reactions. The ab initio results also confirm that thiiranimine is stable toward fragmentation (into an isocyanide plus a thioketone) in agreement with experimental findings for substituted thiiranimines.

Acknowledgment. The authors are indebted to the Belgian Government (Programmatie voor het Wetenschapsbeleid) and to the National Fund for Scientific Research, Belgium (NFWO), for financial support.

Registry No. 1a, 124604-18-8; (*Z*)-HSCH=NH, 135269-13-5; (*Z*)-Me(HS)C=NH, 135269-14-6; Me_2C=NH, 38697-07-3; (*E*)-MeCH=NH, 56003-81-7; H_2C=NH, 2053-29-4; cyclopropylimine, 54376-32-8.

Theoretical Studies of Transition Structures and Stereoselectivities of the [2,3]-Wittig Rearrangement of Sulfur Ylides

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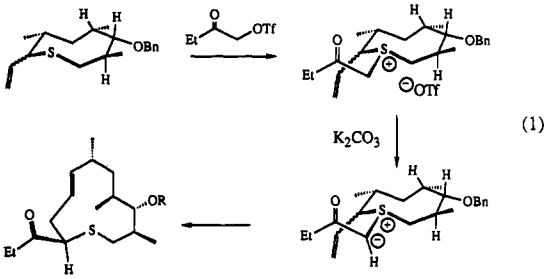
Transition structures of the [2,3]-Wittig rearrangements of allylsulfonium methylide and three substituted cases have been located with the 3-21G(*) and 6-31+G* basis sets. The transition structures have envelope conformations with the partially formed C–C bond nearly eclipsed with the partially broken C–S bond. The forming C–C bond is only formed to a small extent, corresponding to an early transition structure. The lone pair on sulfur prefers to be exo (away from the allyl fragment), primarily to minimize electrostatic repulsions. A formyl group at the anionic center is more stable in the endo configuration, while a methyl substituent prefers the exo configuration. The stereoselectivity of ring expansions of sulfur ylides can be rationalized by the combination of ring strain and the sulfur lone pair exo preference.

Introduction

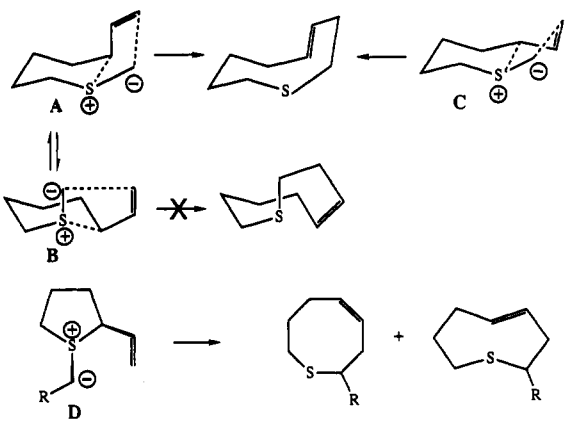
The sulfur ylide mediated ring expansion involving the intramolecular [2,3]-Wittig rearrangement has been developed by Vedejs et al. as a useful method for medium-ring synthesis, as exemplified by eq 1.[1-3]



(1)

General stereoselectivity patterns have been established.[1,4,5] As summarized in Scheme I, six-membered reactants form nine-membered products with an (*E*)-alkene geometry, regardless of whether the reactant is cis (A or B) or trans (C).[4] The same stereoselectivity is observed for larger rings. With five-membered reactants, D, ring expansion occurs only when the two substituents are cis. Both *Z* and *E* products can be formed. The *Z* product is formed exclusively if the starting ylide is stabilized, while more *E* product is formed if the starting ylide is not stabilized. Several examples are given in the scheme. Stabilization is afforded by substitution of an electron-withdrawing group at the ylide anionic center.

