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Silica Gel Triggered Transformations of 3-Methylenecyclopropylmethyl Sulfonates to 3-Methylenecyclobutyl Analogues: Experimental and Computational Studies

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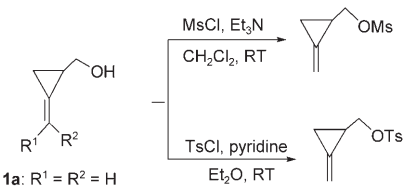
Abstract: Methylenecyclopropylcarbinols **1** treated with sulfonyl chloride and Et_3N form the sulfonated products **3** in almost quantitative yields, which can be transformed to the corresponding 3-methylenecyclobutyl sulfonates **4** with silica gel chromatography work-up. The rational explanation was proposed on the basis of computational studies.

Keywords: density functional calculations · methylenecyclopropylcarbinols · rearrangement · silica gel · synthetic methods

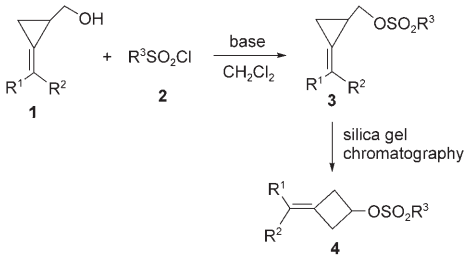
Introduction

Methylenecyclopropanes (MCPs) applied to synthetic transformations have brought about mounting interest in this area over the past decade. The attractive feature of these compounds is their surprising stability along with a high level of strain.[1,2] During our project on MCPs in our laboratory, we have found some novel Lewis acids catalyzed/promoted transformations of MCPs which are quite different from those of transition metals catalyzed reactions.[2,3] Previously, in the chemistry of 3-hydroxylmethyl substituted MCPs (methylenecyclopropylcarbinols) **1**,[4] we found a highly efficient and stereoselective reaction of **1** with iodine or diphenyl diselenide to furnish the corresponding oxabicyclo[3.1.0]hexane derivatives in good to high yields under mild conditions.[5] As a continuing project, we attempted to convert methylenecyclopropylcarbinols **1** to the corresponding sulfonic acid esters. According to previous results, methylenecyclopropylcarbinol **1a** ($R^1 = R^2 = H$) can be easily transformed to its methanesulfonate and toluene-4-sulfonate under mild conditions, which can be obtained as pure products by distillation (Scheme 1).[6]



Scheme 1. Sulfonation of methylenecyclopropylcarbinols **1a**.

As a consequence, we found that the expected esters **3** can be obtained in almost quantitative yields and in addition, their isomers, sulfonic acid 3-methylenecyclobutyl esters **4**, can be obtained from silica gel column chromatography of **3** (Scheme 2).[8] Herein, we will report the details of this silica gel triggered transformations of the rearrange-



Scheme 2. Sulfonation of methylenecyclopropylcarbinols **1**.

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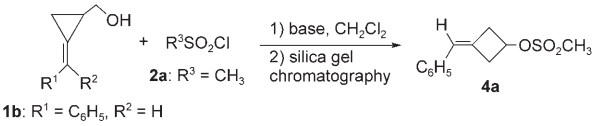
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: Spectroscopic data of all the new compounds shown in Tables S1–S3, the detailed descriptions of experimental procedures and X-ray data for compound **4a**.

ment process along with the reaction mechanism proposed on the basis of computational studies.

Results and Discussion

Experimental studies of the silica gel triggered transformations of 3-methylenecyclopropyl sulfonates to 3-methylenecyclobutyl derivatives: Initially, the reactions of methylenecyclopropylcarbinol **1b** ($R^1 = C_6H_5$, $R^2 = H$) with methanesulfonyl chloride (**2a**) in the presence of various bases were carefully examined. Typical results are shown in Table 1. To our surprise, none of the corresponding expected sulfonated products was obtained in all reactions (Table 1).

Table 1. Optimization for the formation of **4a**.[8]



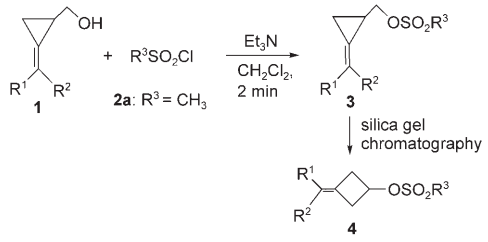
Entry	Base	Yield [%][a] **4a**
1	Et_3N	70
2	DBU	17
3	DBN	15
4	DABCO	59
5	DMAP	53
6	pyridine	11
7	Et_2NH	<10
8	iPr_2NH	60
9	iPr_2NEt	47

[a] Isolated yields by a silica gel column workup.

