Mechanistic Investigation of a Synthetic Route to Biaryls via the Sigmatropic Rearrangement of Arylsulfonium Species

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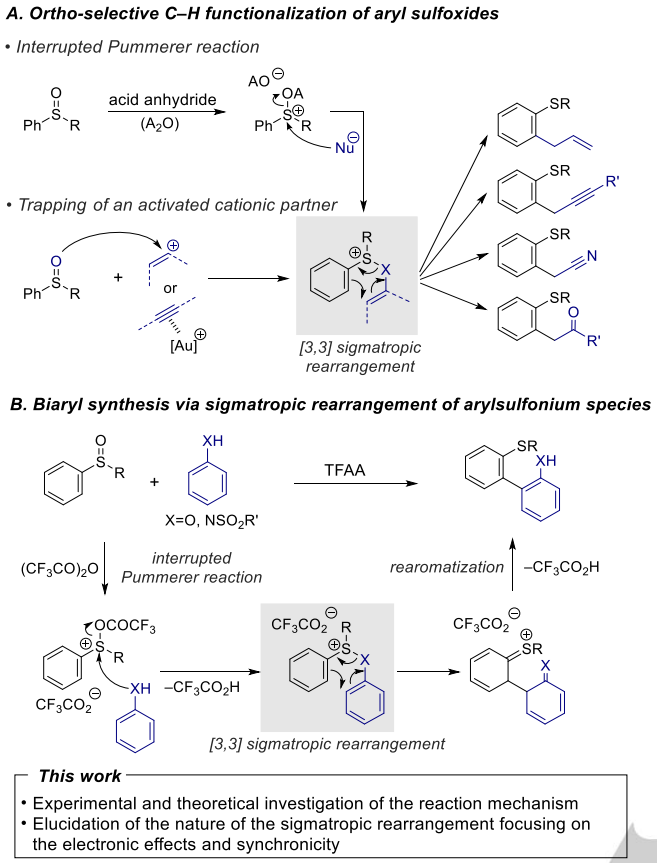
Abstract: A comprehensive mechanistic investigation was conducted on the coupling reaction of aryl sulfoxides with phenols by means of trifluoroacetic anhydride to yield biaryls. NMR experiments revealed that our previously proposed mechanism, which consists of a cascade of an interrupted Pummerer reaction and a rate-determining [3,3] sigmatropic rearrangement, is reasonable. The electronic effects of the substrates have also been evaluated to elucidate the nature of the rearrangement step. Based on experimental observations and theoretical calculations, we conclude that the rearrangement is highly asynchronous and stepwise rather than concerted when electron-rich phenols are employed for the reaction.

Introduction

In the organic synthesis toolkit, [3,3] sigmatropic rearrangements are some of the most powerful reactions for the formation of C–C bonds, given that the well-defined six-membered transition state (TS) of these reactions allows a highly regioselective formation of the C–C bonds at remote sites. In particular, charge-accelerated sigmatropic rearrangements that involve a charged atom in the rearranging skeleton have attracted a great deal of attention, both from a synthetic[1] and mechanistic perspective[2] due to the high reactivity of these substrates relative to their electronically non-biased counterparts.

Over the last decade, several [3,3] sigmatropic rearrangements that involve a positively charged sulfur atom have emerged (Scheme 1A).[3] These transformations exhibit some synthetically useful characteristics: (1) The reaction temperature is typically low (approximately ambient temperature), and (2) the precursors for the rearrangement can usually be prepared *in situ* from stable and readily available sulfoxides. Ever since those early reports on the coupling of aryl sulfoxides with alkynes,[4a] allylsilanes,[4b] and *β*-ketoesters,[4c] the *ortho*-selective C–H functionalizations of aryl sulfoxides via sigmatropic rearrangements have been investigated actively, and many variants, including propargylations[4d] and α-cyanomethylations[4e] have been established.[5]

As part of our continuous interest in the [3,3] sigmatropic rearrangement of such transient sulfonium species,[6] we have reported the synthesis of biaryls from aryl sulfoxides and phenols[7] or *N*-sulfonylanilides[8] (Scheme 1B). This reaction is thought to be initiated by the activation of the aryl sulfoxide by trifluoroacetic anhydride (TFAA), followed by the assembly with the nucleophilic coupling partner via an interrupted Pummerer reaction. A subsequent sigmatropic rearrangement and rearomatization would then furnish the desired biaryls. A similar reaction mechanism has been proposed for the reactions shown in Scheme 1A, based on experimental evidence and theoretical calculations. Recently, Maulide has reported that this kind of rearrangement is on the borderline between concerted and stepwise mechanisms.[9] However, research focusing on the nature of the charge-accelerated sigmatropic rearrangement of arylsulfonium species remains limited.



Scheme 1. *Ortho*-Selective C–H Functionalizations of Aryl Sulfoxides.

