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Direct Transformations of Ketones to γ-Unsaturated Thiols via [2,3]-Sigmatropic Rearrangement of Allyl Sulfinyl Carbanions: A Combined Experimental and Computational Study

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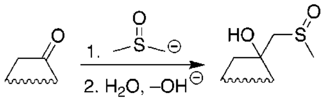
The reaction of a series of ketones with dimsylsodium in dimethyl sulfoxide resulting in the formation of γ-unsaturated thiols was studied experimentally. [2,3]-Sigmatropic rearrangements of β-unsaturated sulfinyl carbanions are involved at the key step of those transformations. DFT computations at the B3LYP/6-31+G* level indicated that such rearrangements, as well as some typical [2,3]-sigmatropic rearrangements, e.g., thermal rearrangements of allyl sulfoxides and Wittig rearrangements of sulfur ylides and lithiated allyloxy methyl anions, are concerted and moderately synchronous processes. Negative (diatropic) nucleus-independent chemical shifts (NICS) and high diamagnetic susceptibility exaltations indicate that the transition structures of these [2,3]-sigmatropic migrations are aromatic.

Introduction

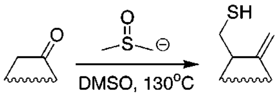
Sulfinyl carbanions play an important role in the chemistry of sulfur compounds.[1] The simplest and the most widely used example, dimsylsodium (DMSS, methyl sulfinyl carbanion), was discovered over 30 years ago by Corey.[2] This reagent is a strong base[3] that can deprotonate different CH acids, such as sulfonium, sulfoxonium[4] and phosphonium salts.[5] Besides, DMSS is rather powerful nucleophile which undergoes addition and substitution reactions with electrophilic substrates. Best known is the reaction of DMSS with carbonyl compounds to give β-hydroxy sulfoxides (Scheme 1).[2] Addition usually proceeds under mild conditions (25 °C or lower) and does not require high temperatures.

DMSS in dimethyl sulfoxide (DMSO) is considered[6] to decompose rapidly at temperatures above 80 °C; hence, reactions at higher temperatures have received little attention. However, we have demonstrated that dimethyl sulfoxonium methylide reacts with ketones in DMSO at 120 °C to give substituted 1,3-dienes with high preparative yields.[7] In this paper, we describe the unusual reaction of ketones with DMSS in DMSO at temperatures above 120 °C. We show that this transformation can be used for the preparation of homoallyl thiols. The key step, a new [2,3]-sigmatropic rearrangement of allyl sulfinyl carbanions, has been studied computationally, together with some other typical [2,3]-sigmatropic migrations used as model reactions.

Scheme 1. Addition of DMSS to Ketones



Scheme 2. γ-Unsaturated Thiol Formation in the DMSS/DMSO System



Experimental Results

One-Step Transformations of Ketones to Homoallyl Thiols in DMSS/DMSO System. The interaction of DMSS with a number of aliphatic, cyclic, and cage ketones (Table 1) in DMSO in the 125−130 °C temperature range resulted in the formation of the corresponding γ-unsaturated thiols (Scheme 2).[8]

The best results (Table 1) were obtained for aliphatic and cyclic ketones. Relatively low yields of compounds **16**−**18** can be attributed to the steric factors. In the case of octanone-2 (**3**) and (1-adamantyl)acetone (**8**), the products arising from the mercaptomethylation of the methyl group are formed preferably. In summary, we have found a new preparative method for direct trans-

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[1] (a) Krief, A. *Tetrahedron* **1980**, *36*, 2531. (b) Field, L. *Synthesis* **1972**, 101. (c) Barrett, G. C. *Rodd's Chem. Carbon Compd.*, 2nd ed.; 1996; Vol. 3, Part A.

[2] (a) Corey E. J.; Chaykovsky M. *J. Am. Chem. Soc.* **1965,** *87*, 1345. (b) Corey E. J.; Mitra R. B.; Uda H. *J. Am. Chem. Soc.* **1964**, *86*, 485.

[3] (a) Becker, H.-D.; Russell, G. A. *J. Org. Chem.* **1963**, *28*, 1896. (b) Russell, G. A.; Becker, H.-D. *J. Am. Chem. Soc.* **1963**, *85*, 3406. (c) Cardenas, C. G.; Khafaji, A. N.; Osborn, C. L.; Gardner P. D. *Chem. Ind.* **1965**, 345. (d) Osborn, C. L.; Shields, T. C.; Shoulders, B. A.; Cardenas, C. G.; Gardner, P. D. *Chem. Ind.* **1965**, 766. (e) Roberts, W.; Whiting, M. C. *J. Chem. Soc.* **1965**, 1290. (f) Argabright, P. A.; Hofmann, J. E.; Schriesheim, A. *J. Org. Chem.* **1965**, *30*, 3233. (g) Russell, G. A.; Weiner S. A. *J. Org. Chem.* **1966**, *31*, 248.

[4] Claus, P. K. *Schwefel-Ylide*; Houben-Weyl, Board E11, S.1344, 1985.

[5] Johnson, A. W. *Ylides and Imines of Phosphorus*; John Wiley & Sons: New York, 1993.

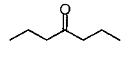
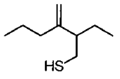
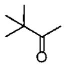
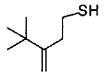
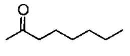
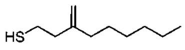
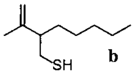
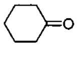
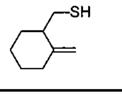
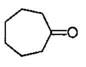
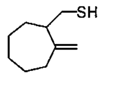
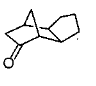
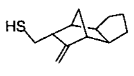
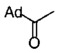
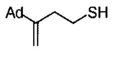
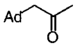
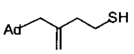
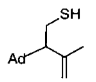
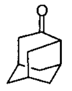
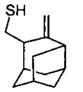
[6] Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.

[7] Yurchenko, A. G.; Kirij, A. V.; Likhotvorik, I. R.; Melnik, N. N.; Zaharzh, P.; Bzezovsky, V. V.; Kushko, A. O. *Synthesis* **1991**, *5*, 393.

[8] Kushko, A. O.; Yurchenko, A. G.; Kirij, A. V.; Likhotvorik, I. R.; Fokin, A. A. *J. Org. Chem. Russ.* **1998**, *34*, 776.

10.1021/jo991672e CCC: $19.00

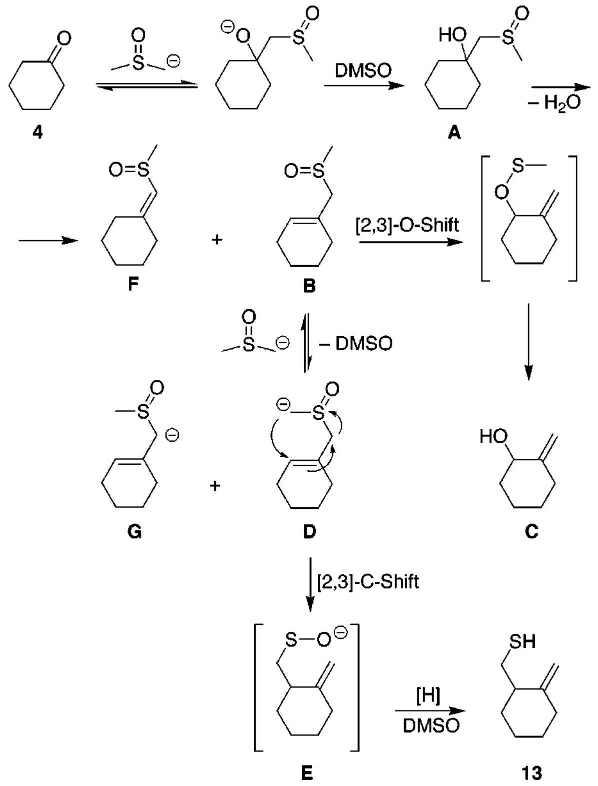
Table 1. Structure and Yields of Homoallylthiols 10–18 Obtained from the Reaction of Ketones 1–9 with Dimsyl Sodium in DMSO

Starting ketone		Structure(s) of the product(s)		Yield, %
	**1**		**10**	69
	**2**		**11**	52
	**3**	 a  b	**12**	71
	**4**		**13**	73
	**5**		**14**	69
	**6**		**15**	53
	**7**		**16**	7
	**8**	 a  b	**17**	16
	**9**		**18**	8

formation of ketones to homoallyl thiols[9] applicable to a wide range of substrates.

Scheme 3 summarizes the reaction of DMSS with cyclohexanone **4**, as a model compound. The key steps of these transformations were confirmed by a series of model experiments. The excess of the base (DMSS) was found to be decisive factor in determining the reaction course. Thus, thiol **13** is formed from **4** with a high yield (71%) only with a 3-fold DMSS excess, whereas the reaction with a 1.2–1.5-fold DMSS excess results in the formation of allylic alcohol **C** with a yield of 73%.[10] β-Hydroxysulfoxide **A**,[11] presumably formed in the first step of the reaction, dehydrates in DMSO at elevated temperatures as described previously for the tertiary alcohols.[10] If DMSS is used in a small excess or in an equimolar amount relative to ketone, the intermediate sulfoxide **B** undergoes a thermal [2,3]-O-sigmatropic rearrangement to give allylic alcohol **C**. Similar transformations were studied previously using unsaturated arylsulfoxides.[12] Unsaturated sulfoxide **B**,[13] independently prepared, also formed allylic alcohol **C** in DMSO when heated at 125–130 °C. With excess DMSS, deprotonation of **B** occurs; carbanion **D**, thus formed, undergoes [2,3]-C-sigmatropic rearrangement to the unstable sulfenic acid anion **E**. The latter forms **13** after the reduction in DMSO.[14]

Scheme 3. Transformations of Cyclohexanone 4 in the DMSS/DMSO System



Thus, one-pot formation of the desired **13** occurs due to the remarkable properties of the DMSS/DMSO system, which acts both as an nucleophile and as a base (addition to **4** and deprotonation of **B**) and also dehydrates **A** to **B**.