We found that the reactions proceeded smoothly to give the corresponding sulfonic acid 3-methylenecyclobutyl ester **4a** in moderate to good yields with the bases shown in Table 1.[8] The structure of **4a** was confirmed unambiguously by an X-ray diffraction analysis (Figure 1).[9] Triethylamine (Et_3N) is the best base for the transformation, leading to the formation of **4a** in 70% yield (Table 1, entry 1). For other bases screened, the yields varied from low to moderate or to good in almost cases (Table 1, entries 2–9). In addition, we also found that increasing amounts of methanesulfonyl chloride (**2a**) or Et_3N or both did not affect the yield of **4a** significantly.

Further studies showed that product **4** was derived from the expected sulfonated product **3** when purified by chromatography on a silica gel column. To survey the generality of the reaction, a variety of 3-methylenecyclopropylcarbinols **1** was examined under these optimal conditions with methanesulfonyl chloride (**2a**).[8] The results are summarized in Table 2. In all reactions, substrates **1** was used, both as the *E* isomers and *Z* isomers. The reactions proceeded smoothly to give the corresponding products **3** in almost quantitative yields and the purities of **3** were $>99\%$, which were determined by crude ^1H NMR spectroscopic data (Table 2) (see also Supporting Information). Products **3** also can be transformed to compounds **4** in moderate to good yields when purified by chromatography on a silica gel column (Table 2).[10] In these cases, we found that for the *Z* isomers, the yields of the rearrangement product **4** were somewhat lower compared with those of the *E* isomers (Table 2, entries 1 vs 9, 3 vs 10, 5 vs 11). For the terminally unsubstituted substrate **1a**, a similar result was obtained, leading to the formation of the corresponding product **4i** in 59% yield which was higher than we expected (Table 2, entry 12).[6]

Table 2. Reactions of methylenecyclopropylcarbinols **1** with methanesulfonyl chloride **2a** under the optimal conditions.



Entry	**1** (R^1/R^2)	Yield [%][a] **3**	Yield [%][b] **4**
1	**1b** (C_6H_5/H)	**3a**, 99	**4a**, 70
2	**1c** [3,4,5-$(MeO)_3C_6H_2$/H]	**3b**, 99	**4b**, 51
3	**1d** (4-BrC_6H_4/H)	**3c**, 99	**4c**, 65
4	**1e** (4-MeC_6H_4/H)	**3d**, 99	**4d**, 36
5	**1f** (4-MeC_6H_4/H)	**3e**, 99	**4e**, 77
6	**1g** (4-FlC_6H_4/H)	**3f**, 99	**4f**, 74
7	**1h** (3-MeC_6H_4/H)	**3g**, 99	**4g**, 54
8	**1i** (2,3-$Cl_2C_6H_3$/H)	**3h**, 99	**4h**, 40
9	**1j** (H/C_6H_5)	**3i**, 99	**4a**, 32
10	**1k** (H/4-BrC_6H_4)	**3j**, 99	**4c**, 31
11	**1l** (H/4-ClC_6H_4)	**3k**, 99	**4e**, 30
12	**1a** (H/H)	**3l**, 70	**4i**, 59

[a] Crude yields. [b] Isolated yields by silica gel column chromatography.

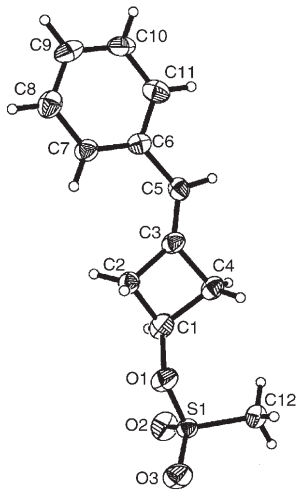
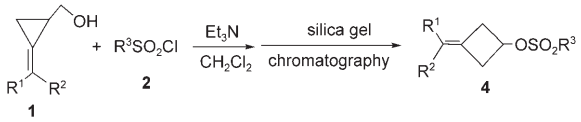


Figure 1. ORTEP drawing of **4a**.