In addition, our arylation reactions can be regarded as a new variant of the benzidine rearrangement,[10] wherein hydrazobenzenes (ArNH–NHAr) are rearranged to 4,4′- or 2,2′-diaminobiaryls under acidic conditions through [5,5] or [3,3] sigmatropic rearrangements. The detailed mechanism of this classical rearrangement step has long been discussed controversially, and no generally accepted mechanism has been established so far.[11] Therefore, the investigation of the nature of the recent sulfur-based analogues is also of interest to gain a better understanding of this series of benzidine-type rearrangements.[12, 5b] Herein, we report a combined experimental and theoretical mechanistic investigation into the synthesis of biaryls via the sigmatropic rearrangement of arylsulfonium species. Initially, we attempted to observe the key precursor for the [3,3] sigmatropic rearrangement and to experimentally determine the electronic effects in order to obtain the premise for the subsequent theoretical study. The pathway of the cascade reaction was then examined computationally to validate our mechanistic hypothesis. Finally, the effects of the conformation of the intermediate and of the substituents on the nature of the rearrangement, especially its synchronicity and activation free energy, were investigated.

Results and Discussion

^{1}H NMR Study to Monitor the Reaction

We performed an *in-situ* NMR study to observe plausible reaction intermediates and verify our working hypothesis.

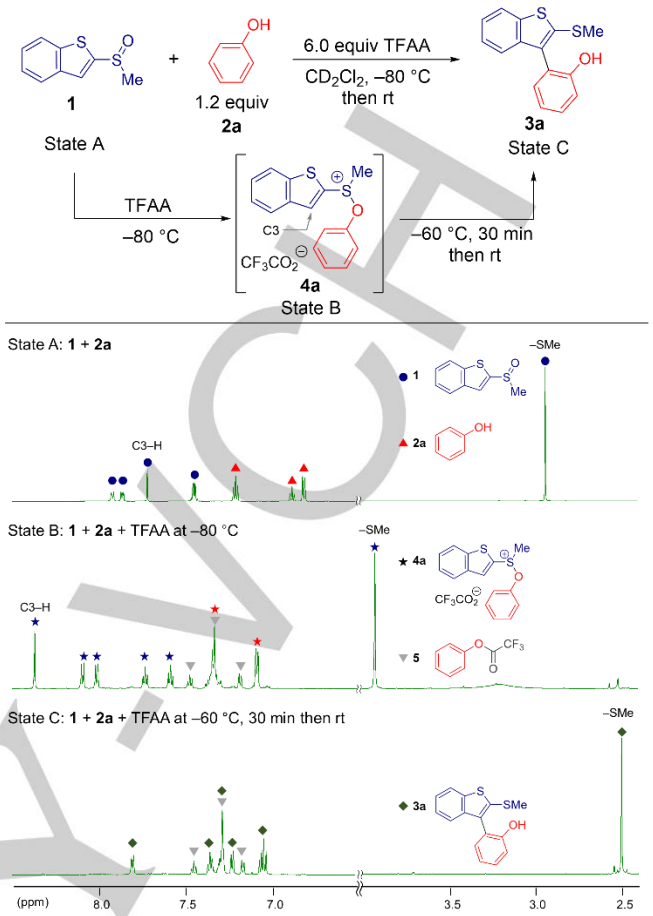


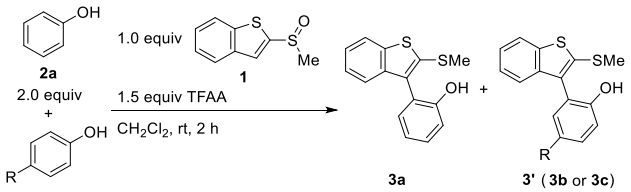
Figure 1. ^{1}H NMR study for the observation of transient intermediate **4a**.

As a model reaction, we chose the coupling reaction of 2-benzothienyl methyl sulfoxide (**1**) with phenol (**2a**) to yield **3a** (Figure 1). Treatment of a mixture of **1** and **2a** (State A) with TFAA at –80 °C in CD_2Cl_2 (State B) resulted in overall downfield shifts in the ^{1}H NMR spectrum.[13] In particular, the signals of C3–H in the benzothienyl group and the methyl group on the sulfonium center showed significant shifts, indicating the formation of the proposed sulfonium intermediate **4a**. At the same time, phenyl trifluoroacetate (**5**) was formed by competitive acylation of part of the phenol. As expected, **4a** rearranged into biaryl product **3a** within 30 min when the mixture was allowed to warm to –60 °C (State C), and accumulation of other intermediates was not detected during the rearrangement. These results suggest that the assembly of the two reaction components is quite facile, and that the rearrangement can be considered as the rate-determining step.