Scheme I



R = H	6	1
R=Me	1	1.4
R=COPh	10	1
$R=CO_2Et$	exclusive	no

Fava et al. have qualitatively rationalized the stereoselectivities based on orbital overlap and ring-strain considerations.[4] Concerted transition states with envelope conformations were assumed to be involved in these reactions.[6,7] For example, conformer A is suggested to be more stable than B because A has good orbital overlap without geometrical distortion about the six-membered ring, while geometrical distortions are necessary for B to achieve good orbital overlap. The variation of stereoselectivity with R group in D was suggested to be the result

(1) Vedejs, E. *Acc. Chem. Res.* **1984**, *17*, 358.
(2) Vedejs, E.; Buchanan, R. A.; Conrad, P. C.; Meier, G. P.; Mullins, M. J.; Schaffhausen, J. G.; Schwartz, C. E. *J. Am. Chem. Soc.* **1989**, *111*, 8421.
(3) Vedejs, E.; Buchanan, R. A.; Conrad, P. C.; Meier, G. P.; Mullins, M. J.; Watanabe, Y. *J. Am. Chem. Soc.* **1987**, *109*, 5878. Vedejs, E.; Powell, D. W. *J. Am. Chem. Soc.*, **1982**, *104*, 2046. Vedejs, E.; Buchana, R. A. *J. Org. Chem.* **1984**, *49*, 1840. Vedejs, E.; Hagen, J. P. *J. Am. Chem. Soc.* **1975**, *97*, 6878.
(4) Cere, V.; Paolucci, C.; Pollicino, S.; Sandri, E.; Fava, A. *J. Org. Chem.* **1979**, *44*, 4128; *Ibid.* **1981**, *46*, 3315. Fava, A.; Paolucci, C.; Pollicino, S.; Sandri, E. *Ibid.* **1978**, *43*, 4826.
(5) Vedejs, E.; Mullins, M. J.; Renga, J. M.; Singer, S. P. *Tetrahedron Lett.* **1978**, 519. Vedejs, E.; Hegan, J. P.; Roach, B. L.; Spear, K. L. *J. Org. Chem.* **1978**, *43*, 1185. Vedejs, E.; Arco, M. J.; Powell, D. W.; Renga, J. M.; Singer, S. P. *Ibid.* 4831.
(6) Baldwin, J. E.; Hackler, R. E.; Kelly, D. P. *J. Chem. Soc., Chem. Commun.* **1968**, 538. Evans, D. A.; Angews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147.
(7) Trost, B. M.; Melvin, L. S., Jr. *Sulfur Ylides*; Academic Press: New York, 1975; Chapter 7.

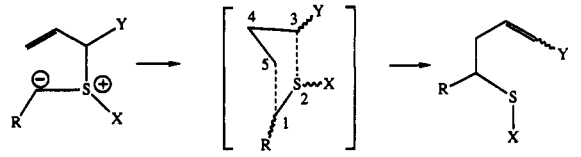
0022-3263/91/1956-5657$02.50/0

of changes in the transition-state geometry caused by the substituents.[4]

In order to provide a better understanding of the stereoselectivities of these reactions, detailed information about the transition structures is necessary. We report theoretical studies that have led to new ideas about the factors controlling the stereoselectivities of these reactions.

Results and Discussion

The transition structures for the reactions of **1a–d** have been located with the 3-21G(*) basis set using Pople's GAUSSIAN 88 program.[8] For the parent reaction, **1a**, transition structures were also located with the 6-31+G and 6-31+G* basis sets. Harmonic vibrational frequency calculations were performed for each of the transition structures. Each is a saddle point. The energies of the transition structures were further evaluated by MP2/6-31+G(*) calculations on the 3-21G(*) geometries (MP2/6-31+G* on 6-31+G* geometries for the parent reaction **1a**).[9] The reactant and product of the parent reaction were also optimized with the 6-31+G* basis set.



