972).



Similar results have been obtained utilizing 2,6-dimethyl-2-cyclohexen-1-one. Attack of **2** should occur predominantly (if not exclusively) trans to the saturated methyl group.<sup>9</sup> Rearrangement with stannic chloride produces a single cyclobutanone **7**<sup>5</sup>—again the

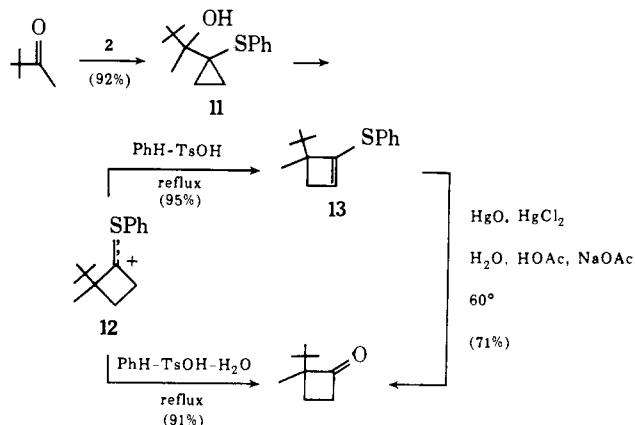


product that demands a predominant retention of configuration at the migration terminus. The stereochemistry of **7** is based upon the  $\text{Eu}(\text{dpm})_3$  (25 mol %) induced shifts of the saturated methyl group relative to the methylene group  $\alpha$  to the carbonyl ( $\Delta\delta_{\text{satCH}_3}:\Delta\delta_{\text{H}_a} = 0.55$ ) compared to this ratio for compound **8** ( $\Delta\delta_{\text{satCH}_3}:\Delta\delta_{\text{H}_a} = 1.2$ ). Confirmatory evidence arises from the fact that hydrogenation ( $\text{Pd}/\text{C}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , 1 atm) of **7** produces two dihydro compounds (ratio 2:1), isomeric with **8**,<sup>10</sup> but neither of which is identical with **8**.<sup>6</sup> They must have the stereochemistry depicted in **9** and **10**.<sup>5</sup>



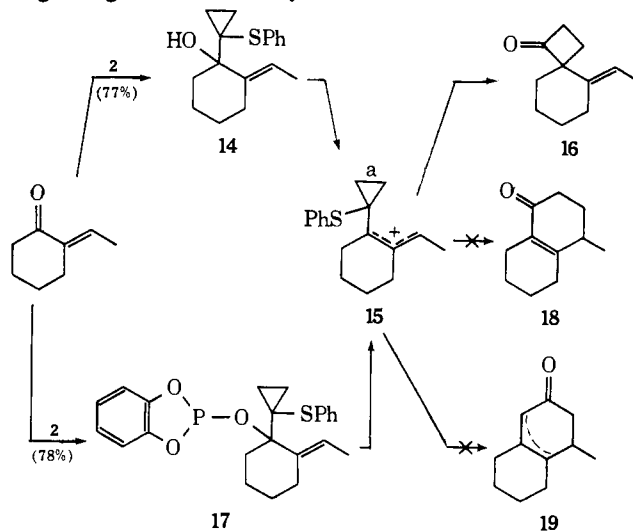
Spiroannellation of pinacolone provided support for the intervention of an  $\alpha$ -phenylthiocyclobutyl cation (e.g., **12**). Rearrangement of the adduct **11** under anhydrous conditions produces the enol thio ether **13**<sup>5</sup> arising from deprotonation of **12**; whereas, in the presence of water, trapping of this intermediate by the water leads to cyclobutanone.<sup>5</sup>

At first glance, the exclusive formation of cyclobut-



ones from  $\alpha,\beta$ -unsaturated carbonyl compounds appears surprising for a carbonium ion reaction.<sup>3</sup> A recent report described the generation and rearrangement of cyclopropylallyl cations in which the products were cyclohexenyl derivatives.<sup>4a</sup> *A priori*, the release of almost all the strain energy of the system should provide a strong driving force for cyclohexenone formation. To test whether conformational or electronic effects accounted for the preferred pathway, spiroannellation of 2-ethylidenecyclohexanone<sup>11</sup> was performed. In this case, the intermediate **15** is restricted to a cisoid conformation. Rearrangement of **14** with aqueous fluoroboric acid (39% yield) or stannic chloride (84% yield) again produced only cyclobutanone **16** as indicated by the carbonyl stretching vibration at  $1773\text{ cm}^{-1}$ , the nmr absorptions at  $\delta$  2.92 (t,  $J = 9\text{ Hz}$ ,  $\text{CH}_2\text{CO}$ ) and 1.63 (d,  $J = 5\text{ Hz}$ ,  $\text{CH}_3\text{C}=\text{C}$ ), and the mass spectral fragmentation peaks at  $m/e$  136 ( $\text{M}^+ - \text{C}_2\text{H}_4$ ) and 122 ( $\text{M}^+ - \text{CH}_2\text{CO}$ ) which are typical for cyclobutanones.<sup>5</sup> Similarly, the phosphite derivative **17** in refluxing tetrahydrofuran containing a trace of hydrochloric acid also led only to **16** (83% yield).

Orbital symmetry demands that the formation of **16**, a suprafacial two-electron [1,2] shift, occurs with retention of configuration of the migrating carbon; whereas, the formation of **18**, a suprafacial four-electron [1,4] shift, must occur with inversion of configuration of the migrating carbon.<sup>12</sup> Cyclohexenone **19** would have



(9) J. Laemmle, E. C. Ashby, and P. V. Roling, *J. Org. Chem.*, **38**, 2526 (1973).