Substituent Effects on the Reaction

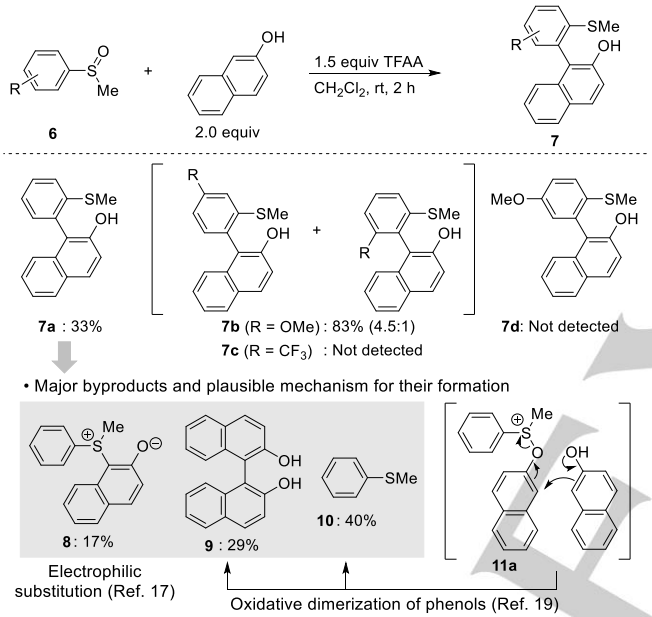
We performed competition reactions using electronically biased phenols to evaluate the electronic effects on the transformation. When phenol (**2a**) competed with *p*-cresol (**2b**; R = Me), electron-rich **2b** was preferentially converted into the coupling product **3b**. This trend was also observed in the competition between **2a** and electron-deficient *p*-(trifluoromethyl)phenol (**2c**; R = CF_3), where **3a** was obtained as the main product (65%).[14] We also tried to observe the rearrangement precursors as in Figure 1, but could not observe **4b**, probably due to its high reactivity at –80 °C, while

the conversion of **4c** was slow even at –30 °C (Table S1). These results indicate a correlation between the reaction activity of the rearrangement precursor and the yield of the desired biaryl.



Substrates	Yield (%)		ratio of
	3a	**3'**	**3'/3a**
2a + **2b** (R = Me)	36	44	1.2
2a + **2c** (R = CF_3)	65	5	0.08

Scheme 2. Substituent effects on the phenols; yields were determined by ^{1}H NMR spectroscopy.



Scheme 3. Substituent effects of the aryl sulfoxides; yields were determined by ^{1}H NMR spectroscopy.

Electron-rich aryl groups on sulfoxides often enhance their reactivity in the rearrangement step of similar reactions.[15] In our reaction system, an *m*-methoxy group significantly promoted the yield of the desired reaction product **7b** compared to that of **7a** (Scheme 3).[7a] In contrast, *m*-trifluoromethyl and *p*-methoxy-substituted sulfoxides **6c** and **6d** did not afford the desired biaryls **7c** and **7d**.[16] Low-temperature ^{1}H NMR measurements revealed an almost quantitative formation of the intermediates **11a,c-d**. However, elevation of the temperature (–30 °C or above) resulted in decomposition of these intermediates (Table S1). Using **6b**, only biaryl product **7b** was observed; **11b** was not seen, not even at –80 °C, probably due to its high reactivity. These results indicate that the success of the overall transformation depends on the competition between the rearrangement and side reactions. In the reaction with **6a**, **8**–**10** were observed as major byproducts. Zwitterion **8** would be expected as the product of the electrophilic substitution of the activated sulfoxide at the most electron-rich position of 2-naphthol.[17] BINOL (**9**) and methyl phenyl sulfide (**10**) may be formed via intermediate **11**, as was reported in the hypervalent-iodine-mediated oxidative functionalization of phenols.[18] A similar reaction mode has also been used for biaryl synthesis and the functionalization of phenols.[19]

Computational Investigation of the Pathway of the Cascade Reaction

We then carried out DFT calculations using the coupling reaction of 2-benzothienyl methyl sulfoxide (**1a**) with phenol (**2a**) as a model reaction.