1a. R = H, X = Y = H
1b. R = Me, X = Y = H
1c. R = CHO, X = Y = H
1d. R = H, X,Y = $(CH_2)_3$

As shown in Figure 1, there are two transition structures, **2** and **3**, for the reaction of the parent system **1a**. These differ by the orientation of the S–H bond. The transition structures correspond to concerted reaction pathways. The breaking C---S bonds are longer than a normal C–S single bond by about 4.0 Å. The forming C---C bonds are quite long. These early transition structures reflect the high exothermicity of the reaction (6-31+G*, 75 kcal/mol; MP2/6-31+G*, 67 kcal/mol) and low activation energy (6-31+G*, 14.2 kcal/mol; MP2/6-31+G*, -2.7 kcal/mol for **2**).[10] The partially formed C---C and C---S bonds are nearly eclipsed in **3**, but are somewhat less so in **2**. The two terminal carbons (C_3 and C_5) of the allyl moiety are partially negatively charged, and the central carbon (C_4) is positively charged. Overall, the allyl moiety bears about 0.025 unit of negative charge according to Mulliken population analysis.

Methyl substitution at the anionic center (reaction of **1b**) slightly increases the forming C---C bond length, while the C---S bond length changes very little. Whereas the two cis transition structures, **4** and **7**, are less eclipsed, nearly perfect eclipsing exists in **5** and **6**, where C–Me and S–H are trans. Formyl group substitution at the anionic center (**1c**) stabilizes the ylide and results in more advanced transition structures (**8–11**), as indicated by about 0.13-Å shortening of the forming C---C bonds and lengthening of the breaking C---S bonds. The formyl group in **8–11** is chosen to be in an s-cis conformation with respect to the sulfur ylide bond. It has been found that a carbonyl bond generally prefers the s-cis conformation in the transition structures of Diels–Alder reactions, which have geometries quite similar to these reactions.[11,12] This conformation becomes more favorable in the case of carboxylic ester substituents,[13] which we try to model in these calculations.

Table I. Calculated Endo/Exo Preferences of Substituents in the Transition Structures

X (kcal/mol) = E(*exo*-SH) – E(*endo*-SH)

Y (kcal/mol) = E(*exo*-R) – E(*endo*-R), R = Me, CHO

	R = H	R = Me		R = CHO	
basis set	X	X	Y	X	Y
3-21G(*)	2.3	2.2	–0.5	2.0	0.2
6-31+G(*)	1.8	1.6	–0.5	1.3	0.1
MP2/6-31+G(*)	1.2	1.1	–0.8	1.1	1.3

There is a clear preference for the S–H bond to be endo (near C_4 of the allyl fragment), or equivalently, there is an exo preference of the S lone pair.[14] This preference is 2.3 kcal/mol with the 3-21G(*) basis set but drops to about 1.2 kcal/mol with the MP2/6-31+G(*) calculations. This exo lone pair preference is mainly due to the electrostatic destabilizing interaction in **3** (and **6**, **7**, **10**, and **11**) between the endo lone pair and the partially negatively charged allyl moiety. Such endo lone pair destabilization is predicted to be even larger in many hetero-Diels–Alder reaction transition structures involving species such as imines, which have unsymmetrical lone-pair distributions.[15]

If it is assumed that the group endo/exo preferences are additive, the inherent preferences of S–H, C–Me, and C–CHO in the transition structures **4–11** can be estimated,[16] as given in Table I. These are calculated as shown in the following examples:

$$X \text{ (kcal/mol)} = E(\textit{exo}\text{-SH}) - E(\textit{endo}\text{-SH})$$

$$Y \text{ (kcal/mol)} = E(\textit{exo}\text{-R}) - E(\textit{endo}\text{-R}), \text{ where R = Me or CHO}$$

In the case of the 3-21G(*) calculations when R = Me

$$E(6) - E(5) = X - Y = 2.7$$

$$E(7) - E(4) = X + Y = 1.7$$

therefore, $X = 2.2$ and $Y = -0.5$.

When R = CHO

$$E(10) - E(9) = X - Y = 1.8$$

$$E(11) = E(8) = X + Y = 2.2$$

therefore, $X = 2.0$ and $Y = 0.2$.