To further examine their generality, we also carried out the transformations for substrates **1** with other sulfonyl chlorides, such as 4-toluenesulfonyl chloride (**2b**) and benze-

nesulfonyl chloride (**2c**) under these optimized conditions. The results are shown in Table 3. Again, all reactions proceeded smoothly to give the corresponding sulfonic acid 3-methylenecyclobutyl esters **4** in moderate yields (Table 3, entries 1–7).[8]

Table 3. Reactions of various **1** with **2** for the formation of **4** under the optimal conditions.[8]



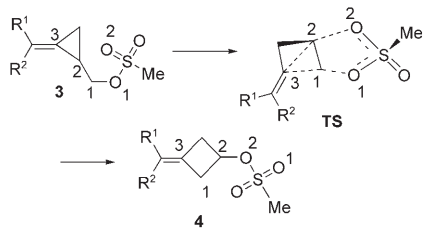
Entry	**1** (R^1/R^2)	**2** (R^3)	Yield [%][a] **4**
1	**1b** (C_6H_5/H)	**2b** (4-MeC_6H_4/H)	**4j**, 50
2	**1d** (4-BrC_6H_4/H)	**2b**	**4k**, 55
3	**1f** (4-ClC_6H_4/H)	**2b**	**4l**, 52
4	**1a** (H/H)	**2b**	**4m**, 32
5	**1b**	**2c** (C_6H_5)	**4n**, 50
6	**1d**	**2c**	**4o**, 37
	1f	**2c**	**4p**, 46

[a] Isolated yields by silica gel column chromatography.

Computational studies for the rearrangement reaction mechanism: Density functional (DFT) calculations have been performed with GAUSSIAN 03 program and the reactants, transition structures, intermediates and the products were fully optimized with B3LYP method on 6-31G* level.[11] For each structure, harmonic vibration frequency calculations were carried out and thermal corrections were made. All structures were shown to be minimum or transition state.

The mechanism for the transformations of 2-methylenecyclopropylmethyl esters **3** to 3-methylene-cyclobutyl derivatives **4** was studied on models in gas phase and on silica gel. In this rearrangement reaction, we found that silica gel acts both as a Lewis acid and a Lewis base, which reduces the energy of the transition state for the transformation and facilitate the reaction significantly.[12]

The proposed mechanism in the gas phase is shown in Scheme 3. In the rearrangement reaction, during the cleavage of C^1–O^1 bond in compound **3**, O^2 attacks C^2 to form a new C–O bond; in addition, C^1 and C^3 form a new C–C bond and the C^2–C^3 bond is broken, which finally leads to the corresponding product **4** (Scheme 3).[13]



Scheme 3.

The calculated reactant ($\mathbf{A_R}$) and transition state ($\mathbf{A_{TS}}$) for **3a** ($R^1 = R^2 = H$) in the gas phase are shown in Figure 2. For the transition structure $\mathbf{A_{TS}}$, the Mulliken charges on the OMs group are −0.689, and +0.689 on the remaining part, so $\mathbf{A_{TS}}$ is heavily polarized and charged. The charges are much larger than that of the reactant $\mathbf{A_R}$, which are −0.332 and +0.332. The calculated reaction barrier is 48.3 kcal mol^{-1}, which indicates that this reaction is impossible in the gas phase at room temperature. To take the effect of the silica gel into account, two silicic acid molecules ($H_6Si_2O_7$) are used to simulate the silica gel surface contacting with the reaction system (Figure 2, models **B**). The initial structure of $\mathbf{B_{TS1}}$ was based on $\mathbf{A_{TS}}$ because of their similar imaginary vibration mode of the carbon skeleton part, many orientations of the silicic acids were tried to find the structure with more hydrogen bonds. Then the structure was optimized with two fixed O–C bond lengths. After the optimization, the restriction of the two bond lengths was released and the structure was optimized as transition state. Two new structures were obtained by slightly changing the geometry structure of $\mathbf{B_{TS1}}$ toward the reactant and the product direction. Then, we got $\mathbf{B_R}$ and $\mathbf{B_{INT}}$ through careful small step optimization. The initial structure of $\mathbf{B_{TS2}}$ was obtained by a relaxed potential energy surface scan with $\mathbf{B_{INT}}$ along O^1–C^2 bond [O^2 is too far from C^2 (4.256 Å) in $\mathbf{B_{INT}}$]. $\mathbf{B_P}$ was obtained from $\mathbf{B_{TS2}}$ by the same way of $\mathbf{B_{INT}}$; contrarily $\mathbf{B_{TS1}}$ will lead to an intermediate $\mathbf{B_{INT}}$, which can be considered as a separated ion pair. The structure of the carbocation $\mathbf{B_{INT}}$, which is easy to rearrange to the final product over a small barrier of 1.2 kcal mol^{-1} through transition structure $\mathbf{B_{TS2}}$, is similar with the results of the former theoretical studies.[14] For models **B**, it is O^1 that attacks C^2 to form a new C–O bond, and the first step is the rate-determining step.