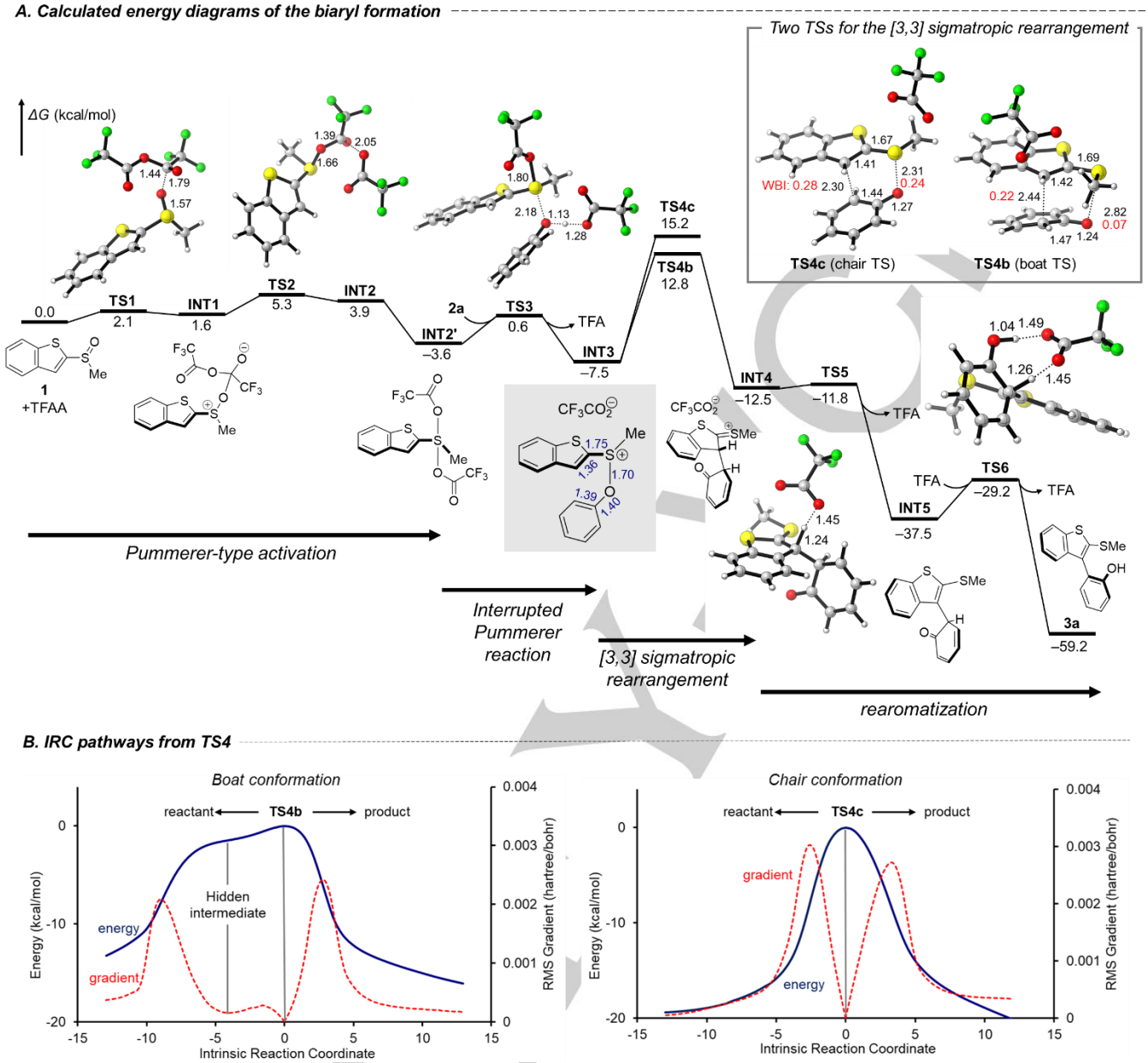


Figure 2. (A) Energy diagram for the overall reaction process; structures of the transition states (TSs) are drawn as ball-and-stick models; bond lengths are given in Angstroms (Å); (B) IRC pathways from **TS4b** and **TS4c**.

All geometry optimization and frequency calculations were performed using the M06-2X functional[20] and 6-31+G(d,p) basis set, unless noted otherwise. All structures were characterized by frequency calculations to confirm their identity as either local minima or first-order saddle points. Free energies at the optimized structures were calculated at the same level of theory at 298.15 K. The effect of the solvent (dichloromethane) on the reaction was evaluated using the solvation model based on density (SMD).[21]

The calculated energy profile is shown in Figure 2A. The reaction begins with the nucleophilic addition of the oxygen atom of **1** to TFAA to form adduct **INT1**. The subsequent elimination of the trifluoroacetate anion results in the formation of ion pair **INT2**, which recombines to give sulfurane **INT2′**. The assembly of **INT2′** with phenol (**2a**) proceeds in a concerted manner with concomitant deprotonation of **2a** by the trifluoroacetate anion to provide **INT3**. The calculation results suggest that the formation of **INT3** is thermodynamically favorable and reversible, which is consistent with the NMR studies.

The C–C-bond-forming step from **INT3** proceeds with cleavage of the S–O bond, which indicates that this step is a concerted sigmatropic rearrangement.[22] The boat-conformation TS (**TS4b**) is more favorable than the sterically less hindered chair one (**TS4c**; $\Delta\Delta G^{\ddagger}$ = 2.4 kcal/mol).[23] Interestingly, the rearrangement is also thermodynamically favorable (ΔG = –5.0 kcal/mol), even though both aromatic rings lose their aromaticity during the process. The subsequent rearomatization of the thionium moiety of **INT4** (**TS5**; $\Delta G^{\ddagger}$ = 0.7 kcal/mol; ΔG = –25.0 kcal/mol) is quite facile to afford **INT5** irreversibly. Finally, tautomerization of the dearomatized phenol moiety of **INT5** with the aid of TFA (**TS6**; $\Delta G^{\ddagger}$ = 8.3 kcal/mol) results in the formation of the target biaryl **3a**. The rate-determining step of the overall transformation is the C–C-bond-forming [3,3] sigmatropic rearrangement (**INT3**→**TS4b**; $\Delta G^{\ddagger}$ = 20.3 kcal/mol),[24] which means that the efficiency of this step would strongly affect that of the overall process.