There also are some interesting features in the Scheme 3. The dehydration of **A** gives **B**, rather than the conjugated isomer **F**. The second question is the intermediacy of the carbanion **G**, which, unlike **D,** is stabilized both by the sulfinyl group and by the CC double bond. Even if we find that **G** is more stable than **D**, the observed rearrangement must proceed from **D** as an

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[9] (a) Miyata, O.; Shinada, T.; Ninomiya, I.; Naito, T. *Tetrahedron* **1997**, *53*, 2421. (b) Nishio, T.; Kato, M. *J. Heterocycl. Chem.* **1997**, *34*, 143. (c) Kang, J.; Kim, J. W.; Lee, J. W.; Kim, D. S.; Kim, J. E. *Bull. Korean Chem. Soc.* **1996**, *17*, 1135. (d) Haque, M. B.; Roberts, B. P. *Tetrahedron Lett.* **1996**, *37*, 9123. (e) Montenegro, E.; Echarri, R.; Claver, C.; Castillon, S.; Moyano, A.; Pericas, M. A.; Riera, A. *Tetrahedron*: *Asymmetry* **1996**, *7*, 3553.

[10] Trofimov, B. A.; Petrova, O. V.; Vasiltsov, A. M.; Mikhaleva, A. I. *Izv. AN USSR, Ser. Khim.* **1990**, 1601.

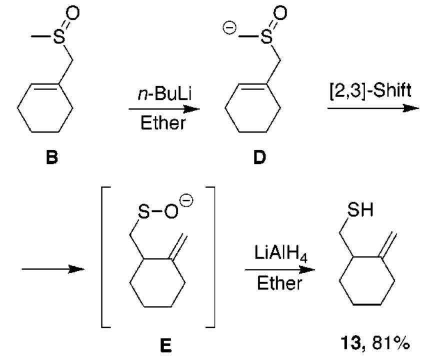
[11] The transformation of independently prepared[10] β-hydroxysulfoxide **A** under similar reaction conditions increase the yield of corresponding homoallylic thiol **13** by 5–10% on the average.

[12] (a) Hoffmann, R. W.; Goldmann, S.; Maak, N.; Gerlach, R.; Frickel, F.; Steinbach, G. *Chem. Ber.* **1980**, *113*, 819. (b) Goldmann, S.; Hoffmann, R. W.; Maak, N.; Geueke, K.-J. *Chem. Ber.* **1980**, *113*, 831. (c) Hoffmann, R. W.; Goldmann, S.; Gerlach, R.; Maak, N. *Chem. Ber.* **1980**, *113*, 845. (d) Hoffmann, R. W.; Gerlach, R.; Goldmann, S. *Chem. Ber.* **1980**, *113*, 856.

[13] Unsaturated sulfoxide **B** was obtained independently by method described elsewhere.[10] The rearrangement of **B** into allylic alcohol **C** in DMSO/KOH was also previously demonstarted.[10]

[14] (a) Hogg, P. R.; Stewart, I. *J. Chem. Soc., Perkin Trans. 2* **1974**, 436. (b) Allison, W. S. *Acc. Chem. Res.* **1976**, *9*, 293. (c) Cooper, R. D.; Jose, G. *J. Am. Chem. Soc.* **1970**, *92*, 2575. (d) Allan, R. D.; Barton, D. H. R.; Girijavallabha, M.; Sammes, P. G. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1456.

Scheme 4. [2,3]-Sigmatropic Rearrangement of Cyclohexen-1-yl DMSO in the Presence of Base



intermediate. Also, the positive counterion can play an important role in the stabilization of carbanions; the structures and the relative stabilities of these species will be studied computationally in this paper.

The [2,3]-Sigmatropic Rearrangement of B to 13 in the Presence of Base. When treated with the DMSS in DMSO, the independently prepared[13] unsaturated sulfoxide **B** also formed thiol **13** (81% yield). We extended our studies to other reacting systems, which are different from the DMSS/DMSO. With the *n*-BuLi in ether followed by the reductive workup with LiAlH$_4$, **B** was also converted with high yield to the thiol **13** (Scheme 4). The key step of this transformation includes a [2,3]-sigmatropic rearrangement of unsaturated sulfinyl carbanion **D** in the presence of base.

To gain the additional information on the mechanism, this [2,3]-sigmatropic rearrangement as well as some related [2,3]-sigmatropic migrations were studied theoretically.

Computational Methods

All calculations were performed at the density functional theory (DFT) level using Becke's three-parameter hybrid method with LYP correlational functional (B3LYP) as implemented in the Gaussian 94[15] and Gaussian 98[16] program packages. The 6-31+G* basis set was used for the geometry optimizations and for characterization of the stationary points by frequency analysis (NIMAG = 0 for minima and 1 for transition structures). The reliability of the B3LYP method was confirmed by comparison with the MP2/6-31+G* energies for key transformations. Reaction pathways along both directions from the transition structures were followed by the IRC method. The ZPVEs were scaled by a factor of 0.98 for energy corrections at the B3LYP/6-311+G**//B3LYP/6-31+G* level.

The synchronicities (S_y)[17] of sigmatropic reactions have been calculated via eq 1:[18]

$$S_y = 1 - (2n-2)^{-1}\sum_{i=1}^{n}\frac{|\delta B_i - \delta B_{\mathrm{av}}|}{\delta \mathrm{B}_{\mathrm{av}}} \qquad (1)$$

$$\delta B_i = \frac{B_i^{\mathrm{TS}} - B_i^{\mathrm{R}}}{B_i^{\mathrm{P}} - B_i^{\mathrm{R}}} \qquad \delta B_{\mathrm{av}} = n^{-1}\sum_{i=1}^{n}\delta B_i$$

where n is the number of the bonds involved in the reaction ($n = 5$ for [2,3]-sigmatropic reaction), $B_{\mathrm{i}}^{\mathrm{TS}}$, $B_{\mathrm{i}}^{\mathrm{R}}$, and $B_{\mathrm{i}}^{\mathrm{P}}$ are Wiberg bond indices[19] for the *i*-bond in the transition structure (TS), reactant (R), and product (P), respectively. According to this definition, if all bonds in the TS are broken or formed to the same extent the reaction is synchronous and $S_y = 1$. In contrast, $S_y = 0$ if at least one bond involved into the rearrangement is unchanged in the TS relative to the starting minimum. The natural bond orbital (NBO) method[20] was used for the B_{i} computations.

Nucleus-independent chemical shifts (NICS)[21] and magnetic susceptibilities χ were computed with the continuous set of gauge transformations (CSGT) method at the B3LYP/6-311+G**//B3LYP/6-31+G* level. NICS are based on the magnetic shielding computed at the centers of the rings; negative (upfield) NICS values indicate diatropic ring currents and the electron delocalization. Magnetic susceptibility exaltations Λ were estimated as the differences in the magnetic susceptibilities (χ), computed for the ground and transition states. To analyze σ and π contributions to the ring shieldings, dissected NICS were computed at the IGLO-III TZ2P level using the Pipek and Mezey localization procedure[22] as implemented in the deMon−Master program.[23]

Computational Results

Since the [2,3]-sigmatropic reactions are widely used in organic synthesis, there have been many recent computational studies.[24] A typical example, the [2,3]-

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[15] (a) Foresman, J. B.; Frisch, M. *Exploring Chemistry with Electronic Structure Mehods*; Gaussian, Inc.: Pittsburgh, 1996. (b) Density functional theory computations were carried out with the Gaussian 94 program. Gaussian 94, Revision D.2: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

[16] Gaussian 98, Revision A.5: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

[17] Moyano, A.; Pericàs, M. A.; Valentí, E. *J. Org. Chem.* **1989**, *54*, 573.

[18] (a) Lecea, B.; Arrietta, A.; Roa, G.; Ugalde, J. M.; Cossío, F. P.*J. Am. Chem. Soc.* **1994**, *116*, 9613. (b) Cossío, F. P.; Morao, I.; Jiao, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1999**, *121*, 6737.

[19] Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.

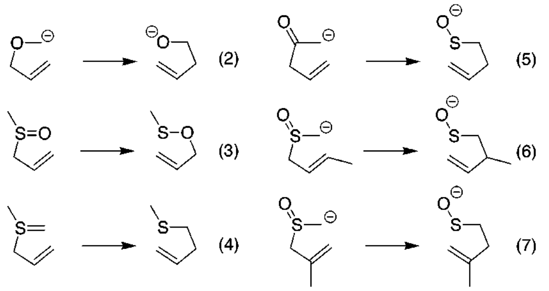
[20] Reed, A. E.; Curtiss, L. A.; Weinhold, F. J. *Chem. Rev.* **1988**, *88*, 899.

[21] (a) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2373. (b) Subramanian, G.; Schleyer, P. v. R.; Jiao, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2824. (c) Jiao, H.; Schleyer, P. v. R.; Mo, Y.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119*, 7075. (d) Schleyer, P. v. R.; Jiao, H.; van Eikema Hommes, N. J. R.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669. (e) Cyrañski, M. K.; Krygowski, T. M.; van Eikema Hommes, N. J. R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1998**, *37*, 187.

[22] Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916.

[23] (a) Malkin, V. G.; Malkina, O. L.; Eriksson, L. A.; Salaub, R. D. *J. Am. Chem. Soc.* **1994**, *116*, 5898. (b) Malkin, V. G.; Malkina, O. L.; Eriksson, L. A.; Salaub, R. D. In *Modern Density Functional Theory;* Seminario, J. M., Politzer, P., Eds.; Elsevier: Amsterdam, 1995; p 273.