The calculated S–H endo preferences in the presence of Me and CHO groups are 1–2 kcal/mol and are only

(8) GAUSSIAN 88: Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A., Gaussian Inc., Pittsburgh, PA, 1988.

(9) The 6-31+G(*) basis set refers here to the 6-31+G basis set with the inclusion of an additional set of d orbitals only on the S atom. The 3-21G(*) basis set means a set of d orbitals only on the S atom.

(10) The slightly negative activation energy for the reaction of **1a** calculated at the MP2/6-31+G* level of theory indicates that the [2,3]-rearrangement of this unstabilized ylide may be concerted with deprotonation. This is similar to the reaction of allyl methylide, where we found that the transition structure located with the 6-31+G* basis set is very similar to the transition structure concerted with deprotonation by Cl^- located with the MP2/6-31+G level of theory. This will be published shortly.

(11) Loncharich, R. J.; Houk, K. N. *J. Org. Chem.* **1989**, *54*, 1129.

(12) Birney, D. M.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 4127.

(13) Loncharich, R. J. Schwartz, T. R.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 14.

(14) The endo and exo positions defined throughout the paper refer to five-membered envelope transition structures, as designated in **2** and **3**.

(15) Wu, Y.-D.; McCarrick, M.; Houk, K. N. Manuscript in preparation.

(16) For the exo/endo preferences of C–Me and C–CHO, only structures with same pattern of substitutions can be compared, that is, **5** to **6**, **4** to **7**, **9** to **10**, and **8** to **11**.