For the silicic acids, the hydrogen atom of the hydroxyl groups are hydrogen-bonded to the oxygen atom of the OMs groups (as a Lewis acid), while the oxygen atoms of the hydroxyl groups and the Si-O-Si linkage are hydrogen-bonded to the hydrogen atoms on the carbon skeleton (as a Lewis base). The reaction energy barrier is greatly reduced to 20.1 kcal mol^{-1}, which is consistent with the experimental results that the transformation is fast at room temperature (several minutes).

Other models with R^1/R^2 = C_6H_5/H, 4-ClC_6H_4/H and 4-MeC_6H_4/H both in the gas phase and in the silica gel (only for the first step) are also calculated and are shown in Figures 3 and 4, respectively.

The calculated activation free energies for the transformations of **3** to **4** with different R^1/R^2 groups in the gas phase and on silica gel for the first step (on B3LYP/6-31G* level) are summarized in Table 4. It is clear that silica gel can efficiently decrease the reaction energy barrier to facilitate the rearrangement step (Table 4).

Recently, hydrogen-bond-promoted reactions have attracted much attention.[15] In these reactions, the catalysts form hydrogen bonds with the substrates to serve as Lewis acids. In model **B**, the silicic acids serve as both a Lewis acid

and a Lewis base. As shown in Figure 2, compared with the reactant $\mathbf{B_R}$, the hydrogen bonds in the transition structure $\mathbf{B_{TS1}}$ become stronger as indicated by the shorter bond lengths. Moreover, many new hydrogen bonds were formed in the transition structure $\mathbf{B_{TS1}}$. In this structure, two hydroxyl groups of the lower silicic acid are found to form cooperatively arranged hydrogen-bond networks.[16] They form hydrogen bonds both with the negatively charged OMs group and the positively charged hydrogen atom on the carbon skeleton. In the chain of the two hydrogen bonds, both become stronger and the polarization is therefore enhanced.[17] All of these results clearly demonstrate that the silicic acids stabilize the transition state much better than the reactant, and subsequently lower the reaction energy barrier in large scale (28.2 kcal mol^{-1}). Likewise, the silicic acids also stabilize $\mathbf{B_{INT}}$ and $\mathbf{B_{TS2}}$ much better than $\mathbf{B_R}$, which can be easily understood since the transition structure and the intermediate are heavily polarized and charged.