Scheme 5. Selected Examples of [2,3]-Sigmatropic Reactions

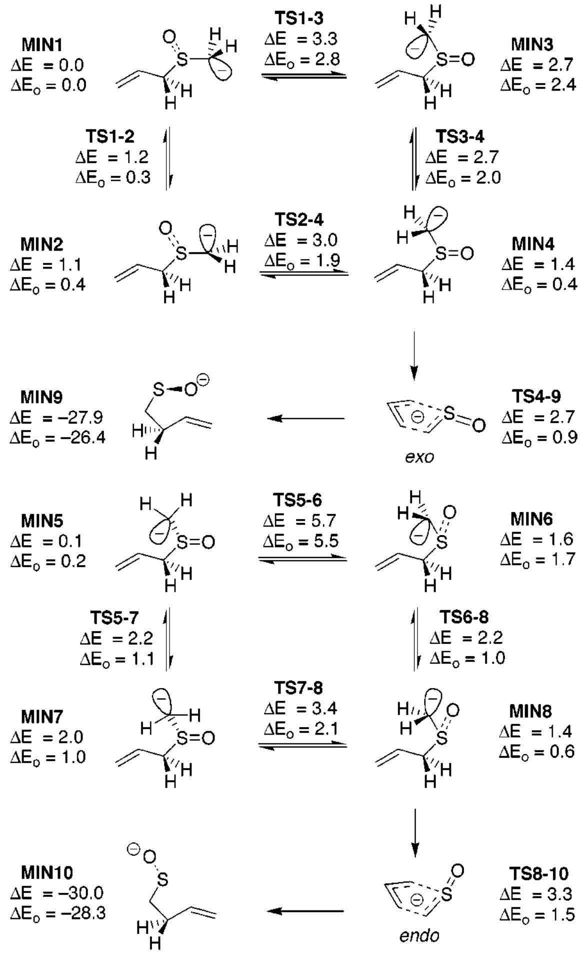


Wittig rearrangement[25] of the allyloxy methylene anion to the homoallylic alcoholate anion (Scheme 5, eq 2), is generally accepted to be a concerted sigmatropic reaction.[26] However, this is not found for the parent nonstabilized allyoxymethyl anion where the computed transition structure is extremely early and describes the carbanion inversion and the C−O bond dissociation. When the carbanion is stabilized by a ethynyl substituent the transition structure is quite different and does describe a true concerted reaction pathway (the [2,3]-migration barrier is 6.0 kcal/mol at MP2/6-31+G*).[27] Likewise, if a Li^+ counterion is included in the TS, the barrier of the concerted reaction is 16.2 kcal/mol at MP2/6-31+G.[28]

A key step of another convenient route to allylic alcohols involves the stereoselective [2,3]-sigmatropic Mislow−Evans rearrangement of allyl sulfoxides (Scheme 5, eq 3) to unstable sulfenates.[29] The experimentally observed stereoselectivities and activation energies were reproduced recently by ab initio calculations (the barriers are 26−28 kcal/mol for 1,2-dimethylallyl phenyl sulfoxide rearrangement[30] and 16 kcal/mol for allyl sulfoxide rearrangement[31] at the different MP correlated levels).

The [2,3]-Wittig rearrangement also have been extended to allylic sulfur ylides and used for the selective preparations of sulfides (Scheme 5, eq 4).[32] Computations by Jursic[33] at HF and by Wu and Houk[34] at correlated MP2 and MP3 levels with the 6-31+G* basis set predicted concerted mechanisms with the barriers about 10−16 kcal/mol for [2,3]-sigmatropic migration in sulfur allyl ylides.

Scheme 6. Relative Energies of the Conformers and [2,3]-Rearrangements of ASC (in kcal/mol from B3LYP/6-311+G//B3LYP/6-31+G* (ΔE) and B3LYP/6-311+G**//B3LYP/6-31+G* + ΔZPVE (ΔE_0) Data)**



The allyl sulfinyl carbanion (ASC) is used here as a model for computational studies of our [2,3]-sigmatropic rearrangement (Scheme 5, eq 5). The influence of alkyl substitution is studied with the crotyl sulfinyl (CSC, eq 6) and the 2-methylallyl sulfinyl carbanions (MSC, eq 7). A set of parent reactions, including the classical [2,3]-Wittig rearrangement of the allyl methylene ether anion to the homoallylic alcoholate anion (eq 2) as well as the rearrangement of the allyl methyl sulfoxide to the methylsulfenic acid allylic ether (eq 3), and the Wittig rearrangement of allylsulfonium methylide to methylhomoallyl sulfide (eq 4), also are computed in order to provide a more comprehensive mechanistic overview of [2,3]-sigmatropic migrations.

[2,3]-Sigmatropic Rearrangements in Allyl Sulfinyl Carbanions. Conformations of ASC. Interconversions of the different ASC conformers (**MIN1**−**MIN8**) are depicted in Scheme 6 (for optimized geometries and absolute energies see Figure 1 and Table 2, respectively). The most stable is anti conformer **MIN1**, where reacting centers (double bond and carbanion) are quite distant, although the differences in energies with other conformers are low (2−3 kcal/mol). Conformers can interconvert via rotation around C−S bond or carbanion inversion.[35] Rotation via **TS1**−**3**, **TS2**−**4**, **TS5**−**6**, and **TS7**−**8** (Figure 2) requires 3−5 kcal/mol and the inversion of the car-

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(24) (a) Houk, K. N.; Li, Y.; Evansek, J. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 682. (b) Wiest, O.; Montiel, D. C.; Houk, K. N. *J. Phys. Chem. A* **1997**, *101*, 8378. (c) Harmata, M.; Glaser, R.; Chen, G. S. *Tetrahedron Lett.* **1995**, *36*, 9145. (d) Okajima, T.; Fukazawa, Y. *Chem. Lett.* **1997**, 81.

(25) (a) Nakai, T.; Mikami, K. *Chem. Rev.* **1986**, *86*, 885. (b) Nakai, T.; Mikami, K. *Org. React.* **1994**, *46*, 105. (c) Marshall, J. A.; Lebreton, J. *J. Am. Chem. Soc.* **1988**, *110*, 2925.

(26) (a) Mikami, K.; Kimura, Y.; Kishi, N.; Nakai, T. *J. Org. Chem.* **1983**, *48*, 279. (b) Takanishi, T.; Nemoto, H.; Kanda, Y.; Tsuji, J.; Fukazawa, Y.; Okajima, T.; Fujise, Y. *Tetrahedron* **1987**, *43*, 5499.

(27) Mikami, K.; Uchida, T.; Hirano, T.; Wu, Y.-D.; Houk, K. N. *Tetrahedron* **1994**, *20*, 5917.

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

(29) (a) Tang, R.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 2100. (b) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147. (c) Hartley, R. C.; Richards, I. C.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1996**, 359.

(30) Jones-Hertzog, D. K.; Jorgensen, W. L. *J. Org. Chem.* **1995**, *60*, 6682.

(31) Jursic, B. S.*THEOCHEM* **1995**, *358*, 131.

(32) (a) Kido, F.; Sinha, S. C.; Abiko, T.; Yoshikoshi, A. *Tetrahedron Lett.* **1989**, *30*, 1575. (b) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 563.

(33) Jursic, B. S. *THEOCHEM* **1995**, *339*, 161.

(34) Wu, Y.-D.; Houk, K. N. *J. Org. Chem.* **1991**, *56*, 5657.

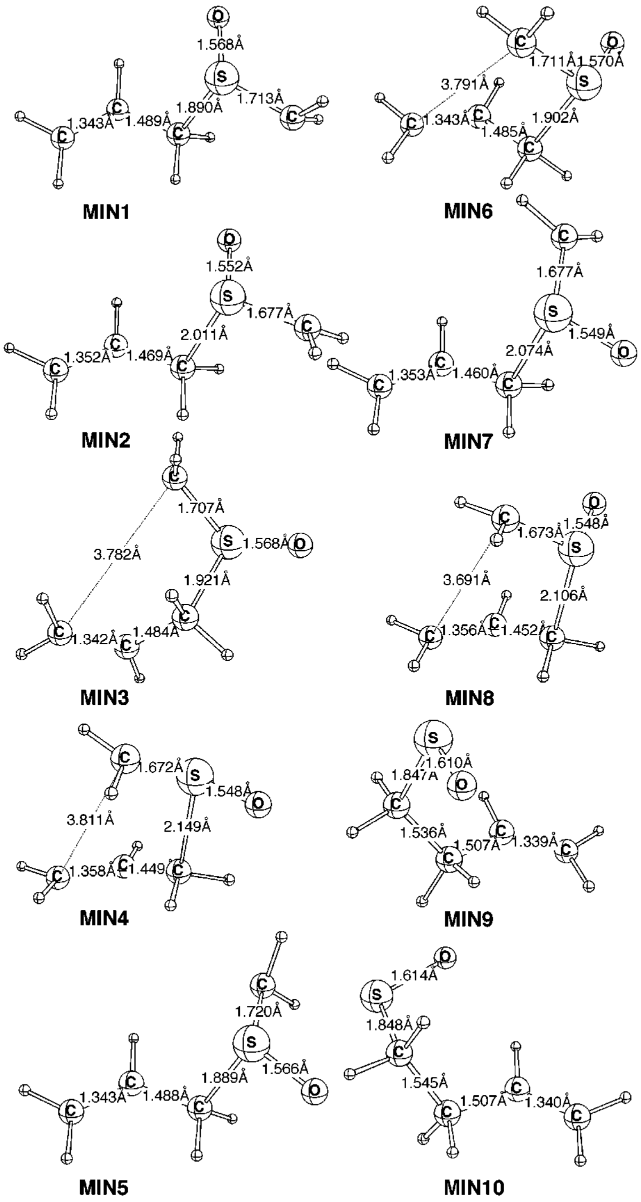

Figure 1. B3LYP/6-31+G*-optimized geometries of ASC minima.

banions via **TS1−2**, **TS3−4**, **TS5−7**, and **TS6−8** (Figure 2) less than 1.0 kcal/mol.

The C−S bond distances depend strongly on the conformations of the carbanion moieties. Due to the considerable hyperconjugative interactions, the C−S bonds are elongated substantially (2.01−2.15 Å, Figure 1) in anti-periplanar conformations of **MIN2**, **MIN4**, **MIN7**, and **MIN8**, vs 1.89−1.92 Å in syn-periplanar forms, **MIN1**, **MIN3**, **MIN5**, and **MIN6**. The proximate minima **MIN3** and **MIN4** considered as starting structures for exo-[2,3]-sigmatropic migrations in ASC; direct endo-migrations are possible only from **MIN6** or **MIN8**.

[2,3]-Sigmatropic Shifts in ASC. The [2,3]-sigmatropic rearrangements of the ASC to conformeric allyl sulfinyl anions (**MIN9** and **MIN10**, Scheme 6) are 25−30 kcal/mol exothermic (at B3LYP/6-311+G**//B3LYP/6-31+G* and at MP2/6-31+G*). Both exo (**TS4−9**) and endo (**TS8−10**) transition structures were located (Figure 2); the IRC procedure indicated that both TSs are connected with reactants in the antiperiplanar conformations of the carbanions (**MIN4** and **MIN8**).