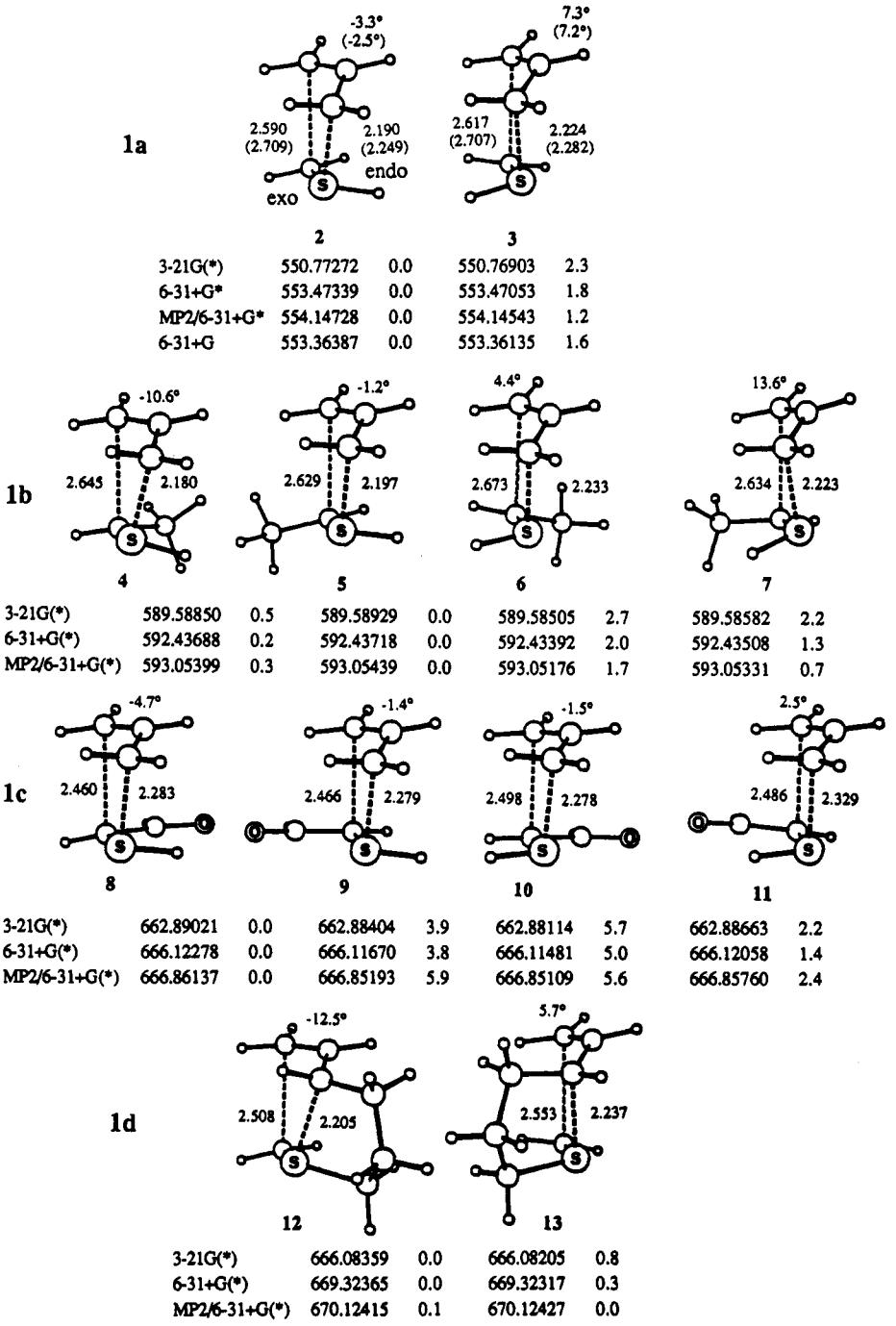


Figure 1. Side views of transition structures of reactions **1a–d** located with the 3-21G(*) basis set. The values below each structure are the calculated total energies (–au) and relative energies (kcal/mol). the 6-31+G(*) and MP2/6-31+G(*) energies of **4–13** were calculated on the basis of 21G(*) geometries, and the MP2/6-31+G* energies of **2** and **3** were calculated on the basis of the 6-31+G* geometries. The geometrical values in parentheses are from 6-31+G* calculations.

slightly different from the preferences calculated from **2** and **3**. There is an about 0.5 kcal/mol preference for the methyl group to be exo. The formyl group, on the other hand, prefers the endo position by 0.1–1.3 kcal/mol. These substituent effects are smaller, but in the same direction, as those in the [2,3]-Wittig rearrangement transition structures with O instead of S.[17] Structure **11** is significantly more stable than **10**, even though **11** has an exo formyl group. This is because **10** is destabilized by electrostatic repulsion between the sulfur lone pair and the formyl oxygen lone pairs. This interaction also occurs in **9**. As will be discussed later, these relative stabilities may be reversed in cyclic systems.

An important factor in determining the stereoselectivities of cyclic cases is that the torsional arrangements around the breaking C---S bond are quite different in the endo S–H and exo S–H transition structures. Figure 2 gives Newman projections sighting along this breaking C---S bond for a number of transition structures. Structure **14** is a Newman projection about the C---S bond for transition structure **2**. The S–H bond is staggered with respect to the C_3–H_{eq} bond, whereas the S–H bond in **15**, which is a Newman projection for **3**, is more nearly eclipsed with the C_3–H_{ax} bond. Consequently, the introduction of a five-membered ring into **14**, by replacing S–H and C_3–H_{eq} with a trimethylene chain, is disfavored because of the torsional strain introduced. This situation corresponds to

(17) Wu, Y.-D.; Houk, K. N.; Marshall, J. A. *J. Org. Chem.* **1990**, *55*, 1421.