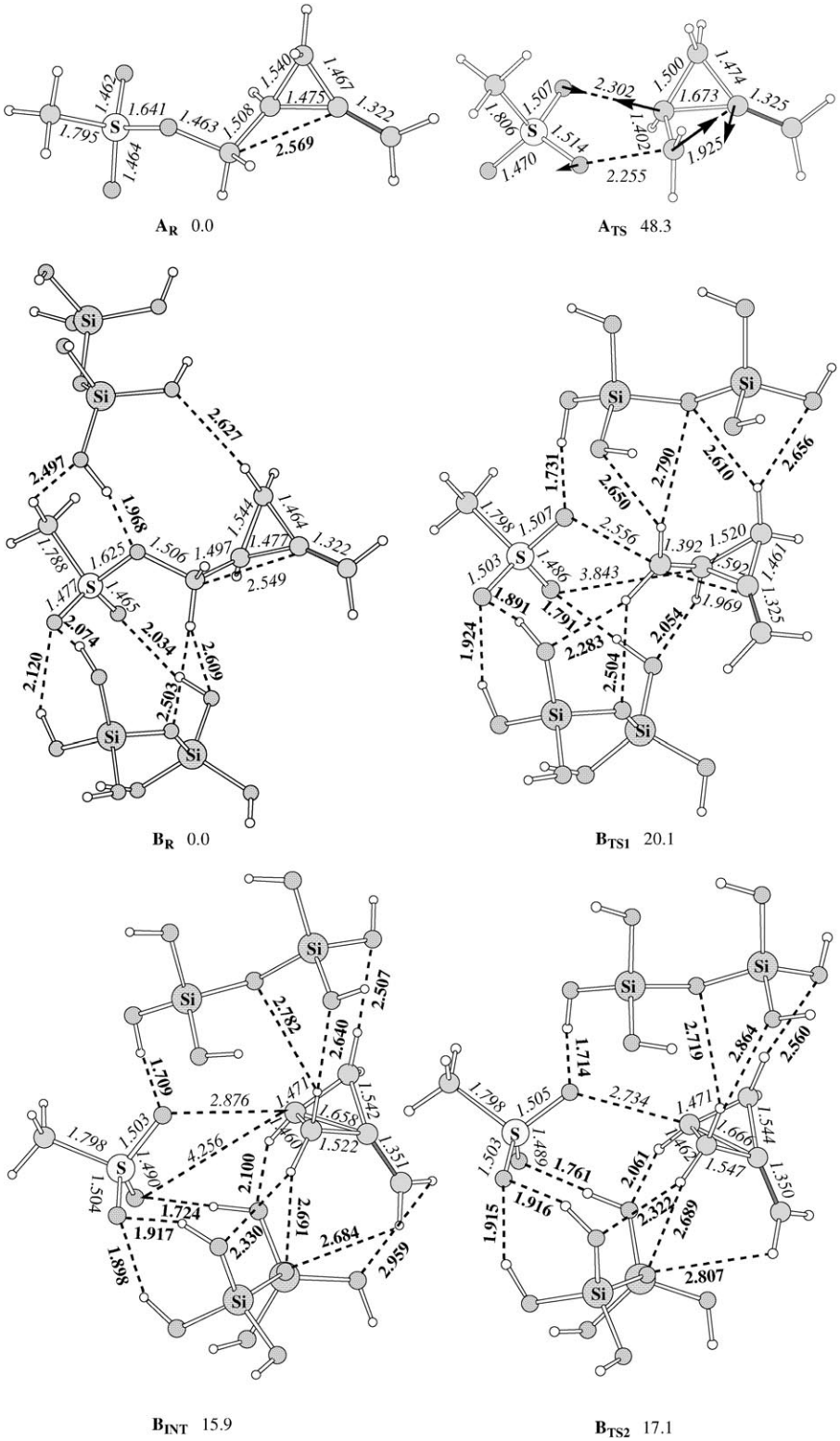


Figure 2. Optimized geometry structures on B3LYP/6-31G* level and their relative free energies (in kcal mol^{-1}, 298 K). The bold numbers are bond lengths (in angstrom) of hydrogen bonds. **A**: the gas phase model. The arrows in the transition structure are the displacement vectors of the imaginary vibration mode. **B**: the system modeled on silica gel.

To further determine that sulfonate migration indeed takes place from C1 to C2, substrate **1m** was synthesized[18] and the corresponding rearrangement was carried out under the optimal conditions. The result is shown in Scheme 4. The reaction also gave the rearranged product **4q-1** in 26% yield along with the desulfonation product **4q-2** in 36% yield, which may be derived from product **4q-1**. Two CH peaks at δ 48.8 and 76.6 ppm were found in the ^{13}C NMR and DEPT spectroscopy of **4q-1** (see Supporting Information), which are consistent with the structure. This result should be a further proof for the sulfonate migration from C1 to C2.