Sigmatropic migrations with the inversion of the carbanions and rotation around the C−S bonds proceed with the formation of C−C and the breaking of C−S bonds; in the TSs both of these bond distances are 2.7−2.8 Å (Figure 2). The barriers of[2,3]-sigmatropic shifts in ASC are extremely low: 0.5 kcal/mol in **MIN4** and 0.9 kcal/mol in **MIN8**.[36] The geometries of the allylic moieties in the TSs are distorted relative to the free C_{2v} allyl anion: the deviations of the CH_2 groups from the CCC plane are 10−15°and the CCC fragment is compressed relative to the free allyl anion[37] (126° vs 133°). The negative charge is delocalized strongly in these TSs: only about 0.5e of the total is located on the allylic moieties. The molecular fragments in the ASC transition structures are strongly bound: the dissociation energies to free $H_2C{=}SO$ and the allyl anion are high (24.4 kcal/mol for **TS4−9** and 23.8 kcal/mol for **TS8−10**).

A more realistic picture of the [2,3]-sigmatropic rearrangement in sulfinyl carbanions, includes the Li^+ counterion in the ASC rearrangement (Scheme 7).

In the presence of the Li^+, the reaction is still exothermic (−22.6 and −21.1 kcal/mol) but the barriers increase (23.0 and 22.3 kcal/mol) relative to free ASC (see Scheme 6). The geometries of the TSs also change significantly: partially formed/broken bonds are much shorter (Figure 2) when Li^+ is included (from 2.4 to 2.5 Å vs 2.7 to 2.8 Å for free ACS rearrangement).[38] The molecular fragments in the TSs are more tightly bound, i.e., B_{23} and B_{15} values (see Table 3) increases (the ASC transition structures are described in more detail below).

[2,3]-Sigmatropic Shifts in Methyl-Substituted ASC. The [2,3]-sigmatropic shifts in CSC (**MIN11** and **MIN13**) and MSC (**MIN15** and **MIN17**), both of which have anti-periplanar conformations of the carbanion moieties, are shown in Scheme 8; the optimized geometries are depicted in Figure 3. The influence of methyl substitution on the barriers of exo-migrations via **TS11−12** (1.0 kcal/mol) and **TS15−16** (1.2 kcal/mol) is small, and the relative barriers are similar to the unsubstituted ASC. The methyl substituents influence the geometries, but not the relative energies of the TSs (Figure 3).

Computations on the CSC and MSC rearrangements clearly indicate that alkyl substitution generally has only a small influence on the [2,3]-sigmatropic migrations in allyl sulfinyl carbanions.

[2,3]-Sigmatropic Migrations in the Cyclohexen-1-yl Methyl Sulfinyl Carbanion. The experimental results on the rearrangement of unsaturated sulfoxide **B** (Scheme 2) were verified computationally. The dehydration of the alcohol **A** (Scheme 2) gives the endocyclic olefin **B** (Scheme 2 and eq 8) rather than the terminal olefin **F** (the latter is 3.0 kcal/mol less stable at DFT, eq 8, relative energies in kcal/mol from B3LYP/6-311+G**//B3LYP/6-31+G* (ΔE) and B3LYP/6-311+G**//B3LYP/6-31+G* + ΔZPVE (ΔE_0) data). The α-deprotonation of the

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(35) Conformers can also interconvert via rotation of the allyl group, however the barriers are slightly higher (4−6 kcal/mol) than the barriers of the CH_2SO group rotation.

(36) Similar barriers (1.2 and 1.5 kcal/mol) were computed for these reactions at MP2/6-31+G* level.

(37) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, *107*, 4793.

(38) We found analogues transition structures including one explicit solvent molecule (dimethyl ether) in **TS4−9** and **TS8−10** modeling [2,3]-sigmatropic rearrangement of ASC in solution; this lowers the barriers to 21.3 and 20.5 kcal/mol, respectively.

Table 2. Computed Absolute Energies (*E*, au), Zero-Point Vibrational Energies (ZPVE, kcal/mol), and Number of the Imaginary Modes (NIMAG) for Optimized Structures

structure	*E*, B3LYP/ 6-31+G*	*E*, B3LYP/ 6-311+G**// B3LYP/6-31+G*	ZPVE (NIMAG) B3LYP/6-31+G*	structure	*E*, B3LYP/ 6-31+G*	*E*, B3LYP/ 6-311+G**// B3LYP/6-31+G*	ZPVE (NIMAG) B3LYP/6-31+G*
MIN1	629.98890	630.07636	61.77 (0)	**D**	786.04559	786.16809	119.97 (0)
MIN2	629.98674	630.07448	60.66 (0)	**E**	786.09244	786.21367	122.51 (0)
MIN3	629.98428	630.07207	61.43 (0)	**F**	786.65494	786.77518	130.47 (0)
MIN4	629.98577	630.07404	60.75 (0)	**G**	786.06412	793.73647	120.77 (0)
MIN4Li	637.54502	637.63420	64.43 (0)	**D-Li**	793.60832	793.73187	123.70 (0)
MIN5	629.98847	630.07609	61.78 (0)	**E-Li**	793.63924	793.76386	125.95 (0)
MIN6	629.98619	630.07369	61.83 (0)	**G-Li**	793.61412	793.73647	123.41 (0)
MIN7	629.98507	630.07315	60.77 (0)	**TSD-E**	786.03804	786.16211	118.85 (1)
MIN8	629.98583	630.07405	60.96 (0)	**TSD-E-Li**	793.56488	793.69008	122.65 (1)
MIN8Li	637.54546	637.63457	64.56 (0)	**TS1−2**	629.98671	630.07438	60.83 (1)
MIN9	630.03456	630.12084	63.24 (0)	**TS1−3**	629.98314	630.07096	61.56 (1)
MIN9Li	637.58284	637.67226	65.70 (0)	**TS2−4**	629.98304	630.07152	60.58 (1)
MIN10	630.03798	630.12412	63.42 (0)	**TS3−4**	629.98403	630.07193	60.91 (1)
MIN10Li	637.58064	637.66997	65.67 (0)	**TS5−6**	629.97954	630.06721	61.53 (1)
MIN11	669.30321	669.40006	78.47 (0)	**TS5−7**	629.98492	630.07286	60.67 (1)
MIN12	669.35053	669.44656	80.91 (0)	**TS6−8**	629.98497	630.07283	60.49 (1)
MIN13	669.30334	669.40064	78.72 (0)	**TS7−8**	629.98237	630.07085	60.42 (1)
MIN14	669.35248	669.44825	81.20 (0)	**TS4−9**	629.98104	630.07203	59.91 (1)
MIN15	669.30516	669.40267	78.43 (0)	**TS4−9Li**	637.50443	637.59535	63.05 (1)
MIN16	669.35352	669.44916	81.19 (0)	**TS8−10**	629.98205	630.07109	59.90 (1)
MIN17	669.30584	669.40362	78.68 (0)	**TS8−10Li**	637.50592	637.59668	63.18 (1)
MIN18	669.35403	669.44995	81.12 (0)	**TS11−12**	669.29786	669.39695	77.44 (1)
MIN19	594.63608	594.71509	84.39 (0)	**TS13−14**	669.29671	669.39585	77.50 (1)
MIN20	630.59489	630.68099	70.93 (0)	**TS15−16**	669.29985	669.39908	77.36 (1)
MIN21	239.32890	239.39373	63.69 (0)	**TS17−18**	669.29888	669.39822	77.43 (1)
MIN22	594.72583	594.80313	86.73 (0)	**TS19−22**	594.63107	594.71104	83.83 (1)
MIN23	630.60471	630.69134	71.32 (0)	**TS20−23**	630.56710	630.65461	70.19 (1)
MIN24	239.40855	239.47184	64.94 (0)	**TS21−24**	239.30462	239.37083	62.03 (1)
B	786.65870	786.77944	130.13 (0)				

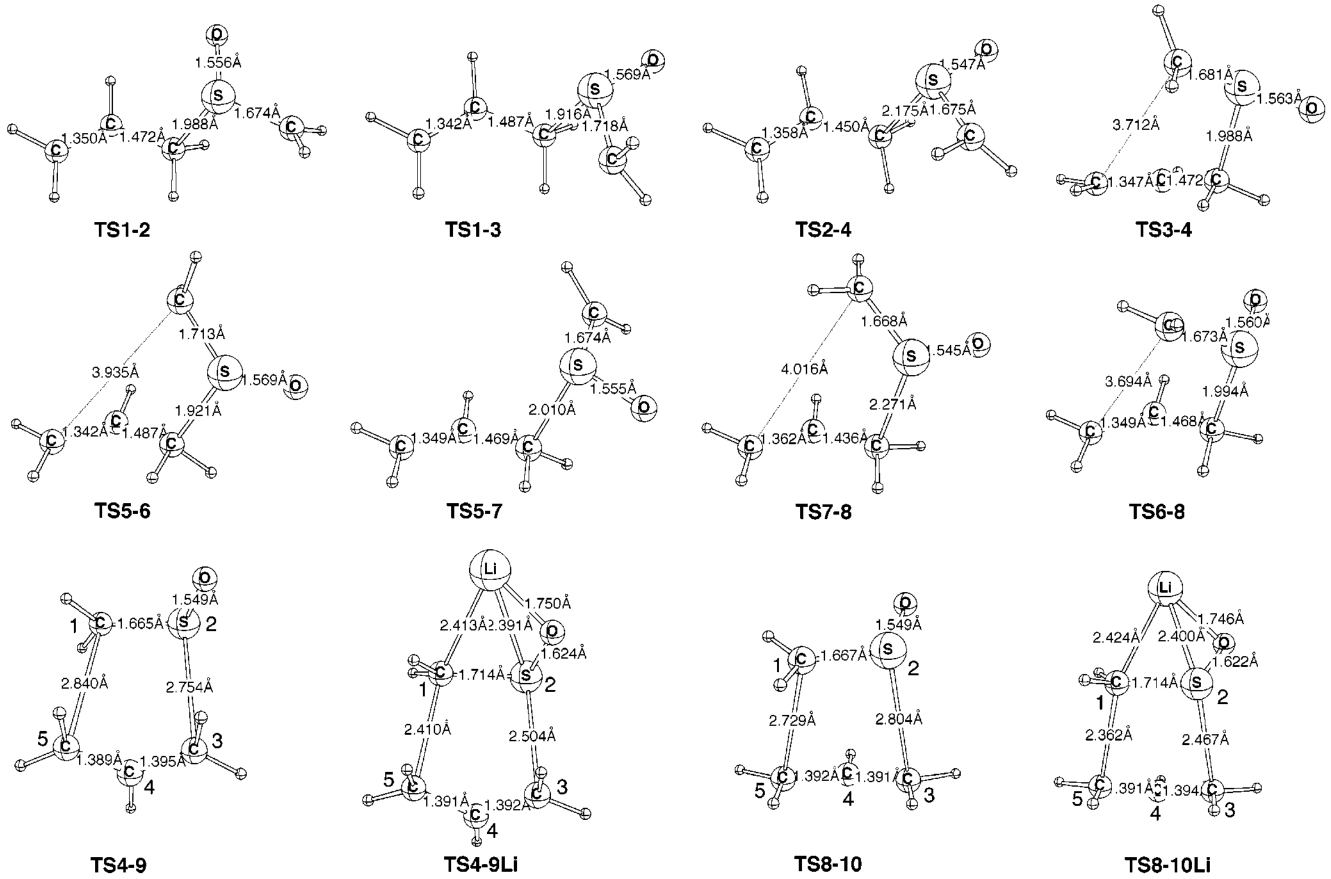

TS1-2 TS1-3 TS2-4 TS3-4
TS5-6 TS5-7 TS7-8 TS6-8
TS4-9 TS4-9Li TS8-10 TS8-10Li

Figure 2. B3LYP/6-31+G*-optimized geometries for ASC transition structures.