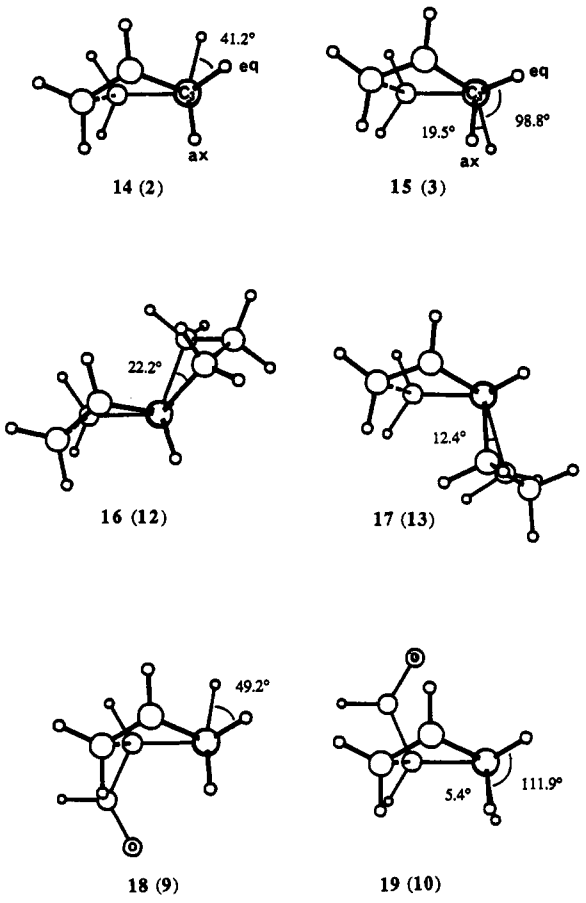
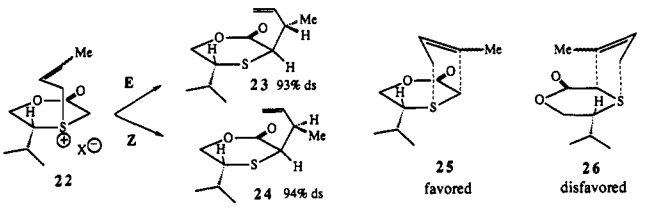


Figure 2. Newman projections sighting along the C---S bond for various transition structures.

the transition structure leading to the formation of the *E* product. Replacement of S–H and C_3–H_{ax} of **15** with a trimethylene chain will introduce less strain; this will lead to the *Z* product. This qualitative conclusion was verified by calculations on the reaction of **1d**. The transition structures are shown in **12** and **13**, and Newman projections are given in **16** and **17**. The five-membered ring with one long C---S bond prefers an envelope conformation with near eclipsing about the long bond; this minimizes strain in the five-membered ring.[18] This is quite general for five-membered rings, since the torsional force about the long bond is smallest. A comparison of **14** to **16** shows that the trimethylene causes the allyl moiety to rotate to reduce the torsional angle about the C---S bond. This relieves ring strain in the five-membered ring with some sacrifice of orbital overlap as indicated by the increase of the dihedral angle between the two partially formed bonds. A comparison of **17** to **15** shows that much less rotation of the allyl moiety is required. Transition structure **13** is calculated to be 0.1 kcal/mol more stable than **12** with the MP2/6-31+G(*) basis set, while a 0.6 kcal/mol preference for the formation of *Z* product is observed experimentally.[4] Structure **13** is destabilized by the endo lone pair, but the destabilization caused by the ring strain in **12** is even larger so that the *Z* product is formed preferentially.

The trends shown in Scheme I can also be rationalized in this way. When a substituent is introduced on the anionic center of **12**, it must occupy the exo position to avoid steric interactions with the S–CH_2 ring. For the same reason, a substituent at the anionic center of the transition structure **13** must be endo. Since a methyl group favors the exo position, it will cause the stability of **12** (plus exo Me) to increase relative to **13** (plus endo Me). Thus, the *E* product is very slightly favored experimentally. A formyl group favors the endo position, and the formation of *Z* product will be enhanced by this or other carbonyl groups. Moreover, the lateness of transition structures introduced by the stabilizing formyl group at the anionic center increases the importance of orbital overlap and reduces the mobility of the allyl moiety. This will force the transition structure for the *E* product to be more like **14** than **16**. This disfavors the formation of the *E* product, in agreement with Fava's analysis.[4] Structures **18** and **19**, which are the Newman projections sighting along the C---S bonds of the formyl-substituted transition structures **9** and **10**, respectively, show that the staggering in **18** is better than that in **14** and that **19** is more eclipsed than **15**.