Conclusion

In summary, we have found that 3-methylenecyclopropylcar-

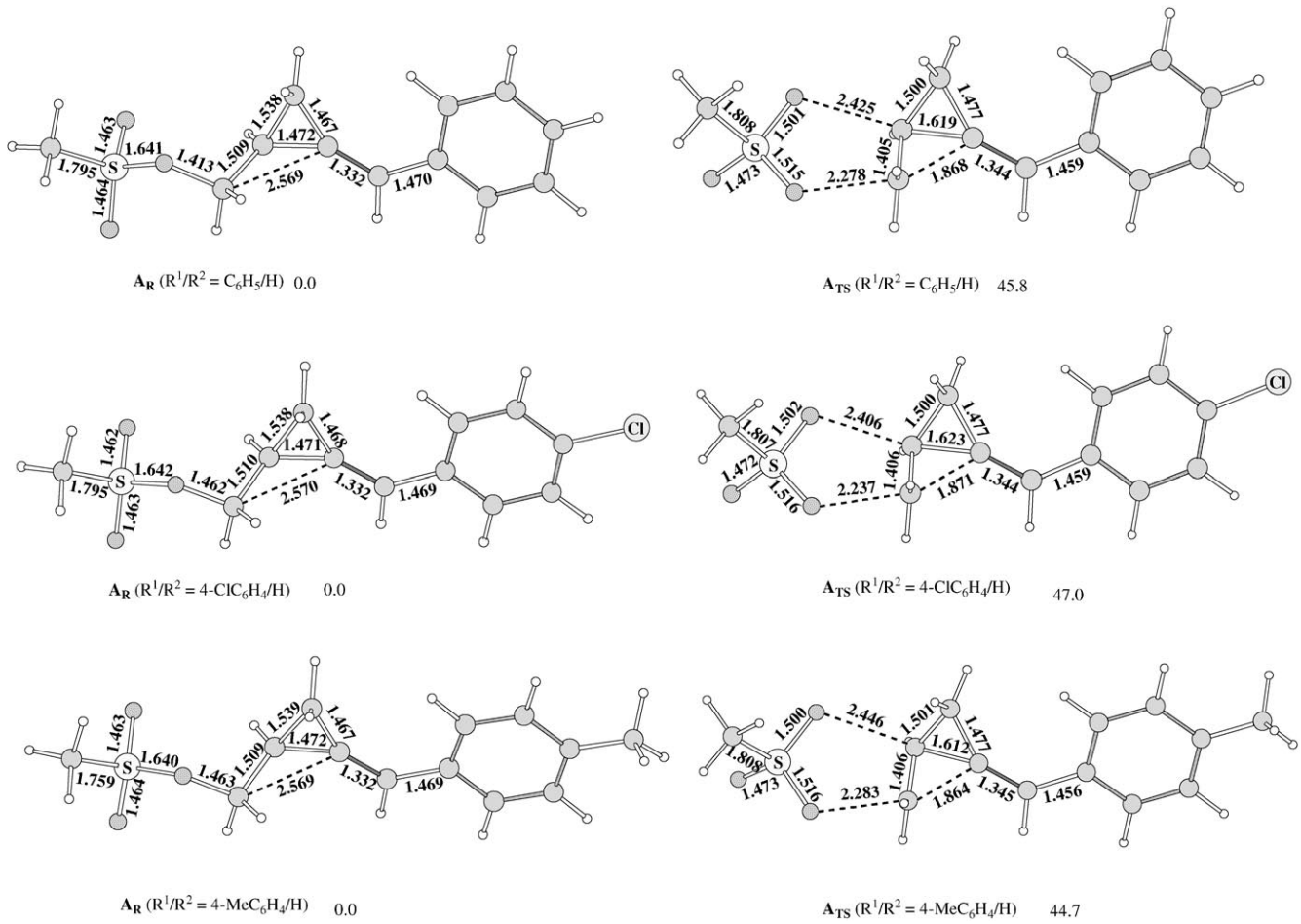
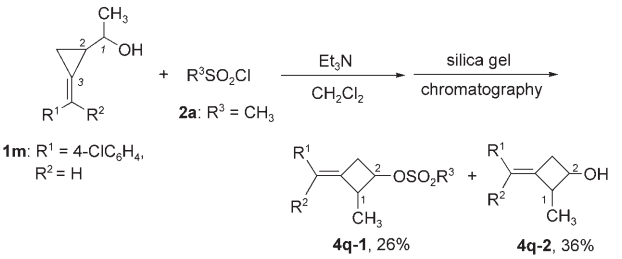


Figure 3. Optimized reactants and transition structures in gas phase for $R^1/R^2 = C_6H_5/H$, 4-ClC_6H_4/H, 4-MeC_6H_4/H and their relative free energies (in kcal mol^{-1}, 298 K).

Table 4. Calculated activation free energies of the transformation of **3** to **4** with different R^1/R^2 groups in the gas phase and in the silica gel for the first step (on B3LYP/6-31G* level).

R^1/R^2	ΔG [kal mol^{-1}] in the gas phase	on silica gel
H/H	48.3	20.1
C_6H_5/H	45.8	16.6
4-ClC_6H_4/H	47.0	17.2
4-MeC_6H_4/H	44.7	16.8



Scheme 4. Rearrangement of substrate **1m** under optimized conditions.[8]

binols **1** treated with sulfonation reagents **2** can give the expected sulfonates **3**, which can be transformed into their isomers, 3-methylenecyclobutyl sulfonates **4** when using silica gel column as work-up step. Density functional theory (DFT) studies suggest that silica gel, which serves as both a Lewis acid and a Lewis base, can stabilize the separated charges in the transition state by forming hydrogen bonds. Silica gel accelerates the reaction significantly and acts as an effective catalyst for the transformation. Furthermore, the reaction also introduces a new and simple synthetic method for methylenecyclobutyl carbinols derivatives because of its easy manipulation and simple experimental procedure. Efforts are underway to elucidate the mechanistic details and to determine its scope and limitations.

