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Brønsted Acid Mediated Novel Rearrangements of Diarylvinylidenecyclopropanes and Mechanistic Investigations Based on DFT Calculations

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Abstract: Diarylvinylidenecyclopropanes undergo a novel rearrangement in the presence of the Brønsted acid Tf_2NH (Tf: trifluoromethanesulfonyl) to give the corresponding naphthalene derivatives in good to high yields upon heating, whereas in the presence of the Brønsted acid toluene-4-sulfonic acid (*p*-TSA), the corresponding triene derivatives are afforded in moderate to good yields under mild conditions. Cor-

Introduction

Vinylidenecyclopropanes, **1**, are one of the most remarkable organic compounds that are known in the research field of highly strained small rings. They have an allene moiety connected to a cyclopropyl ring and yet they are thermally stable and reactive substances in organic synthesis. Thus far, thermal and photochemical skeletal conversions of vinylide-necyclopropanes have attracted much attention from mechanistic, theoretical, spectroscopic, and synthetic viewpoints.^[1,2] Many intriguing transformations with these interesting substances have been explored under mild conditions. Moreover, we have recently been investigating the Lewis acid or

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901172. It contains ¹H and ¹³C NMR spectra for the rearranged products **2**, **3a**, **4**, **5**, and **7**, the GC–MS spectra of the propene capture, the NMR study of **7a**, the calculated NMR spectra for **7a**, the optimized structures for the compounds in Scheme 3, and the total energies and geometrical coordinates of the structures in Scheme 3 and Figure 2.

responding mechanistic studies on the basis of density functional theory (DFT) with the Gaussian03 program by using the B3LYP method have re-

Keywords: Brønsted acids • diarylvinylidenecyclopropanes • Lewis acids • naphthalenes • reaction mechanisms • regioselectivity • trienes vealed that the pK_a value of the Brønsted acid, as well as the entropy and solvent effects, plays a significant role in this reaction; these factors can discriminate the differences in the reactivity and regioselectivity among the Brønsted acids used in this reaction. In the presence of Lewis acid Sn(OTf)₂, a butatrienecyclopane can produce the corresponding ring-opened products in moderate yields.

Brønsted acid catalyzed/mediated ring-opening reactions of **1** with various electrophiles and have found some novel reaction patterns of these substrates.^[3,4] As an interesting example, we have found that naphthalene derivative **2a** was formed in 50% yield in the Sn(OTf)₂-catalyzed reaction of diphenylvinylidenecyclopropane **1a**, bearing 4 methyl groups on the cyclopropane ring, in 1,2-dichloroethane (DCE) upon heating at 80 °C (Scheme 1).

However, because the reaction mechanism remains obscure and Lewis acids such as $BF_3 \cdot OEt_2$, $Zr(OTf)_4$, $Sn-(OTf)_2$, and lanthanide triflates $(Ln(OTf)_3; Ln: Yb, Sc, and Y)$ produce naphthalene derivative **2a** in only moderate yields,^[3b] we attempted to examine the Brønsted acid mediated reactions of diarylvinylidenecyclopropanes **1** under similar conditions and to determine the detailed reaction mechanism. In this paper, we wish to report the Brønsted acid mediated rearrangement of diarylvinylidenecyclopropanes **1**



Scheme 1. Rearrangement of diphenylvinylidenecyclopropane 1a in the presence of the Lewis acid $Sn(OTf)_2$ in DCE at 80 °C.



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to form the corresponding naphthalene derivatives 2 or triene derivatives 4 in good to high yields under mild conditions, along with an investigation of the reaction mechanism by a DFT study, which has been supported by the detection of the released propene molecule. In addition, we will disclose in this paper that the pK_a value of the employed Brønsted acid, entropy, and solvent effects can significantly affect the reactivity and regioselectivity of the reaction.

Results and Discussion

An initial examination was performed by using diphenylvinylidenecyclopropane 1a as a substrate in the presence of the Brønsted acid trifluoromethanesulfonic acid (TfOH) $(pK_a = 4.2 \text{ in acetic acid at } 20 \,^{\circ}\text{C})^{[5]}$ in DCE, and the results of these experiments are summarized in Table 1. We found

Table 1. TfOH-catalyzed/mediated rearrangement of diphenylvinylidenecyclopropane **1a** in a variety of solvents.