Conformation Effects on Synchronicity

In the TSs **TS4b** and **TS4c**, both the cleaving S–O bond and the forming C–C bond of the boat TS (**TS4b**) are much longer than those of the chair TS (**TS4c**), indicating that **TS4b** is the more dissociative TS.[2] Indeed, the Wiberg bond index (WBI) of the S–O bond of **TS4b** is only 0.07 whereas that of the forming C–C bond has not been well developed (WBI: 0.22). The asynchronous character of the favorable boat TS was also supported by intrinsic reaction coordinate (IRC) calculations (Figure 2B).

The energy diagrams of the rearrangement from both the boat and chair conformations have no energy minima along the IRC, albeit that the former has a nearly flat region before **TS4b**. The RMS gradient shows a small dip around the flat region, which suggests the existence of a "hidden intermediate".[2e, 25]

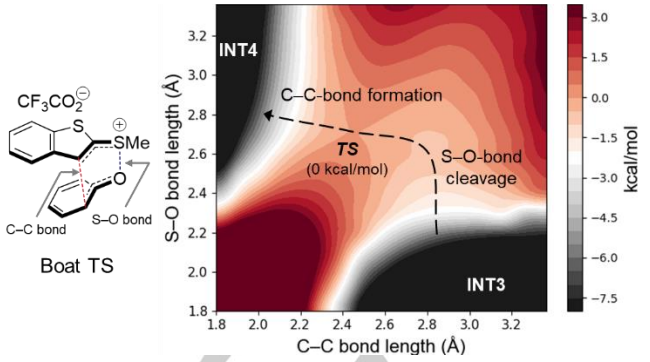


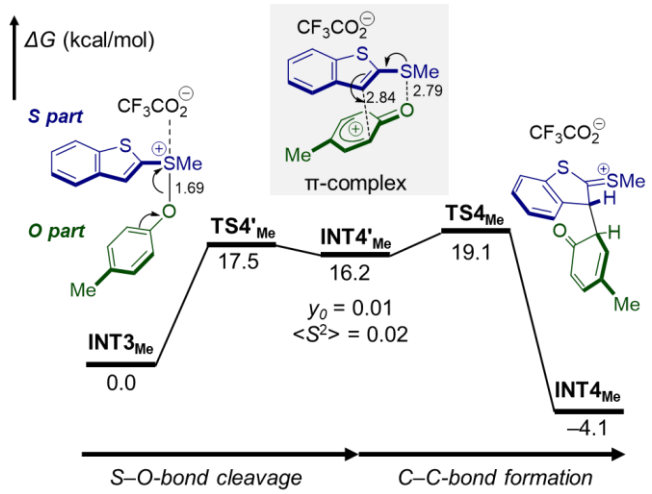
Figure 3. Potential energy surface around **TS4b**.

To trace the structural changes during the rearrangement, we performed a coordinate scan along the cleaving S–O bond and the forming C–C bond of **TS4b** (Figure 3). The obtained potential energy surface (PES) shows that the S–O-bond cleavage precedes the C–C-bond formation in the early stage of the rearrangement from **INT3**. The energetically nearly flat region reached after the initial elongation of the S–O bond corresponds to the hidden intermediate in Figure 2B, which can be regarded as a π-complex of the benzothienyl and phenol moieties.

Computationally Revealed Substituent Effects

The rearrangement is highly affected by the electronic nature of the phenol. When an electron-withdrawing trifluoromethyl group is placed at the *para*-position of phenol **2c**, the process becomes more synchronous (Figure S19). In contrast, the "hidden intermediate" is no longer hidden when an electron-donating group is introduced at the *para*-position of phenol **2b** (Figure 4).[26,27] In this case, the rearrangement proceeds sequentially via S–O-bond cleavage and C–C-bond formation. The transient intermediate **INT4′**$_{Me}$ is an open-shell species, with negligible singlet biradical character (y_0 = 0.01) based on the Yamaguchi scheme.[28] Viewed from the perspective of charge distribution, the electron density of the cresol moiety (O part = green) significantly decreases during the S–O-bond cleavage to reach a minimum at **INT4′**$_{Me}$ and then begins to increase again as the C–C-bond formation proceeds.

Based on the negligible diradical character and charge distribution, **INT4′**$_{Me}$ can thus be considered to consist of a predominant contribution from a canonical structure of a complex of 2-benzothienyl methyl sulfide and a phenoxonium cation.



Bond index and charge distribution

Structure		$INT3_{Me}$	$INT4'_{Me}$	$INT4_{Me}$
WBI	S–O	0.75	0.07	0.01
	C–C	0.00	0.06	0.95
NPA charge	*S part*	+1.27	+0.72	+0.92
	O part	–0.39	+0.26	+0.06

Figure 4. Stepwise rearrangement with *p*-cresol, calculated at the UM06-2X/6-31+G(d,p) level of theory using the SMD (dichloromethane).