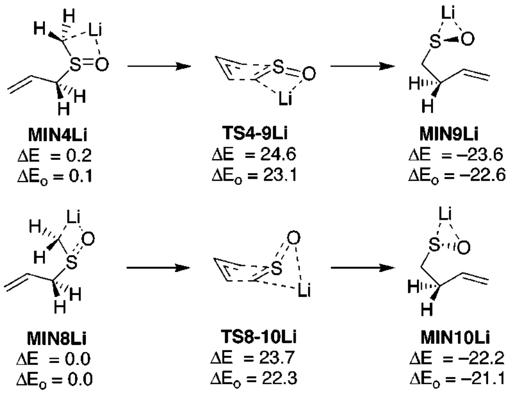
unsaturated sulfoxide **B** from the CH_2 group is more favorable than from the CH_3 group: the proximate minimum of suitable for [2,3]-sigmatropic rearrangement structure (**D**) is 9.8 kcal/mol less stable than the isomeric

Table 3. Bond Indices (B_i), Nucleus-Independent Chemical Shifts (NICS, ppm-cgs), Magnetic Susceptibility Exaltations (Λ, ppm-cgs) for TSs, and Synchronicities (S_y) Computed for Some [2,3]-Sigmatropic Reactions

structure	B_{12}[a]	B_{23}	B_{34}	B_{45}	B_{15}	δB_{av}	NICS[b] CSGT-B3LYP/6-311+G**	NICS$_t$[b] IGLO-III TZ2P	NICS$_\sigma$[c] IGLO-III TZ2P	NICS$_\pi$[c] IGLO-III TZ2P	Λ[d]	S_y
TS4−9	1.44	0.22	1.49	1.53	0.14	0.32	−14.8	−16.2	−4.1	−9.1	−11.2	0.71
TS4−9Li	1.26	0.32	1.49	1.49	0.34	0.55	−19.1	−19.9	−3.0	−12.8	−14.7	0.84
TS8−10	1.44	0.20	1.51	1.51	0.22	0.38	−16.6	−17.0	−4.1	−9.0	−8.8	0.77
TS8−10Li	1.27	0.34	1.47	1.50	0.35	0.52	−20.0	−21.1	−3.0	−13.3	−15.4	0.87
TS11−12	1.43	0.24	1.46	1.52	0.19	0.35	−15.0	−15.0	−3.1	−9.5	−9.6	0.78
TS13−14	1.42	0.23	1.47	1.50	0.21	0.36	−16.3	−16.7	−3.8	−9.9	−8.7	0.78
TS15−16	1.44	0.22	1.45	1.49	0.20	0.35	−16.3	−16.4	−3.7	−9.4	−12.2	0.77
TS17−18	1.43	0.19	1.48	1.47	0.22	0.40	−16.8	−17.1	−4.1	−9.5	−9.1	0.76
TS19−22	1.40	0.41	1.31	1.70	0.20	0.23	−16.7	−17.3	−6.5	−5.2	−11.4	0.61
TS20−23	1.16	0.37	1.48	1.47	0.33	0.85	−22.6	−23.6	−4.4	−11.2	−12.0	0.57
TS21−24	1.21	0.36	1.35	1.64	0.24	0.64	−18.7	−19.8	−2.9	−9.8	−10.0	0.59

[a] Atom numbering as in Figures 2, 3, and 5. [b] NICS total. [c] The sum of the contributions only from the $\sigma-$ and π-bonds in five-membered rings without the contributions from the other bonds of the TSs. [d] Calculated as a difference between magnetic susceptibilities (χ) of the transition structure and reactant.

Scheme 7. [2,3]-Sigmatropic Rearrangement in the Complex of the ASC with Li$^+$



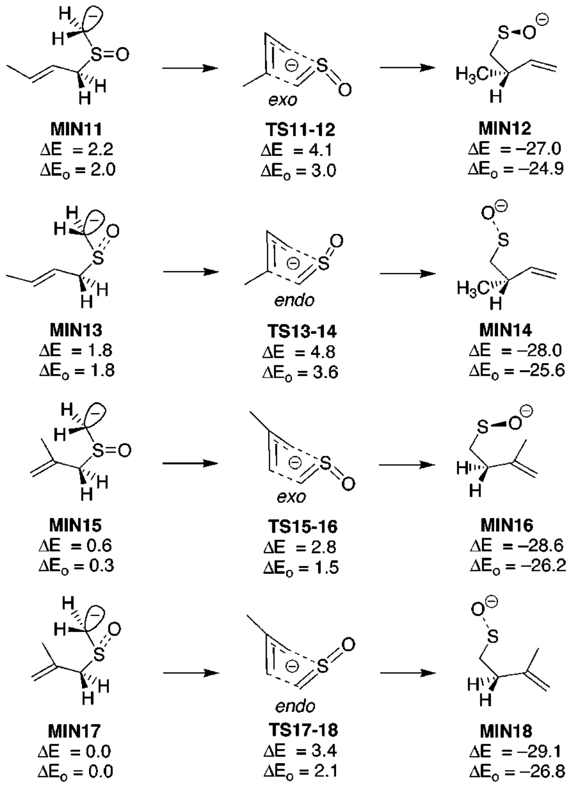
conjugated carbanion **G** (eq 9). However, when a Li$^+$ counterion is present, the relative stabilities changed dramatically: localized structure **D-Li** has nearly the same stability as conjugated carbanion **G-Li** (eq 10). Thus, computations show that the possible starting minimum for [2,3]-sigmatropic migration (**D**, Scheme 2 and eq 9) is stabilized more by the counterion than the alternative isomeric carbanion **G** and the rearrangement via **D** can proceed efficiently in *n*-BuLi/ether or DMSS/DMSO reacting systems.

The [2,3]-sigmatropic rearrangements in **D** also were computed (Scheme 9) and follow the same trends found for substituted ASCs: the reaction is exothermic (−26.1 kcal/mol), and the barrier of the rearrangement is low (2.6 kcal/mol). The geometry of five-membered ring in the **TSD-E** (Figure 4) are also similar to ASC case.

With the Li$^+$ added to cyclohexen-1-yl sulfinyl carbanion (**D-Li**) the barrier of the rearrangement increases (25.1 kcal/mol) and the geometry of the five-membered ring in the **TSD-E-Li** is similar to the **TS4−9Li** of the [2,3]-sigmatropic migration in ASC. Thus, computations on a larger systems confirmed that the substitution influent only slightly on the [2,3]-sigmatropic shifts in the allyl sulfinyl carbanions.

Comparing with Typical [2,3]-Sigmatropic Migrations. In accord with the Woodward−Hoffmann rules[39] as well as the concepts of Evans[40] and Zimmerman,[41] pericyclic reactions occur concertely via transition states that have aromatic character. The nature of the transition structures of some pericyclic reactions recently has been analyzed systematically for some cycloaddition reactions, Cope and Claisen rearrangements, and H-shifts.[42] Strongly exalted diamagnetic susceptibilities (Λ) as well as high negative NICS values were shown to be associated with the aromaticity of the transition struc-

Scheme 8. [2,3]-Sigmatropic Shift in Methyl-Substituted ASC (Relative Energies in kcal/mol from B3LYP/6-311+G//B3LYP/6-31+G* (ΔE) and B3LYP/6-311+G**//B3LYP/6-31+G* + ΔZPVE (ΔE_0) Data)**



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(39) Woodward, R. B.; Hoffmann, R. *The Conservation of the Orbital Symmetry*; Verlag Chemie: Weinheim, 1970.

(40) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1938**, *34*, 11.

(41) Zimmerman, H. *Acc. Chem. Res.* **1971**, *4*, 272.

(42) (a) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1763. (b) Jiao, H.; Schleyer, P. v. R. *J. Chem. Soc., Perkin Trans.* **1994**, 407. (c) Herges, R.; Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1376. (d) Jiao, H. Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *34*, 334. (e) Jiao, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1995**, *117*, 11529. (f) Jiao, H.; Schleyer, P. v. R. *J. Phys. Org. Chem.* **1998**, *11*, 655.