	Brøns solviv RT	ted acid ent,	2a	+	Ja Ja
Entry	Brønsted acid	Solvent	t	Yield	[%] ^[a]
				2 a	3a
1	HOTf (1.0 equiv)	DCE	2 min	34	complex mixture
2	HOTf (0.1 equiv)	DCE	4 d	26	40
3	HOTf (0.2 equiv)	DCE	6 h	40	42
4	HOTf (0.4 equiv)	DCE	2 h	40	45
5	HOTf (0.6 equiv)	DCE	2 min	62	33
6	HOTf (0.6 equiv)	THF	4 d	trace	_
7	HOTf (0.6 equiv)	Et ₂ O	4 d	trace	-

a Yield of isolated product.

that the corresponding naphthalene derivative 2a was produced under various conditions, along with enyne product 3a. With TfOH (1.0 equiv) as a promoter in DCE at room temperature (20°C), the reaction proceeded extremely quickly to give 2a in 34% yield within 2 min, along with a complex mixture of many unidentified products and 3a (Table 1, entry 1). However, with less TfOH (0.1 equiv) as the promoter under otherwise identical conditions, 2a was obtained in 26% yield, along with 3a in 40% yield, after 4 days (Table 1, entry 2). An increase in the employed amount of TfOH significantly accelerated the reaction rate (Table 1, entries 3–5). In the presence of TfOH (0.6 equiv), 2a was produced in 62% yield, along with 33% yield of 3a (Table 1, entry 5). However, the reaction did not take place in Et₂O or tetrahydrofuran (THF), presumably because the oxygen atom in these solvents could capture the proton of TfOH and impair the catalytic ability of TfOH (Table 1, entries 6 and 7).

Interestingly, with Tf₂NH (1.0 equiv; $pK_a = 7.8$ in acetic acid at 20°C)^[5] as the promoter in this reaction at room temperature (20°C), 2a was produced in 71% yield as the sole product after 3 days (Table 2, entry 1). Solvent effects were also examined with Tf_2NH (1.0 equiv) as the promoter,

Table 2. Brønsted acid promoted rearrangement of diphenylvinylidenecyclopropane 1a in DCE at different temperatures.

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(1.0 e	quiv)

1a — 2a + 3a						
Entry	Brønsted acid	t	T [°C]	Yield [%] ^[a]		
				2 a	3a	
1	Tf ₂ NH	3 d	20	71	-	
2 ^[b]	Tf ₂ NH	4 d	20	-	-	
3 ^[c]	Tf ₂ NH	2 d	20	87	-	
4 ^[d]	Tf_2NH	7 d	20	40	_	
5 ^[e]	Tf_2NH	3 d	20	52	_	
6	Tf ₂ NH	11 h	50	92	-	
7	Tf_2NH	10 min	84	99	_	
8 ^[f]	Tf ₂ NH	90 min	84	76	_	
9 ^[g]	Tf ₂ NH	10 min	84	92	_	
10	Tf ₂ NH	11 d	0	50	_	
11	p-TSA	10 min	84	71	16	
12	p-TSA	5 h	50	93	_	
13	MeSO ₃ H	11 h	50	85	_	
14	CF ₃ CO ₂ H	2 d	50	71	_	
15	Me - SO ₃ H	4 d	50	_[h]		
16	H ₂ N - SO ₃ H	4 d	50	_[h]		
17		4 d	50	_[h]		
18		4 d	50	_[h]		
19	$HO_2C - CO_2H$	4 d	50	_[h]		
20		4 d	50	_[h]		

[a] Yield of isolated product. [b] With n-pentane as the solvent. [c] With dichloromethane as the solvent. [d] With benzene as the solvent. [e] With chloroform as the solvent. [f] With 0.1 equiv of Tf_2NH . [g] With 0.5 equiv of Tf₂NH. [h] No reaction occurred.