Notably, a similar π-complex, *i.e.*, Dewar's complex, has been proposed as the intermediate of such benzidine rearrangements,[10,11] and some computational studies have suggested the existence of such π-complexes for benzidine-rearrangement-type transformations.[12] Moreover, Maulide has proposed that the [3,3] rearrangements of some kinds of aryl(enol)sulfonium species proceed in a stepwise manner, and that the nature of the intermediate can be represented by a π-complex of an aryl sulfide and an enol cation.[9]

In addition to the bond-reorganization mode, the electronic nature of the phenol affects the activation free energy. The rearrangements with electron-rich phenols show more asynchronous character with lower calculated energies ($\Delta G^{\ddagger}$ = 24.8, 20.3, and 19.1 kcal/mol for R = CF_3, H, and Me, respectively).[29] This tendency is qualitatively consistent with our experimental results (Scheme 2).

For a qualitative interpretation of the trend, a valence-bond diagram was employed.[30] As shown in Figure 5, the relative energies of three species, namely, the initial state, the putative π-complex, and the product state, can be expected to determine the nature of the process. When an electron-withdrawing trifluoromethyl group is placed at the phenol moiety (*cf.* reaction with **2c**), the corresponding π-complex should be relatively destabilized due to the partial cationic character of the phenol moiety. This would lead to the direct intersection of the PESs of the initial and product states, resulting in a relatively synchronous rearrangement with a high activation barrier. In contrast, the PES of the π-complex can intersect with both of those of the initial and product states at lower energies when R = Me (**2b**) due to the stabilization ability of the cation, leading to a more asynchronous but energetically favorable process.

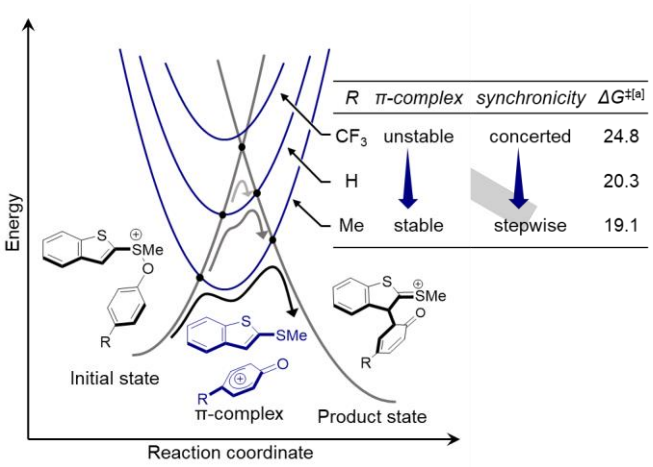


Figure 5. Valence-bond diagram of the rearrangement process. [a] Activation free energy for the rearrangement step(s); all values are given in kcal/mol.

Considering the above, the rearrangements, and especially the rearrangements involving electron-neutral or -rich phenol moieties, can be regarded as consisting of two elementary steps: (1) oxidation of the phenol moiety with S–O-bond cleavage to form a π-complex composed of the aryl sulfide and the phenoxonium; (2) intramolecular nucleophilic addition of the aryl group on the sulfur atom to form the phenoxonium moiety, rather than a conjugate addition of the intramolecular phenoxide moiety to the arylsulfonium species of **INT3**. This mechanistic scenario is consistent with the high reactivity observed for *m*-methoxyphenyl methyl sulfoxide (**6b**; Scheme 3), whose *ortho*-position should be the most nucleophilic among the four sulfoxides (**6a**-**d**). When the aryl group on the sulfur atom is not sufficiently nucleophilic, as *e.g.* in the case of **6a**, the electrophilic 2-naphthol moiety would be trapped by an external nucleophile, *i.e.*, 2-naphthol, to give BINOL (*cf.* **11**→**9** in Scheme 3).[19] The activation free energies for the rearrangement steps were estimated to be 20.4, 19.8, 21.7, and 25.5 kcal/mol for R = H, *m*-OMe, *p*-OMe, and *m*-CF_3, respectively, which qualitatively reproduces the observed trend of the reactivity.[31]

IBO Analysis

In addition, we performed the intrinsic bond orbital (IBO) analysis developed by Knizia[32] along the IRC of the rearrangement of the sulfonium intermediate derived from phenyl methyl sulfoxide and phenol (**2a**) (Figure 6). This analysis is able to associate quantum chemistry with the classical curly arrows that are commonly used for the interpretation of reaction mechanisms in organic chemistry. We chose three important orbitals, *i.e.*, the aromatic π-bonds in the phenoxy moiety (blue) and sulfonium moiety (green) and the S–O σ-bond (red) (Figure 6). In the early stage of the rearrangement, the orbital in the phenoxy moiety (blue) is converted into the C–O π-orbital with concomitant conversion of the S–O σ-bond (red) into a lone pair on the sulfide (**A**→**B**). Subsequently, the C–C π-orbital in the sulfonium moiety (green) forms the C–C bond between the two aryl fragments (**B**→**C**→**D**). Importantly, the mechanistic scenario based on the IBO analysis is consistent with the discussion above.