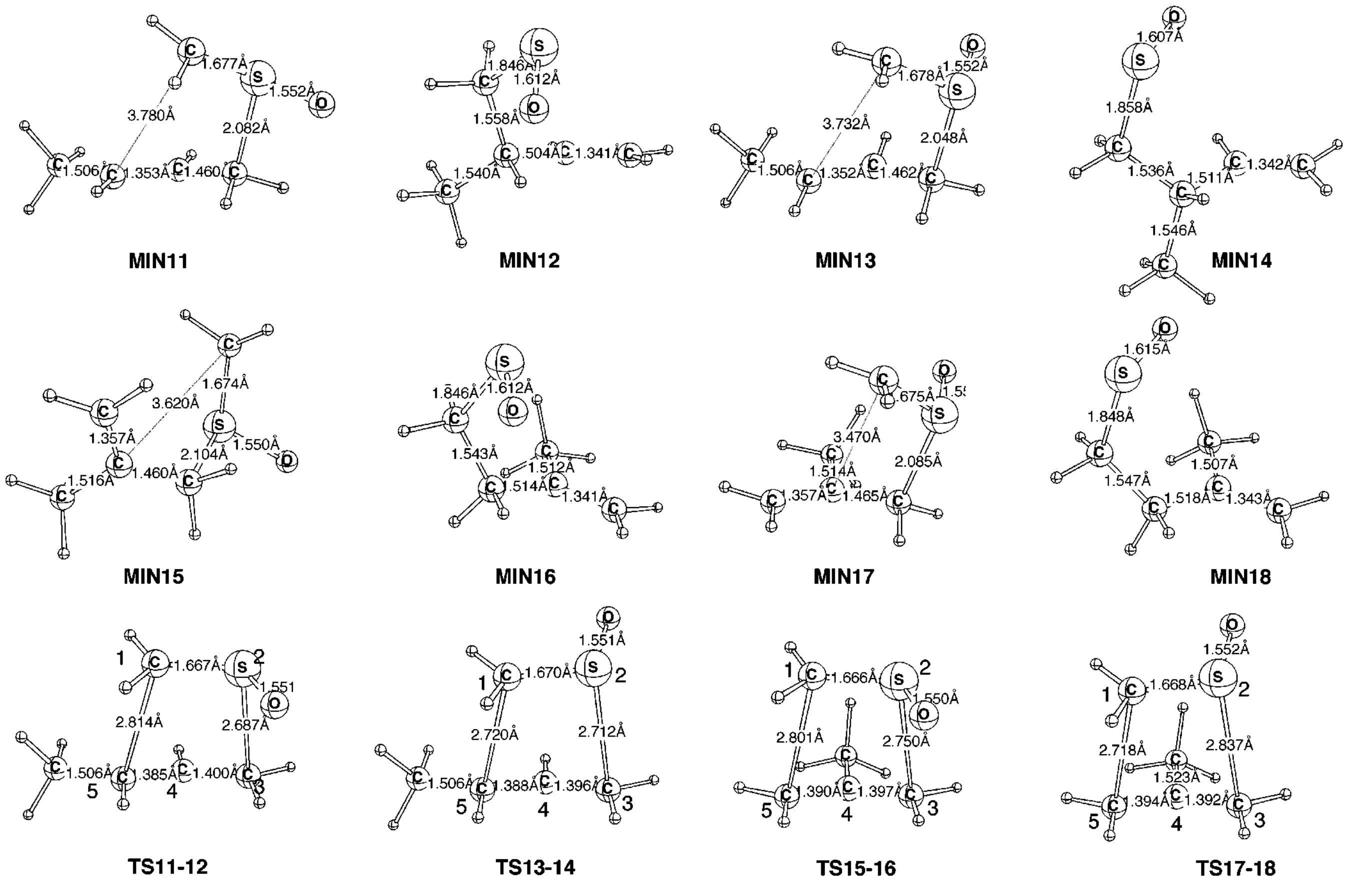
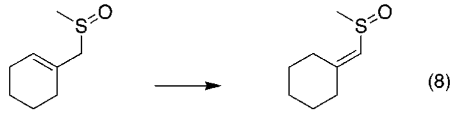
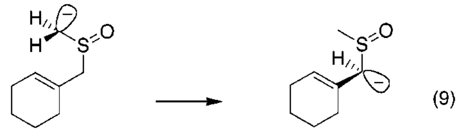


Figure 3. B3LYP/6-31+G*-optimized geometries for methyl-substituted ASC.



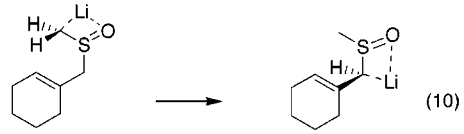
B $\Delta E = 0.0$ $\Delta E_0 = 0.0$

F $\Delta E = 2.7$ $\Delta E_0 = 3.0$



D $\Delta E = 0.0$ $\Delta E_0 = 0.0$

G $\Delta E = -10.6$ $\Delta E_0 = -9.8$



D-Li $\Delta E = 0.0$ $\Delta E_0 = 0.0$

G-Li $\Delta E = -2.9$ $\Delta E_0 = -3.1$

tures of pericyclic reactions. In these paper, we will demonstrate that magnetic properties also are helpful in understanding the nature of the transition structures of [2,3]-sigmatropic rearrangements. In addition to the representative examples of ASCs rearrangements, some typical [2,3]-sigmatropic migrations were computed (Scheme 10; for optimized geometries see Figure 5) in order to find out if there are similar trends in the mechanisms of these transformations.

The [2,3]-sigmatropic migrations in allyl sulfonium methylide (**MIN19**) to methyl homoallyl sulfide (**MIN22**) is more exothermic (−52.9 kcal/mol) than the allyl methyl sulfoxide (**MIN20**) rearrangement (6.1 kcal/mol) to allyl methyl sulfenate (**MIN23**). As expected from Hammond postulate,[43] the first highly exothermic reaction is characterized by an earlier **TS19−22** with only a slightly elongated partially broken CS bond (2.34 Å, Figure 5); the reaction barrier is only 2.0 kcal/mol. In contrast, the barrier of sulfoxide rearrangement in **MIN20** is higher (15.8 kcal/mol), and the CS bond distance in **TS20−23** is longer (2.52 Å). As found previously,[28] the transition structure of [2,3]-sigmatropic migration in the allyloxy methyl anion could be located only if Li^+ counterion is involved (from **MIN21** via **TS21−24**); this reaction is 47.8 kcal/mol exothermic and has a barrier 13.1 kcal/mol at DFT (16.2 kcal/mol at MP2/6-31G[28]). IRC procedures applied to these TSs indicated the concerted character of sigmatropic migrations.

The TS geometries for model [2,3]-sigmatropic migrations are quite different (Figures 2, 3, and 5). The C−C bond distances in the allylic moieties of **TS4−9, TS8−10**, **TS11−12, TS13−14, TS15−16, TS17−18,** and **TS20−23** are equalized (1.39−1.40 Å), but the values for **TS19−22** and **TS21−24** differ considerably. The same differences have found for the "long" bonds, which are formed/broken in the course of the rearrangement.

Despite such pronounced geometrical differences, *all* TSs of [2,3]-sigmatropic migrations computed in this paper have strong cyclic electron delocalization. This

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[43] Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

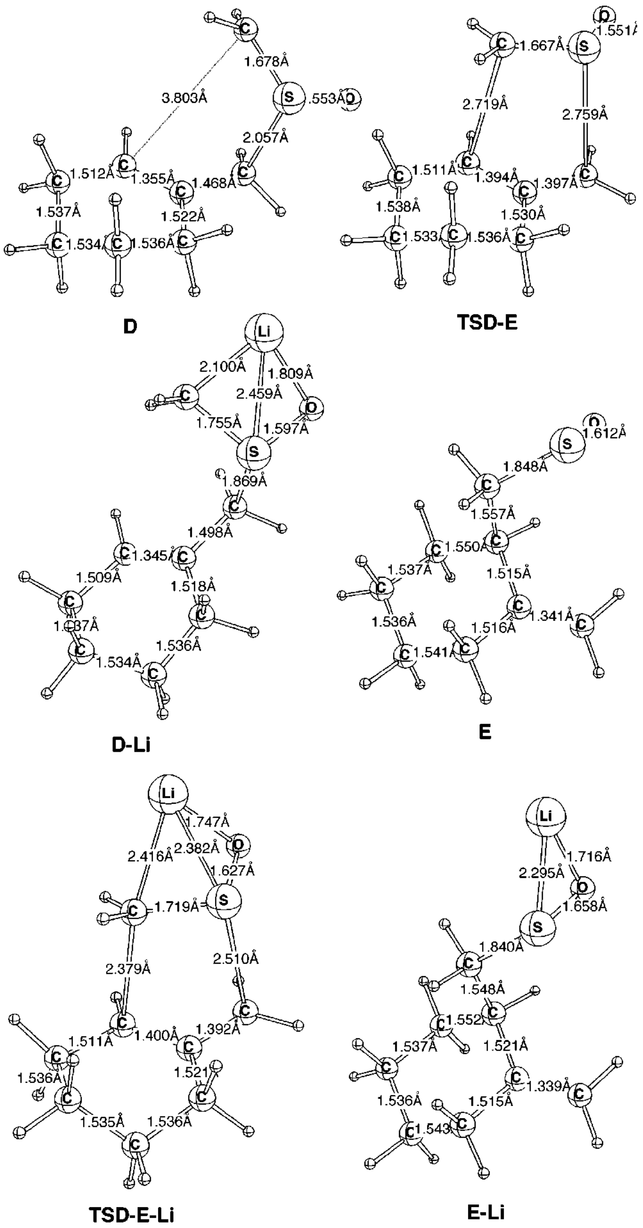
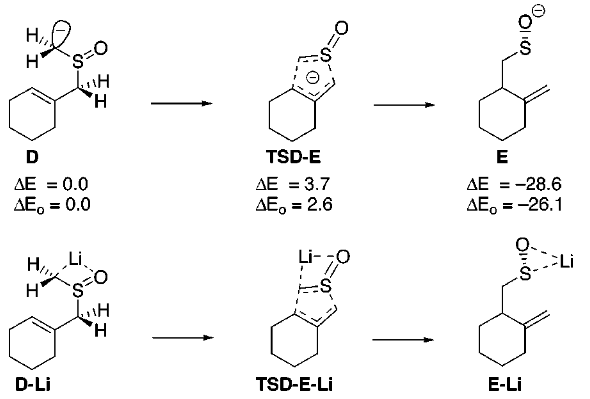
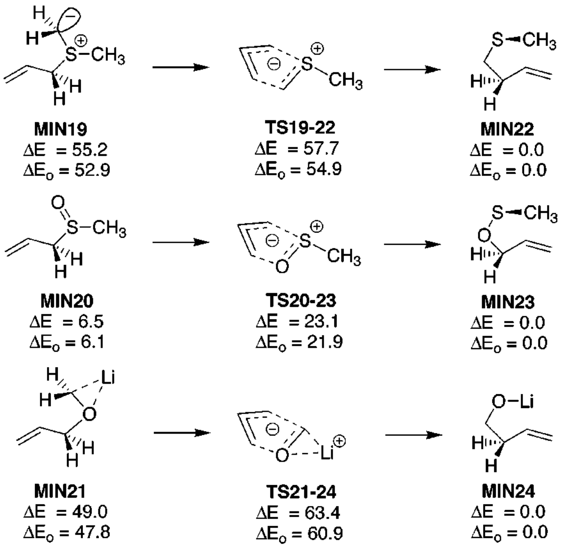


Figure 4. B3LYP/6-31+G* geometries for [2,3]-sigmatropic migrations in cyclohexen-1-yl methyl sulfinyl carbanions.