Experimental Section

General methods: Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass spectra were recorded by EI/MALDI methods, and HRMS was measured on a Finnigan MA^+ mass spectrometer. Organic solvents used were dried by standard methods when necessary. Satisfactory CHN microanalyses were obtained with a Carlo–Erba 1106 analyzer. All reactions were monitored by TLC

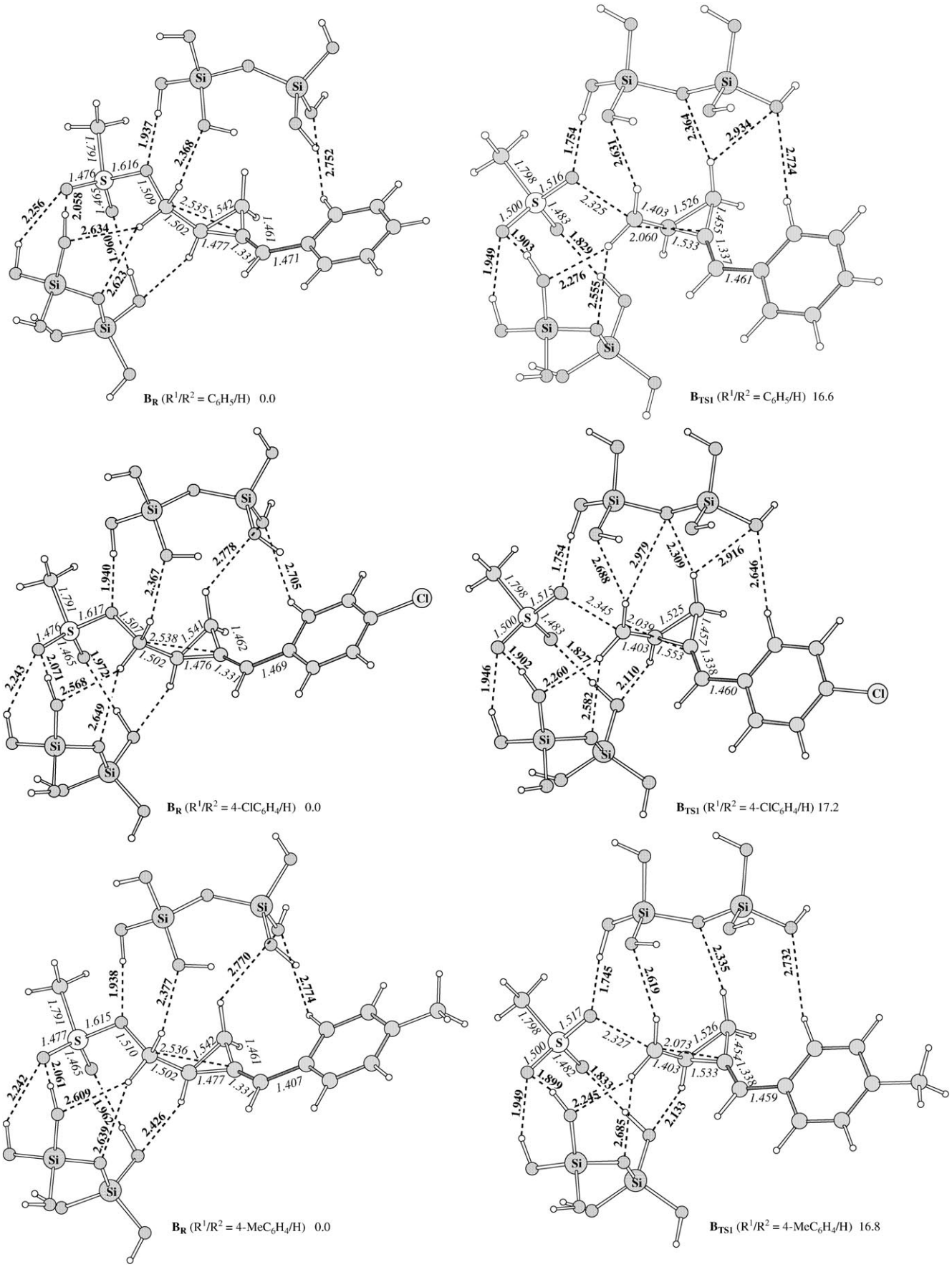


Figure 4. Optimized reactants and transition structures on silica gel for the first step for $R^1/R^2 = C_6H_5/H$, 4-ClC_6H_4/H and 4-MeC_6H_4/H and their relative free energies (in kcal mol^{-1}, 298 K).

plate with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

General reaction procedure for the formation of product 3: Compound **1b** (0.4 mmol), Et_3N (0.5 mmol) and dichloromethane (2.0 mL) were added successively into a Schlenk tube under an argon atmosphere and the reaction mixture was stirred for about 30 min at room temperature. Then compound **2a** (0.5 mmol) was added and the reaction was monitored on TLC plates. The reaction was usually completed within 2 min. The reaction was quenched with H_2O and extracted with CH_2Cl_2. The combined organic layers were washed with 1.0 M aqueous HCl solution, saturated aqueous $NaHCO_3$ solution, and dried over anhydrous $MgSO_4$. The solution was concentrated under reduced pressure. Then the crude product was analyzed with ^1H NMR spectroscopy.