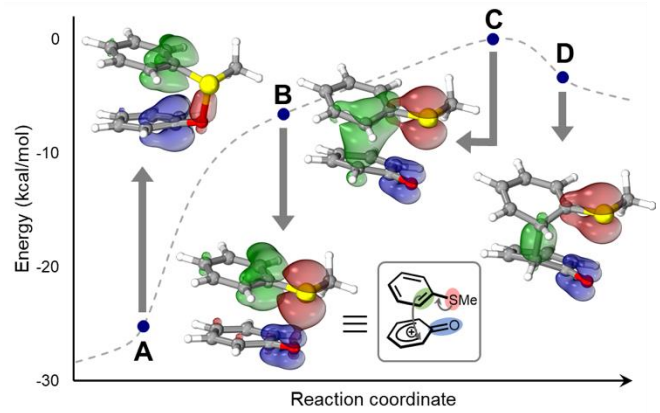


Figure 6. Intrinsic bond orbital (IBO) analysis along the IRC of the [3,3] sigmatropic rearrangement, calculated at the RM06-2X/def2-TZVP//RM06-2X/6-31+G(d,p) level of theory.

Conclusions

We conducted a mechanistic investigation focusing on the overall reaction mechanism for our coupling reaction of aryl sulfoxides with phenols, including the nature of the rearrangement. The experimental study confirmed the formation of an S–O-tethered intermediate via an interrupted Pummerer reaction and a subsequent rearrangement, as well as electronic effects on the transformation. Theoretical calculations supported the experimental observations and revealed a highly asynchronous, sometimes completely stepwise, nature of the rearrangement on the basis of the structures, charge distribution, and IBO analysis around the various transition states.

Acknowledgements

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Keywords: sigmatropic rearrangement • aryl sulfoxide • phenol • DFT calculation • mechanistic study

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[10] For a relevant review, see: D. V. Banthorpe, E. D. Hughes, C. Ingold, *J. Chem Soc.* **1964**, 2864-2901.

[11] For recent computational studies, see: a) S. Yamabe, H. Nakata, S. Yamazaki, *Org. Biomol. Chem.* **2009**, *7*, 4631-4640; b) G. Ghigo, S. Osella, A. Maranzana, G. Tonachini, *Eur. J. Org. Chem* **2011**, 2326-2333; c) G. Ghigo, A. Maranzana, G. Tonachini, *Tetrahedron* **2012**, *68*, 2161-2165.

[12] For recent examples of the synthesis of biaryls via [3,3] or [5,5] sigmatropic rearrangements of hydrazobenzenes and analogues that possess other heteroatom–heteroatom linkers such as N–O bonds, see: a) G.-Q. Li, H. Gao, C. Keene, M. Devonas, D. H. Ess, L. Kürti, *J. Am Chem Soc.* **2013**, *135*, 7414-7417; b) C. K. De, F. Pesciaioli, B. List, *Angew. Chem., Int. Ed.* **2013**, *52*, 9293-9295; *Angew. Chem.* **2013**, *125*, 9463-9465; c) H. Gao, D. H. Ess, M. Yousufuddin, L. Kürti, *J. Am Chem Soc.* **2013**, *135*, 7086-7089; d) L. Guo, F. Liu, L. Wang, H. Yuan, L. Feng, L. Kürti, H. Gao, *Org. Lett.* **2019**, *21*, 2894-2898.

[13] As **4** is very sensitive to moisture, an excess of TFAA was used not only as an activator, but also as a dehydrating agent.

[14] The formation of the rearrangement of precursor **4** might be the selectivity-determining step. However, this possibility was ruled out, because the addition of **2a** to pre-formed **4c** resulted in the preferential

formation of **3a**. For further details, see the Supporting Information (Scheme S1).

[15] For diaryl sulfoxides that possess two different aryl groups, it has been reported that rearrangements occur preferentially with the more electron-rich aromatic ring; for selected examples, see: a) J. A. Fernández-Salas, A. J. Eberhart, D. J. Procter, *J. Am. Chem. Soc.* **2016**, *138*, 790-793; b) B. Peng, X. Huang, L.-G. Xie, N. Maulide, *Angew. Chem., Int. Ed.* **2014**, *53*, 8718-8721; *Angew. Chem.* **2014**, *126*, 8862-8866. See also refs. 4a-b.

[16] A strong electron-donating group such as a methoxy group at the *para*-position on the aryl group may not promote the desired rearrangement because it can potentially neither assist the C–C-bond formation nor stabilize the resulting thionium cation via a resonance effect (for details, see: *Computationally Revealed Substituents Effects* in the main text). Furthermore, such groups at the *para*-position are known to promote aromatic Pummerer-type reactions that lead to the formation of several by products.

[17] D. Chen, Q. Feng, Y. Yang, X.-M. Cai, F. Wang, S. Huang, *Chem. Sci.* **2017**, *8*, 1601-1606.