and the results are listed in entries 2-5 of Table 2. In dichloromethane, 2a was formed in 87% yield as the sole product (Table 2, entry 3), but in other solvents, such as npentane, benzene, or chloroform, 2a was produced in lower yields (Table 2, entries 2, 4, and 5). We next examined the influence of the reaction temperature with Tf₂NH as the promoter. We found that 2a could be produced in 92 and 99% yields at 50°C and under reflux conditions (84°C) after 11 h and 10 min, respectively (Table 2, entries 6 and 7). With a catalytic amount of Tf₂NH as the promoter, a prolonged reaction time was required and the yields of product 2a were lower (Table 2, entries 8 and 9). At 0°C, the reaction was sluggish under otherwise identical conditions to those in entry 7 of Table 2, and 2a was produced in 50%

yield after 11 days (Table 2, entry 10). On the other hand, with the Brønsted acid p-TSA as the promoter, 2a was obtained in 71% yield, along with **3a** in 16% yield, at 84°C after 10 min (Table 2, entry 11). At 50°C, 2a was obtained in 93% yield as the sole product after 5 h (Table 2, entry 12). Other Brønsted acids, such as MeSO₃H ($pK_a > 7.0$ in acetic acid at 20 °C)^[5] and CF₃CO₂H (pK_a=11.4 in acetic acid at 20 °C),^[5] are not as effective as Tf₂NH under similar conditions (Table 2, entries 13 and 14). A sterically more hindered aromatic sulfonic acid provided 2a in 59% yield, along with 3a in 4% yield, at 50°C (Table 2, entry 15). Weak Brønsted acids, such as aromatic carboxylic acids, did not catalyze this reaction (Table 2, entries 16-20). Therefore, the p K_a value of the employed Brønsted acid significantly affected the reaction outcome. The best conditions for the formation of the corresponding naphthalene derivative 2a were found to be those in DCE at 84°C with 1.0 equiv of Tf_2NH (Table 2, entry 7).

By using these optimized reaction conditions, we next examined the rearrangement of a variety of diarylvinylidenecyclopropanes **1**. The results are shown in Table 3. From

Table 3. Rearrangement of a variety of diarylvinylidenecyclopropanes 1 promoted by the Brønsted Acid Tf₂NH in DCE at 84 $^{\circ}$ C.



[a] Yield of isolated product or product mixtures. [b] The ratio of 2 and 2' was determined by ¹H NMR spectroscopic data. 2 f/2 f' 1:1, 2g/2g' 1:1, 2h/2h' 1:1.8.

symmetrical diarylvinylidenecyclopropanes **1b** and **1c**, with electron-donating groups on the benzene rings, the corresponding naphthalene derivatives **2b** and **2c** were obtained in high yields (Table 3, entries 1 and 2). From symmetrical diarylvinylidenecyclopropanes **1d** and **1e**, with electronwithdrawing groups on the benzene rings, the corresponding naphthalene derivatives **2d** and **2e** were formed in moderate yields (Table 3, entries 3 and 4). From unsymmetrical diarylvinylidenecyclopropanes **1f–h**, the corresponding naphthalene derivatives were obtained as isomeric mixtures of **2** and **2'** in good total yields (Table 3, entries 5–7).

Interestingly, with the moderate Brønsted acid p-TSA (1.0 equiv) as the promoter at room temperature (20 °C), the rearrangement of **1a** proceeded slowly in DCE, to give

2,4-dimethyl-3-(2',2'-diphenylvinyl)-penta-1,3-diene (4a) as the sole product in 76% yield after 5 days, rather than products 2a or 3a (Table 4, entry 1).^[7] With hexane, toluene,

Table 4. Rearrangement of diphenylvinylidenecyclopropane **1a** promoted by the Brønsted acid *p*-TSA in a variety of solvents.

	1a <u>p-TSA</u> si	(1.0 equiv) ► 2 olvent ►	¦a + 3a + ⟨		=<	
Entry	Solvent	T [°C]	<i>t</i> [d]	Yield	[%] ^[a]	
				2 a	3a	4 a
1	DCE	20	5	-	-	76
2	hexane	20	4	no rea	action	
3	toluene	20	4	no rea	action	
4	CH_2Cl_2	20	4	14	14	70
5	DCE	0	30	-	-	46
6	THF	20	4	no rea	action	
7	Et_2O	20	4	no rea	action	

[a] Yield of isolated product.

THF, or diethyl ether as the solvent, no reaction occurred under otherwise identical conditions (Table 4, entries 2, 3, 6, and 7). When this reaction was carried out in dichloromethane, **4a** was formed in 70% yield, along with **2a** and **3a**, both in 14% yields (Table 4, entry 4). It should be noted that when this reaction was carried out at 0°C in DCE with *p*-TSA as the promoter, the reaction became extremely sluggish and gave **4a** in 46% yield after 30 days.