General reaction procedure for the formation of product 4: Compound **1b** (0.4 mmol), Et_3N (0.5 mmol) and CH_2Cl_2 (2.0 mL) were added successively into a Schlenk tube under an argon atmosphere and the reaction mixture was stirred for about 30 min. Then compound **2a** (0.5 mmol) was added and the reaction was completed within 2 minutes. The reaction was quenched with H_2O and extracted with CH_2Cl_2. The combined organic layers were washed with 1.0 M aqueous HCl solution, saturated aqueous $NaHCO_3$ solution and dried over anhydrous $MgSO_4$. Then the reaction mixture was purified by chromatography on a silica gel column (Huanghai GF_{254} 300–400 mesh silica gel).

Crude compound **3a**: ^1H NMR ($CDCl_3$, 300 MHz, TMS): $\delta = 1.43$–1.48 (m, 1H), 1.77–1.84 (m, 1H), 2.00–2.04 (m, 1H), 3.02 (s, 3H), 4.10 (dd, $J = 8.1$, 10.5 Hz, 1H), 4.27 (dd, $J = 6.6$, 10.5 Hz, 1H), 6.87 (d, $J = 1.5$ Hz, 1H), 7.22–7.37 (m, 3H, Ar), 7.52 (d, $J = 7.8$ Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): $\delta = 10.5$, 12.2, 37.8, 72.9, 120.7, 123.2, 126.8, 127.5, 128.5, 136.9; IR (Nujol): $\tilde{\nu} = 3033$, 3029, 2939, 1781, 1744, 1598, 1494, 1454, 1355, 1174 cm^{-1}; MS (EI): m/z (%): 238 (2) [M^+].

Product **4a**: White solid; m.p. 96–98 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS): $\delta = 3.05$ (s, 3H), 3.24–3.29 (m, 2H), 3.32–3.51 (m, 2H), 5.10–5.19 (m, 1H), 6.29–6.32 (m, 1H), 7.17–7.35 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): $\delta = 38.3$, 41.3, 41.6, 70.9, 124.0, 126.7, 127.2, 128.5, 131.1, 136.8; IR (Nujol): $\tilde{\nu} = 3080$, 3037, 3020, 2970, 2955, 1325, 1953, 1446, 1334, 1169, 1111 cm^{-1}; MS (EI): m/z (%): 238 (3) [M^+], 142 (100), 141 (39), 131 (35), 115 (53), 91 (51); elemental analysis calcd (%) for $C_{12}H_{14}O_3S$: C 60.48, H 5.92; found: C 60.78, H 6.01.

Acknowledgements

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[9] Crystal data of **4a**: empirical formula: $C_{12}H_{14}O_3S$; formula weight: 238.29; crystal color, habit: colorless, prismatic; crystal system: orthorhombic; absorption correction: empirical; lattice parameters: $a = 5.6596(11)$, $b = 6.3042(12)$, $c = 33.191(6)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$; $V = 1184.2(4)$ Å^3; space group: $P2(1)2(1)2(1)$; $Z = 4$; $\rho_{calcd} = 1.337$ g cm^{-3}; $F_{000} = 504$; diffractometer: Rigaku AFC7R; residuals: R; Rw: 0.0801, 0.1698. CCDC-280669 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif/

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[13] An example for the sulfoxide (S–O bond) participating in a [2,3]-sigmatropic rearrangement towards the formation of a new carbon–heteroatom bond, see: a) D. A. Evans, G. C. Andrews, *Acc. Chem. Res.* **1974**, *7*, 147–155; for an example for the cyclopropyl group participating in a [1,3]-sigmatropic rearrangement, see: b) G. D. Andrews, J. E. Baldwin, *J. Am. Chem. Soc.* **1976**, *98*, 6705–6706, and

references therein. For an example for the S–S bond participating in a [2,3]-sigmatropic rearrangement towards the formation of a new carbon–heteroatom bond, see: c) J. K. Kim, M. L. Kline, M. C. Caserio, *J. Am. Chem. Soc.* **1978**, *100*, 6243–6245.

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[18] Substrate **1m** was synthesized from methylation of the corresponding aldehyde with methylmagnesium bromide and the diastereoisomers can be separated by silica gel column chromatography. We only use one of the diastereoisomers for the rearrangement reaction. At present stage, we did not determine the relative configuration of **1m** shown in Scheme 4. It also should be noted that only one isomer was obtained for product **4q-1** or **4q-2**, respectively.

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