(10) B. M. Trost and M. Preckel, *J. Amer. Chem. Soc.*, **95**, 7862 (1973).

(11) T. A. Spencer, R. W. Britton, and D. S. Watt, *J. Amer. Chem. Soc.*, **89**, 5727 (1967).

(12) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

resulted from a  $\sigma_{2a} + \pi_{2s}$  (or  $\sigma_{2s} + \pi_{2a}$ ) addition of cyclopropyl bond a (see 15) across the allyl unit analogous to that observed in nondirected systems.<sup>4a</sup> Thus, the 1,2 shift represents least nuclear motion<sup>13</sup> and therefore should predominate. It is interesting to note that, in this case, the restraints imposed by the principle of least motion are enough to overcome the thermodynamic driving force for release of strain energy. These results have important implications for synthetic applications. In addition to the high stereoselectivity in spiroannulations, 1-lithiocyclopropyl phenyl sulfide fully complements the behavior of diphenylsulfonium cyclopropylide in terms of both stereochemistry of spiroannulation and chemospecificity<sup>14</sup> with conjugated enones.

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(13) J. Hine, *J. Org. Chem.*, **31**, 1236 (1966).

(14) For a definition of the term "chemospecificity" see B. M. Trost and T. N. Salzman, *J. Amer. Chem. Soc.*, **95**, 6840 (1973).

(15) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient.

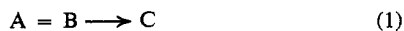
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## Calculation of Steric Effects in Reactions

Sir:

There is increasing interest in reactions which show acceleration due to forced proximity of reacting groups, particularly with respect to possible relationships to enzymatic catalysis.<sup>1-4</sup> Results are often discussed in such terms as preferred reaction trajectories and occasionally with such phrases as "orbital steering." There have, however, been important successes in quantitative calculations of energies of postulated transition states where steric factors have played a considerable role.<sup>5-8</sup> The purpose of this communication is to describe another quantitative procedure for evaluating steric effects which in several cases has given results of comparable accuracy.

We first define a formalism which, like transition state theory, is a thermodynamic model



(1) M. L. Bender, "Mechanisms of Homogeneous Catalysis from Protons to Proteins," Wiley-Interscience, New York, N. Y., 1971.

(2) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969.

(3) T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms," W. A. Benjamin, Reading, Mass., 1966.

(4) D. R. Storm and D. E. Koshland, Jr., *J. Amer. Chem. Soc.*, **94**, 5815 (1972).

(5) F. H. Westheimer, *J. Chem. Phys.*, **15**, 252 (1947); F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 523.

(6) E. W. Garbisch, Jr., S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, *J. Amer. Chem. Soc.*, **87**, 2932 (1965).

(7) M. Simonetta, G. Favini, C. Mariani, and P. Gramaccioni, *J. Amer. Chem. Soc.*, **90**, 1280 (1968).

(8) J. L. Fry, E. M. Engler, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 4628 (1972).

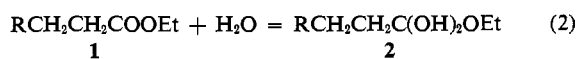
A designates reactants, B some intermediate structure, and C products. Superficially this may appear to be nothing more than a restatement of the transition-state concept, for it is commonly assumed that calculations cannot succeed unless B is a really good model of the transition state.

There are indeed reactions for which B must be the transition state, but the point of the formalism is that this is not at all a general requirement. Suppose that we are comparing examples of a cyclization reaction where there are large rate differences due to remote steric factors. It should be possible to discover many working models for B any one of which could represent reasonably well the relative differences in steric energies between reactants and transition states but none of which was a really accurate model of the transition state. Other examples are to be found among the successes of linear free energy relationships. In these reaction series the structure of B need not even have been clearly defined. Further examples are presented below. It is also possible to state the corollary that we are not justified in assuming that a given model B is a good representation of the transition state just because it gives a good rate correlation.

We do not claim originality for the approach, but we do believe that specific recognition of the basis of this formalism will lead to more fruitful treatment of reaction models. We shall now apply the formalism to the treatment of steric factors, but clearly the formalism is general and applicable to other effects as well.

To implement the formalism for treatment of steric effects, we must define precise structures for the B<sub>i</sub> and we must find a way to calculate the free energy change from A<sub>i</sub> to B<sub>i</sub>. In most cases we cannot hope to find adequate thermodynamic values even for reactants, and the B<sub>i</sub> will not generally represent stable molecules. Developments in molecular mechanics and in related parameterized computations hold great promise.<sup>8-14</sup> For the present we propose to use hydrocarbon models for the A<sub>i</sub> and B<sub>i</sub> in the calculation of relative steric effects. The justification for this approximation is that for many reactions the hydrocarbon part of the molecule is responsible for most of the steric effect. With some caution we can go further and use methyl groups as surrogates for such heteroatoms as oxygen. As in all uses of models their utility will depend on the extent to which they give a reliable account of experiments. If the models prove generally useful, then the approximations are justified. If not, then we must search further.

To calculate steric hindrance in the classical example of ester hydrolysis, eq 2, we shall postulate that the



total steric effect will be represented in going from starting ester 1 to tetrahedral intermediate 2. As hydrocarbon models, we will use the isoalkanes 3 as the

(9) E. J. Jacob, H. B. Thompson, and L. S. Bartell, *J. Chem. Phys.*, **47**, 3736 (1967); L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968).

(10) R. H. Boyd, *J. Chem. Phys.*, **49**, 2574 (1968).

(11) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, **93**, 1637 (1971).

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(13) A. Warshel and M. Karplus, *J. Amer. Chem. Soc.*, **94**, 5612 (1972).

(14) N. Bodor, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, **94**, 5303 (1972).