voltages.¹¹ A recent report¹² 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 "oneelectron 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 $C_5H_5^+$ 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.

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

Sir:

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

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actions involve carbonium ions and are nonstereospecific, (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 spiroannelations with enones. These results have special significance in light of their synthetic consequences¹⁻³ and their comparison to the behavior of cyclopropylcarbinyl systems not possessing such directing groups.⁴

Reaction of the organolithium 2 with 4-*tert*-butylcyclohexanone produces an adduct as a 99:1 mixture of two isomers.^{5,6} By analogy to organometallic additions to this ketone,⁷ the major product was assigned the stereochemistry depicted in 3. Treatment with 1 equiv of anhydrous stannic chloride followed by hydrolysis produces primarily cyclobutanone 5.² 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.^{2,8}

(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. Lalande, 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 phenylthiomethyllithium 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).

⁽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).

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



product that demands a predominant retention of configuration at the migration terminus. The stereochemistry of 7 is based upon the Eu(dpm)₈ (25 mol %) induced shifts of the saturated methyl group relative to the methylene group α to the carbonyl ($\Delta \delta_{satCH_3}: \Delta_{Ha}$ = 0.55) compared to this ratio for compound **8** ($\Delta \delta_{satCH_3}: \Delta \delta_{Ha} = 1.2$). Confirmatory evidence arises from the fact that hydrogenation (Pd/C, C₂H₅OH, 1 atm) of 7 produces two dihydro compounds (ratio 2:1), isomeric with **8**, ¹⁰ but neither of which is identical with **8**.⁶ They must have the stereochemistry depicted in **9** and **10**.⁵



Spiroannelation of pinacolone provided support for the intervention of an α -phenylthiocyclobutyl cation (e.g., 12). Rearrangement of the adduct 11 under anhydrous conditions produces the enol thio ether 13⁵ arising from deprotonation of 12; whereas, in the presence of water, trapping of this intermediate by the water leads to cyclobutanone.⁵

At first glance, the exclusive formation of cyclobut-

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



nones from α,β -unsaturated carbonyl compounds appears surprising for a carbonium ion reaction.³ A recent report described the generation and rearrangement of cyclopropylallyl cations in which the products were cyclohexenyl derivatives.^{4a} 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, spiroannelation of 2-ethylidenecyclohexanone¹¹ 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 cm⁻¹, the nmr absorptions at δ 2.92 (t, J = 9 Hz, CH₂CO) and 1.63 (d, J = 5 Hz, CH₃C=C), and the mass spectral fragmentation peaks at m/e 136 (M⁺ - C₂H₄) and 122 (M⁺ -CH₂CO) which are typical for cyclobutanones.⁵ 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.¹² Cyclohexenone 19 would have



⁽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 $_{\sigma}2_{a} + _{\pi}2_{s}$ (or $_{\sigma}2_{s} + _{\pi}2_{a}$) addition of cyclopropyl bond a (see 15) across the allyl unit analogous to that observed in nondirected systems.^{4a} Thus, the 1,2 shift represents least nuclear motion¹³ 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 spiroannelations, 1-lithiocyclopropyl phenyl sulfide fully complements the behavior of diphenylsulfonium cyclopropylide in terms of both stereochemistry of spiroannelation and chemospecificity¹⁴ with conjugated enones.

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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.¹⁻⁴ 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.⁵⁻⁸ 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

$$A = B \longrightarrow C \tag{1}$$

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- (5) F. H. Westheimer, J. Chem. Phys., 15, 252 (1947); F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed.,
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 (6) E. W. Garbisch, Jr., S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, J. Amer. Chem. Soc., 87, 2932 (1965).

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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_i and we must find a way to calculate the free energy change from A_i to B_i . In most cases we cannot hope to find adequate thermodynamic values even for reactants, and the B_1 will not generally represent stable molecules. Developments in molecular mechanics and in related parameterized computations hold great promise.8-14 For the present we propose to use hydrocarbon models for the A_i and B_i 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

$$RCH_2CH_2COOEt + H_2O = RCH_2CH_2C(OH)_2OEt$$
(2)
1 2

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

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