Scheme II



For the formulation of transition structures with the six-membered ylide with cis substituents, the five-membered ring in **12** and **13** is replaced with a chairlike six-membered ring. These transition structures have not been calculated, but a qualitative understanding can be achieved from inspection of **14** and **15**. Minimal torsional strain exists in the six-membered analogue of **14**, since a six-membered ring prefers an all-staggered conformation, with a torsional angle of 50–60°, near the 41° value present in **14**. The transition structure analogous to **14** will give the *E* product. There will be considerable torsional strain in the six-membered transition structure corresponding to **15**, which leads to *Z* product, because of the eclipsing about the C---S bond. Therefore, the formation of the *E* product will be favored for such cases.[4]

The only reasonable transition structure for the six-membered ylide with trans substituents involves the replacement of the C_3–H_{eq} bond and the exo S–H bond in the transition structure **15** with a tetramethylene chain. This structure will lead to the formation of the *E* product. As shown in **15**, the dihedral angle between the C_3–H_{eq} and S–H bonds is 99°. This transition structure is not as favorable as it is when formed from cis ylides. This supports the Fava explanation of the fact that cis ylides are much more reactive than their trans analogues.[4] In addition, the transition structure from trans ylides is also disfavored by the endo lone pair.

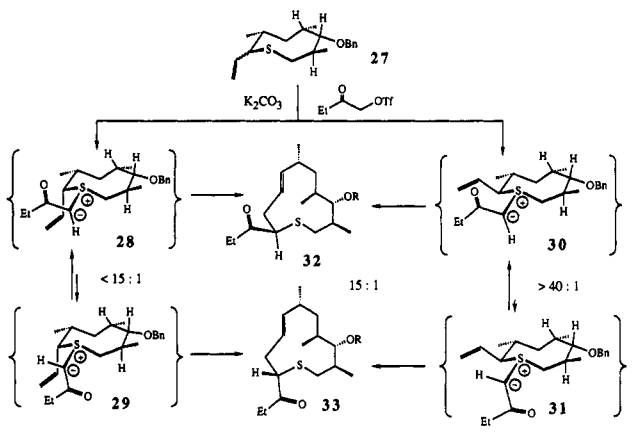
Our results rationalize qualitatively the stereoselectivity of the reaction of **22** reported recently by Kurth et al. and shown in Scheme II.[19] The transition structure with the endo six-membered ring, **25**, is favored over the transition structure with the exo six-membered ring, **26**, leading to a large preference for **23** from the *E* reactant and **24** from the *Z* reactant. Our results indicate that **26** is destabilized relative to **25** both by the exo carbonyl group and the endo sulfur lone pair, even though it should be favorable sterically.

The interesting stereoselectivities of ring expansion of eight-membered ring sulfur ylides reported recently by

(18) This analysis is similar to that made earlier to rationalize the stereoselectivities of intramolecular ene reactions: Loncharich, R. J.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 6947.

(19) Kurth, M. J.; Tahir, S. H.; Olmstead, M. M. *J. Org. Chem.*, **1990**, *55*, 2286.

Scheme III



Vedejs et al. can also be rationalized.[2] As shown in Scheme III, Vedejs et al. observed that the α-monosubstituted ylides derived from a 1:1 mixture of diastereomers (27) gave 32 and 33 in a ratio of 15:1. Significantly higher stereoselectivity (>40:1, 32:33) was observed with one of the separated isomers.[20] Vedejs et al. proposed that the isomer corresponding to 30 is responsible for the high >40:1 preference for 32. This means that the stereoselectivity derived from 28 and 29 is less than 15:1. This is consistent with our findings. Structures 28 and 30 are more stable than 29 and 31, respectively, because the α-propanoyl group is anti to the S-CH_2 to minimize steric interactions. The structure 30 is further favored by having an endo propanoyl group, while 28 is disfavored by having an exo propanoyl group.