Scheme 9



Scheme 10



could be verified easily from the magnetic properties,[44] which are *very* similar for all transition structures studied (Table 3). Thus, the magnetic susceptibility exaltations (Λ), calculated as a differences in the magnetic susceptibilities (χ) of the starting ground states and corresponding transition states, vary only from -9 to -15. The negative Λs indicate the aromatic character of all TSs. The magnitudes agree well with Λ's computed for five-membered aromatic transition and ground states with six delocalized electrons. For instance, $\Lambda = -8.9$ previously been computed for the C_s transition structure of the 1,5-H shift in cyclopentadiene and -17.2 for aromatic cyclopentadienyl anion $C_5H_5^-$ in D_{5h}.[44]

Recently, NICS[21] was shown to be an effective absolute probe for aromaticity, i.e., requiring no reference compounds or increment schemes. Thus, NICS simply can be applied for transition states.[42f] The NICS values, computed in the geometrical centers of five-membered rings of all TSs (Table 3), are negative (from -14.8 to -22.6 at CSGT-B3LYP/6-311+G**//B3LYP/6-31+G*). This also indicates the strong aromaticity (compare with -12.6 computed in the center of the aromatic *cyclo*-$C_5H_5^-$ in D_{5h}).[44] The NICS values computed with CSGT-B3LYP method are similar to $\mathrm{NICS_t}$ computed by IGLO-III/TZ2P.

We also employed the dissected NICS_σ and NICS_π to characterize the separate contributions of σ- and π-bonds to the ring currents in TSs.[23] Only the contributions from the five-membered ring bonds are taken into account for NICS_σ and NICS_π (Table 3). The Pipek-Mezey localization procedure[22] gives three "double" bonds (6π-electrons) in the five-membered rings of **TS4−9**, **TS8−10**, **TS11−12**, **TS13−14**, **TS15−16**, and **TS17−18** (Chart 1). The sum of the π-contributions (NICS_π) from these "double" bonds to the local shieldings in the centers of these TSs (Table 3) is nearly constant (from -9.0 to -9.9). Both **TS4−9Li** and **TS8−10Li** are strongly polarized by Li^+: only one double bond is localized in the allylic fragment and 4π-electrons are localized on the $CH_2{=}S$ moiety. Likewise, 6π-electrons are localized for **TS20−23** and **TS21−24**, but not for the *early* **TS19−22.** In the latter, the localization procedure shows a $4\pi + 2\sigma$ electron system (Chart 1). Despite the π-contribution decrease in that case ($\mathrm{NICS}_\pi = -5.2$), the $\mathrm{NICS_t}$ in the center of the **TS19−22** still remains highly negative due to the larger σ-contri-

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(44) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209.

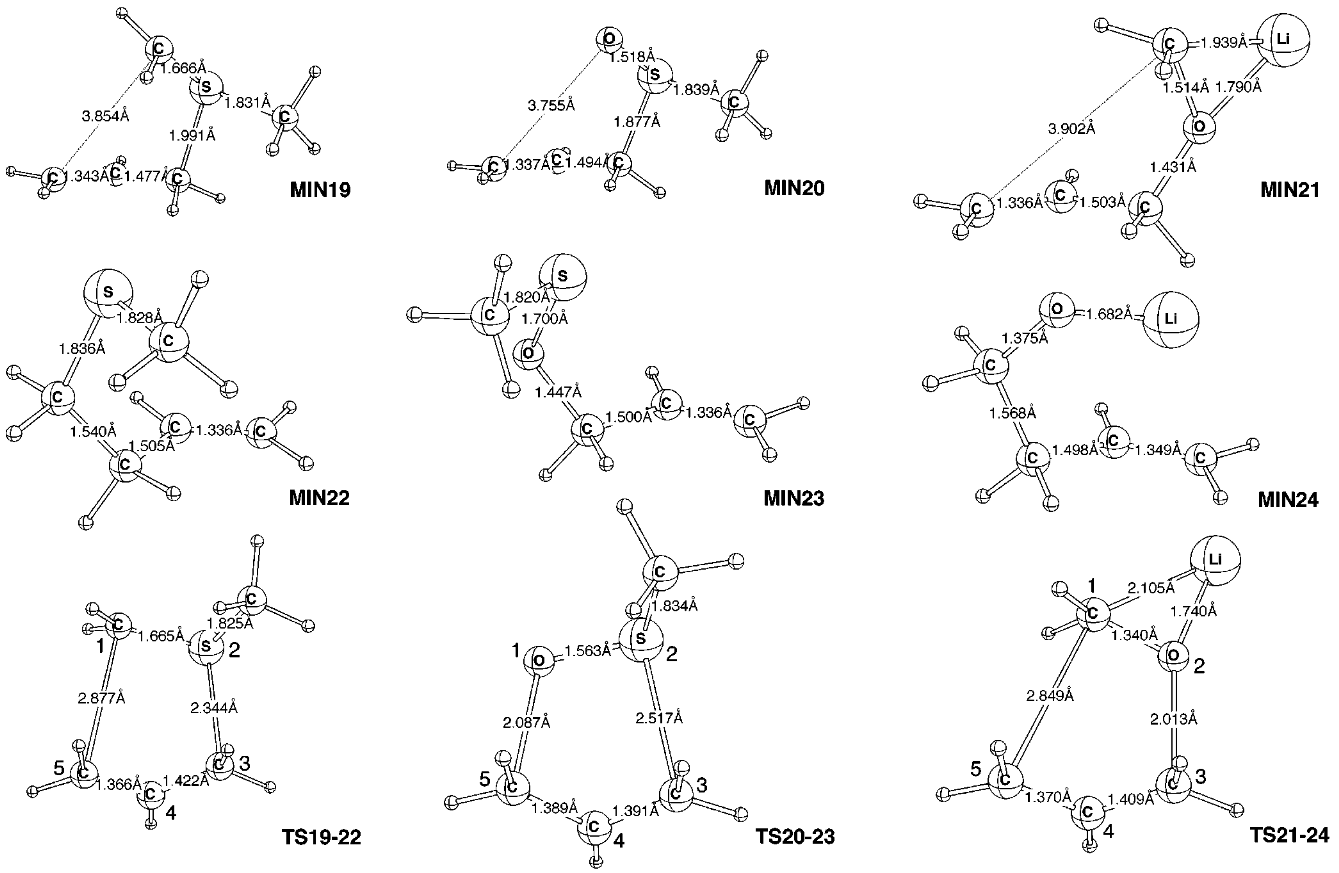
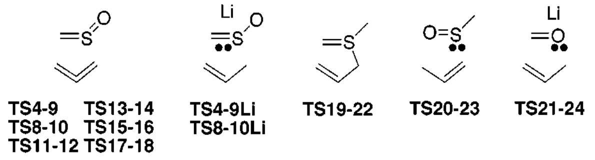


Figure 5. B3LYP/6-31+G* geometries for ground and transition sates for [2,3]-sigmatropic migrations in allyl methyl sulfur ylide (**MIN19**, **MIN22**, **TS19–22**), allyl methyl sulfoxide (**MIN20**, **MIN23**, **TS20–23**), and allyloxy methyl lithium (**MIN21**, **MIN24**, **TS21–24**).

Chart 1



bution ($NICS_\sigma = -6.5$) to the total shielding (Table 3). Thus, dissected NICSs indicate that both σ- and π-bonds can contribute to *in-plane* cyclic ring currents.

Such magnetic properties (*in-plane* ring currents effects) of transition structures also give evidence for concerted reaction mechanisms.[45] In addition, we used bond index criteria to estimate the synchronicity S_y for [2,3]-sigmatropic reactions.[18] Synchronicities were computed (Table 3) for model rearrangements in the sulfur ylides (**TS19–22**, $S_y = 0.61$), the sulfoxides (**TS20–23**, $S_y = 0.57$), and for the Wittig rearrangement (**TS21–24**, $S_y = 0.59$). These S_y values are understandable since the TSs are located far from the "halfway" point ($\delta B_{av} = 0.5$) of the reaction. For example, for the early **TS19–22**, $\delta B_{av} = 0.23$ and $S_y = 0.61$. In contrast, for the late **TS20–23**, $\delta B_{av} = 0.85$; the synchronicity also is low ($S_y = 0.57$). For the [2,3]-shifts in allyl sulfinyl carbanions via **TS4–9**, **TS8–10**, **TS11–12**, **TS13–14**, **TS15–16**, and **TS17–18** the synchronicities generally are higher (from 0.71 to 0.78). The complexation with the Li^+ even increases the synchronicity of the ACS rearrangement: $\delta B_{av} = 0.55$, $S_y = 0.84$ for **TS4–9Li** and $\delta B_{av} = 0.52$, $S_y = 0.87$ for **TS8–10Li**. This agrees with the increase in the aromatic manifestation of these TSs relative to free forms **TS4–9** and **TS8–10** (see Table 3). In general, the calculated synchronicities S_y of [2,3]-shifts in allyl sulfinyl carbanions are similar to those computed for concerted, synchronous cycloaddition reactions ($\delta B_{av} = 0.43...48$ and $S_y = 0.7...0.9$).[18]

Thus, [2,3]-sigmatropic rearrangements can be classified as concerted (based on IRC calculations and magnetic properties of the TSs[46]) pericyclic reactions with moderate synchronicity.

Our results indicate that [2,3]-sigmatropic migrations proceed through strongly cyclic electron delocalized (*in-plane* aromatic) transition structures despite varieties in the charges and the nature of the participating atoms. Since the geometries of TSs are very different, magnetic properties (NICS and magnetic susceptibilities) verify the aromaticity, whereas geometric criteria[47] may be misleading if applied to the transition structures.

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[45] (a) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Ya. *Aromaticity and Antiaromaticity. Electronic and Structural Aspects*; John Wiley and Sons: New York, 1994. (b) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669. (c) Schleyer, P v. R.; Jiao, H.; Glukhovtsev, M. N.; Chandrasekhar, J.; Kraka, E. *J. Am. Chem. Soc.* **1994**, *116*, 10129.

[46] Some 1,3-dipolar cycloaddition reactions also proceed via an aromatic transition structures (see, for example: Morao, I.; Lecea, B. Cossío, F. P. *J. Org. Chem.* **1997**, *62*, 7033).

[47] (a) Katritzky, A. R.; Karelson, M.; Sild, S.; Krygowski, T. M.; Jug, K. *J. Org. Chem.* **1998**, *63*, 5228. (b) Krygowski, T. M.; Cyrañski, M. *Adv. Mol. Struct. Res.* **1997**, *3*, 227. (c) Krygowski, T. M.; Cyrañski, M. *Tetrahedron* **1996**, *52*, 1713.