[18] a) L. Kürti, P. Herczegh, J. Visy, M. Simonyi, S. Antus, A. Pelter, *J. Chem. Soc., Perkin Trans. 1* **1999**, 379-380; b) K. Morimoto, K. Sakamoto, T. Ohshika, T. Dohi, Y. Kita, *Angew. Chem., Int. Ed.* **2016**, *55*, 3652-3656; *Angew. Chem.* **2016**, *128*, 3716-3720.

[19] a) K. Higuchi, T. Tago, Y. Kokubo, M. Ito, M. Tayu, S. Sugiyama, T. Kawasaki, *Org. Chem. Front.* **2018**, *5*, 3219-3225; b) Z. He, A. P. Pulis, D. J. Procter, *Angew. Chem., Int. Ed.* **2019**, *58*, 7813-7817; *Angew. Chem.* **2019**, *131*, 7895-7899; c) Z. He, G. J. P. Perry, D. J. Procter, *Chem. Sci.* **2020**, *11*, 2001-2005.

[20] Y. Zhao, D. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.

[21] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

[22] We think that the rearrangement is a pericyclic rather than a pseudopericyclic reaction based on its orbital connectivity and the geometrical features of the structure. For further details, see the Supporting Information (Figure S18).

[23] The pair of aromatic rings in the TS might be stabilized by π-π interactions. However, a quantitative evaluation is difficult because the effects of the underdeveloped C–C bond in **TS4b** on the stacked structure would be non-negligible.

[24] Considering that the reaction proceeded at –60 °C, the experimental activation barrier may be by a few kcal/mol lower than the computationally obtained values (20 kcal/mol). However, the potential error can be expected to be insufficient to change the rate-determining step of the overall transformation.

[25] a) E. Kraka, D. Cremer, *Acc. Chem. Res.* **2010**, *43*, 591-601; b) H. S. Rzepa, C. Wentrup, *J. Org. Chem.* **2013**, *78*, 7565-7574.

[26] Substituents on either aryl sulfoxides or phenols did not have a significant effect on the interplanar distance between the two aromatic rings in the transition state. For further details, see the Supporting Information (Figures S21 and S22).

[27] Preliminary investigations have revealed that the reaction of benzothienyl methyl sulfoxide **1a** with methanesulfanilide proceeds through a concerted but asynchronous rearrangement similar to that with phenol.

[28] K. Yamaguchi, *Chem. Phys. Lett.* **1975**, *33*, 330-335.

[29] The rearrangement from the methyl or trifluoromethyl-substituted intermediate (derived from **1** with **2b** or **2c**) also favors the boat conformation, as in the case with **2a**. For details, see the Supporting Information (Figure S20).

[30] a) S. Shaik, A. Shurki, *Angew. Chem., Int. Ed.* **1999**, *38*, 586-625; *Angew. Chem., Int. Ed.* **1999**, *111*, 616-657; b) D. Usharani, W. Lai, C. Li, H. Chen, D. Danovich, S. Shaik, *Chem. Soc. Rev.* **2014**, *43*, 4968-4988; c) E. E. Kwan, Y. Zeng, H. A. Besser, E. N. Jacobsen, *Nat. Chem.* **2018**, *10*, 917-923; d) D. E. Ortega, R. Ormazábal-Toledo, R. Contreras, R. A. Matute, *Org. Biomol. Chem.* **2019**, *17*, 9874-9882; e) K. Yasui, M. Kamitani, H. Fujimoto, M. Tobisu, *Bull. Chem. Soc. Jpn.* **2020**, *93*, 1424-1429.

[31] In principle, $\Delta G^{\ddagger}$ does not correspond to the product yields. However, $\Delta G^{\ddagger}$ could be an indicator of product yields because a lower $\Delta G^{\ddagger}$ would indicate preferential formation of the rearranged product compared to the other by products.

[32] a) G. Knizia, *J. Chem. Theory. Comput.* **2013**, *9*, 4834-4843; b) G. Knizia, J. E. M. N. Klein, *Angew. Chem., Int. Ed.* **2015**, *54*, 5518-5522; *Angew. Chem.* **2015**, *127*, 5609-5613.

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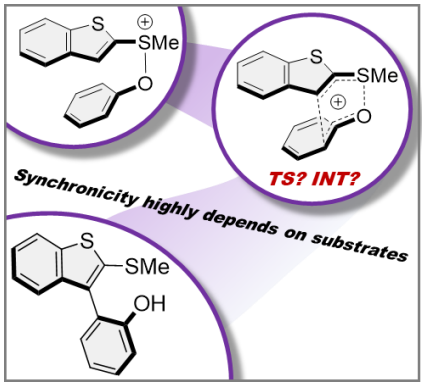

Experimental and computational investigations revealed that, depending on the structure and electronic features of the substrates in the coupling reaction of aryl sulfoxides with phenols, the reaction pathway of the rate-determining [3,3] sigmatropic rearrangements of the interrupted Pummerer intermediates can vary due to changes in energy synchronicity. As an extreme case, when an electron-rich phenol is involved, the rearrangement is no longer concerted, but instead stepwise via a π-complex of the corresponding aryl sulfide and phenoxonium cation.