In summary, the transition structures for [2,3]-sigmatropic rearrangements of sulfur ylides correspond to concerted reaction pathways. The forming C---C bond is formed to a small extent, indicating a very asynchronous transition structure. Ylide-stabilizing substituents such as the formyl group make the transition structure more advanced along the reaction coordinate. There is a general tendency for the two partially formed bonds to be eclipsed, which promotes maximal orbital overlap at both termini of the allyl fragment; this tendency is stronger with ylide-stabilizing substituents. The sulfur lone pair prefers to be exo with respect to the allyl moiety; methyl and formyl substituents at the anionic center favor the exo and endo orientations, respectively. The formation of the *Z* ring expansion product from a five-membered ylide is favored to minimize ring strain in the five-membered ring. The formation of the *E* product from a six-membered ylide benefits from ring strain and sulfur lone-pair orientation effects.

Acknowledgment. We are grateful to the National Institutes of Health for financial support of this research and to Professor Edwin Vedejs for helpful comments. This work was supported in part by a grant of computer time made possible under a joint study with the IBM Corporation on the IBM 3090/600J Supercomputer at the UCLA Office of Academic Computing.

Registry No. 1a, 10152-76-8; 1b, 5296-62-8; 1c, 120983-16-6; 1d, 135285-63-1.

(20) The reasoning for conformation of the eight-membered ring and the equatorial alkylation of 27 can be found in ref 2.

Electron-Donating Ability of the Cyclopropyl Substituent in the Solvolyses of an α-CF_3-Substituted Secondary-Alkyl Tosylate

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Received May 10, 1991

The solvolysis rates of cyclopropyl(trifluoromethyl)carbinyl tosylate (1) have been determined in a series of aqueous alcohol, aqueous trifluoroethanol, and carboxylic acid solvents. Analysis of the rate data for % internal-return isomerization and salt effects and correlation with Y_{OTs} values indicates that 1 underwent solvolysis by the k_Δ pathway. Comparison of the relative ability [k(c-Pr)/k(Ph)] of cyclopropyl and phenyl groups to stabilize carbocation-like transition states in solvolysis reactions of the secondary systems RCH(Y)CH_3 and RCH(Y)CF_3 reveals that replacement of phenyl with cyclopropyl increases the rate in both systems by a factor of 10^2.

Introduction

The unusual electron-donating ability of the cyclopropyl group to an adjacent electron-deficient center is well-known.[1,2] In solvolysis reactions, the rate enhancements observed for a cyclopropyl substituent at the α position have been used in support of a mechanism involving neighboring-group participation by the three-membered ring.[3,4] In earlier papers from this laboratory,[5] we measured, in a wide range of solvents, the response of the cyclopropyl substituent effect to solvent ionizing power. The results clearly supported the contention that cyclopropylcarbinyl sulfonates undergo solvolysis by a k_Δ pathway. As an extension of our study of the substituent effect–solvent response relationship, we became interested

(1) For recent reviews, see: (a) de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809-826. (b) Tidwell, T. T. In *The Chemistry of The Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987; Part 1, Chapter 10.

(2) (a) Brown, H. C.; Peters, E. N. *J. Am. Chem. Soc.* **1973**, *95*, 2400-2401 and references cited therein. (b) Allen, A. D.; Gong, L.; Tidwell, T. T. *J. Am. Chem. Soc.* **1990**, *112*, 6396-6397.

(3) For a review, see: (a) Richey, H. G., Jr. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, Chapter 25. (b) Wiberg, K. B.; Hess, B. A., Jr.; Ashe, A. J., In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, Chapter 26.

(4) Roberts, D. D.; Snyder, R. C., Jr. *J. Org. Chem.* **1979**, *44*, 2860-2863 and references cited therein.

(5) (a) Roberts, D. D. *J. Org. Chem.* **1964**, *29*, 294-297. (b) Roberts, D. D.; Watson, T. M. *J. Org. Chem.* **1970**, *35*, 978-981. (c) Roberts, D. D. *J. Org. Chem.* **1970**, *35*, 4059-4062. (d) Roberts, D. D. *J. Org. Chem.* **1984**, *49*, 2521-2526.

0022-3263/91/1956-5661$02.50/0