Conclusions

We have demonstrated that the reaction DMSS with a number of aliphatic, cyclic, and cage ketones resulted in the formation of γ-unsaturated thiols. Successive reactions, i.e., the addition of DMSS to ketone, dehydration to β-hydroxysulfoxide, [2,3]-sigmatropic rearrangement in allyl sulfinyl carbanion, and reduction of sulfenic acid derivatives occur as a one-pot process in DMSO. The best preparative yields (60−75%) were obtained for cyclic and branched sterically nonhindered ketones.

The [2,3]-sigmatropic rearrangements in allyl sulfinyl carbanions are highly exothermic (from −26 to −29 kcal/mol at DFT) and the barriers computed for the rearrangements in the free anions are low (0.5−3 kcal/mol). The complexation with the Li$^+$ counterion increases the barrier of the rearrangement significantly (21−23 kcal/mol) but does not change the nature of the transition structures, which bond indexes show to be even more tightly bound. Alkyl substitution has only a small influence on the barriers and the geometries of the transition structures. The [2,3]-sigmatropic migrations in allyl sulfenyl carbanions are concerted and moderately synchronous ($S_y = 0.7...0.8$) processes. Some typical [2,3]-sigmatropic migrations (in allyl sulfoxides, allyl sulfur ylides, and Wittig rearrangement) proceed via similar reaction pathways. Even though the TSs of [2,3]-sigmatropic rearrangements formed earlier or later on the reaction coordinate and are show pronounced bond length differentiation, all these TSs are aromatic based on their magnetic properties (NICS and Λ). Localized orbital calculations show that both σ- and π-bonds are contribute to the NICS values at the centers of the transition structures of [2,3]-sigmatropic migrations.

Experimental Section

General Procedure for the Preparation of Homoallylthiols from Ketones. The suspension of NaH (24 mmol) in dry DMSO (20 mL) under dry argon is stirred at 70 °C until the hydrogen evolution is completely interrupted, then the temperature is increased up to 120−130 °C. To the solution of dimsylsodium thus obtained, the ketone (**1**−**9**) (8 mmol) in 5 mL of DMSO was added. The reaction mixture was allowed to stand at this temperature for 30 min, and then it was cooled, diluted with 50 mL of cold water, and extracted with dichloromethane (3 × 30 mL). Combined extracts were washed with water and dried over sodium sulfate and solvent removed in a vacuum. The residue was purified by column chromatography on silica gel (eluant: hexane/ether 5:1). The yields of corresponding homoallylthiols (**10**-**18**) are given in Table 1.

2-Ethyl-3-propyl-but-3-ene-1-thiol (10) was prepared from heptan-4-one **(1)** as a colorless oil. ^{1}H NMR (200 MHz, δ): 0.70−2.60 (16H, m), 4.72 (1H, m), 4.8 (1H, m). ^{13}C NMR (50.3 MHz, δ): 9.99, 12.26, 19.44, 23.96, 26.48, 34.35, 49.42, 109.09, 149.00. MS *m*/*z* (rel intensity) 158 (32). Anal. Calcd for $C_9H_{18}S$: C, 68.29; H, 11.46; S, 20.25. Found: C, 68.31; H, 11.63; S, 20.01.

3-*tert*-Butyl-but-3-ene-1-thiol (11) was prepared from pinacoline **(2)** as a colorless oil. ^{1}H NMR (200 MHz, δ): 1.02 (9H, s), 2.00−2.60 (5H, m), 4.52 (1H, m), 4.80 (1H, m). ^{13}C NMR (50.3 MHz, δ): 26.30, 27.20, 29.91, 36.12, 106.71, 152.02. MS *m*/*z* (rel intensity) 144 (62). Anal. Calcd for $C_8H_{16}S$: C, 66.60; H, 11.18; S, 22.22. Found: C, 66.32; H, 10.81; S, 22.43.

3-Hexyl-but-3-ene-1-thiol (12a) and 3-Methyl-2-pentyl-but-3-ene-1-thiol (12b). The mixture of products was prepared from octan-2-one **(3)** as a colorless oil. ^{1}H NMR (200 MHz, δ): 1.20−1.50 (11H, m), 1.54 (2H, m), 1.80−3.00 (5H, m), 4.70−4.83 (2H, m) MS *m*/*z* (rel intensity) 172 (28). Anal. Calcd for $C_{10}H_{20}S$: C, 69.70; H, 11.70; S, 18.60. Found: C, 69.91; H, 11.43; S, 18.26.

(2-Methylenecyclohexyl)methanethiol (13) was prepared from cyclohexanone **(4)** as a colorless oil. ^{1}H NMR (200 MHz, δ): 1.00−2.90 (12H, m), 4.61 (1H, s), 4.76 (1H, s). ^{13}C NMR (50.3 MHz, δ): 24.33, 27.28, 28.71, 33.02, 34.87, 46.86, 107.24, 151.03. MS *m*/*z* (rel intensity) 142 (21). Anal. Calcd for $C_8H_{14}S$: C, 67.54; H, 9.92; S, 22.54. Found: C, 67.62; H, 9.81; S, 22.66.

(2-Methylenecycloheptyl)methanethiol (14) was prepared from cycloheptanone **(5)** as a colorless oil. ^{1}H NMR (200 MHz, δ): 1.20 (8H, m), 2.00−2.50 (6H, m), 4.72 (1H, m), 4.85 (1H, m). ^{13}C NMR (50.3 MHz, δ): 30.84, 31.40, 31.65, 32.23, 33.94, 34.28, 50.08, 114.08, 153.53. MS *m*/*z* (rel intensity) 156 (25). Anal. Calcd for $C_9H_{16}S$: C, 69.17; H, 10.32; S, 20.51. Found: C, 68.74; H, 10.54; S, 20.32.

8-Methylene-9-mercaptomethyltricyclo[5.2.1.0^{2,6}]-decane (15) was prepared from tricyclo[5.2.1.0^{2,6}]decane-8-one **(6)** as a colorless oil. ^{1}H NMR (200 MHz, δ): 0.8−2.8 (16H, m), 4.63 (1H, s), 4.84 (1H, s). ^{13}C NMR (50.3 MHz, δ): 25.76, 26.68, 27.62, 29.87, 30.32, 42.36, 45.65, 45.79, 48.35, 49.57, 101.58, 156.60. MS *m*/*z* (rel intensity) 194 (26). Anal. Calcd for $C_{12}H_{18}S$: C, 74.17; H, 9.33; S, 16.50. Found: C, 74.21; H, 9.27; S, 16.32.

3-Adamantan-1-yl-but-3-ene-1-thiol (16) was prepared from methyl(1-adamantyl)ketone **(7)** as a colorless oil. ^{1}H NMR (200 MHz, δ): 1.60 (12H, m), 2.36 (3H, m), 2.70 (2H, m), 2.95 (3H, m), 3.67 (1H, s), 4.80 (1H, s). ^{13}C NMR (50.3 MHz, δ): 26.76, 28.73, 35.08, 35.30, 37.43, 39.16, 106.12, 155.30. MS *m*/*z* (rel intensity) 222 (17). Anal. Calcd for $C_{14}H_{22}S$: C, 75.61; H, 9.97; S, 14.42. Found: C, 75.57; H, 10.11; S, 14.23.

2-Adamantan-1-ylmethyl-prop-2-ene-1-thiol (17a) and 2-Adamantan-1-yl-3-methyl-but-3-ene-1-thiol (17b). The mixture of products was prepared from (1-adamantyl)acetone **(8)** as a colorless oil. ^{1}H NMR (200 MHz, δ): 1.40−1.87 (17H, m), 2.35−2.75 (5H, m), 4.66 (1H, m), 4.82 (1H, m). MS *m*/*z* (rel intensity) 236 (17). Anal. Calcd for $C_{15}H_{24}S$: C, 76.21; H, 10.23; S, 13.56. Found: C, 76.33; H, 10.12; S, 13.51.

4-Methylen-5-mercaptomethylprotoadamantane (18) was prepared from protoadamantan-4-one **(9)** as a colorless oil. ^{1}H NMR (200 MHz, δ): 1.00−2.20 (16H, m), 4.71 (1H, m), 4.81 (1H, m) ^{13}C NMR (50.3 MHz, δ): 28.25, 28.67, 29.48, 33.68, 33.85, 33.00, 37.88, 40.62, 43.17, 47.86, 108.32, 152.57. MS *m*/*z* (rel intensity) 194 (23). Anal. Calcd for $C_{12}H_{18}S$: C, 76.21; H, 10.23; S, 13.56. Found: C, 74.33; H, 10.12; S, 13.51.

Rearrangement of Methyl (Cyclohexene-1-yl)methylsulfoxide (B). A. In the Absence of Base in DMSO. Sulfoxide **B** (158 mg) in 1 mL of DMSO was heated to 130 °C and allowed to stand for 30 min. The solution was cooled, diluted with 15 mL of water, and extracted with dichloromethane (3 × 5 mL). Combined extracts were washed with water, dried over sodium sulfate, and concentrated. The reaction mixture (130 mg) contained 73% of allylic alcohol **C** and 27% of unreacted sulfoxide **B** from GC/MS data.

B. In the Presence of DMSS in DMSO. To the solution of dimsylsodium (146 mg) prepared as described above the solution of sulfoxide **B** (316 mg) in 2 mL of dry DMSO was added. The reaction mixture was allowed to stand for 30 min at 130 °C, cooled, diluted with 3 mL of water, and extracted with dichloromethane (3 × 10 mL). Combined extracts are washed with water, dried over sodium sulfate, and concentrated. The reaction mixture (320 mg) contained 81% of thiol **13**, 10% of allylic alcohol **C**, and 9% of unreacted sulfoxide **B**.

C. In the Presence of *n*-BuLi in Ether. To the solution of sulfoxide **B** (316 mg) in 5 mL of dry ether 2.3 mL of 1.6 M solution of *n*-BuLi in ether was added dropwise under stirring at 0 °C. The reaction was heated to reflux for 2 h, cooled, quenched with 0.2 g of $LiAlH_4$, diluted with 3 mL of water, and extracted with ether (3 × 10 mL). Combined extracts were washed with water, dried over sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel (eluant: hexane/ether 5:1), and 230 mg (81%) of thiol **13** was obtained.

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