We examined the rearrangement of a variety of diarylvinylidenecyclopropanes 1 with *p*-TSA as the promoter in DCE. The results are summarized in Table 5. From symmet-

Table 5. Rearrangement of a variety of diarylvinylidenecyclopropanes 1 promoted by the Brønsted acid *p*-TSA in DCE at room temperature.

R		— <u>p-TSA</u> —	(1.0 equiv) CE, RT	R^1	\rightarrow	$\begin{pmatrix} R^2 & R^3 \\ \downarrow & \downarrow \\ \downarrow \\$
Entry	R ² Substrate	\mathbf{R}^1	R ²	R ²	4	R ¹ 4' Product, yield [%] ^{[a}
1	1b	Me	Me	Н	1 d	4b , 84
2	1c	MeO	MeO	Η	7 h	4c , 92
3	1d	Cl	Cl	Η	12 d	4d , 69
4	1e	F	F	Н	5 d	4e , 78
5 ^[b]	1f	Н	Cl	Н	14 d	4f + 4f', 35
6 ^[b]	1g	Н	MeO	Н	12 h	4g + 4g', 98

[a] Yield of isolated product or product mixture. [b] **4f**/**4f**' 3:2, **4g**/**4g**' 1:1. [c] Only **4h**' was obtained, as determined from the NOESY spectrum, along with 42 % of **2h**'.

Me

2 d

Me

rical diarylvinylidenecyclopropanes **1b–e**, the corresponding penta-1,3-diene derivatives **4b–e** were produced in moderate to good yields, although the reaction proceeded slowly

7[c]

1h

Η

4h'. 35

for diarylvinylidenecyclopropanes **1d** and **1e** with electronwithdrawing groups on the benzene rings (Table 5, entries 1–4). From unsymmetrical diarylvinylidenecyclopropanes **1f** and **1g**, the corresponding penta-1,3-diene derivatives were obtained as isomeric mixtures of **4** and **4'** in moderate to good total yields (Table 5, entries 5 and 6). In the case of diarylvinylidenecyclopropane **1h**, the corresponding penta-1,3-diene derivative **4h'** was formed, along with the corresponding naphthalene derivative **2h'**, both in moderate yields (Table 5, entry 7).

We also synthesized two other diarylvinylidenecyclopropanes, **1i** and **1j**, which have two cycloalkyl groups on the cyclopropane ring, to examine their rearrangement behavior in the presence of various Brønsted acids under the standard conditions. The results of these experiments are summarized in Table 6. We found that, in the presence of a strong

Table 6. Optimization of the reaction conditions of the Brønsted acid promoted rearrangement of diarylvinylidenecyclopropane **1i** in DCE.



[a] Yield of isolated product.

Brønsted acid, such as Tf_2NH , complicated product mixtures were formed (Table 6, entry 1). The moderately strong Brønsted acid *p*-TSA produced the 1-(1-cyclohexylideneallyl)cyclohexene derivative **5a** in 10% yield, along with other unidentified products (Table 6, entry 2). Fortunately, with trifluoroacetic acid (2.0 equiv) as the promoter at room temperature, **5a** was obtained in 52% yield after 40 h and 38% yield after 96 h, presumably due to the partial decomposition of **5a** during the prolonged reaction time (Table 6, entries 3 and 4). The use of CF₃CO₂H (1.2 equiv) under otherwise identical conditions produced **5a** in 65% yield at 80°C (Table 6, entry 5). It should be noted that with Sn(OTf)₂ as a Lewis acid in this reaction, **5a** was produced in 45% yield after 3 h at room temperature (Table 6, entry 6).

With diarylvinylidenecyclopropane **1j**, the corresponding 1-(1-cyclopentylidene-allyl)cyclopentene derivative **5b** was obtained in 50% yield at 50°C by using CF_3CO_2H (1.0 equiv) as the promoter (Scheme 2).

Theoretical study: A reasonable explanation for the intriguing results described above could basically be that the pK_a value of the employed Brønsted acids can dominate the re-



Scheme 2. Rearrangement of diarylvinylidenecyclopropane 1j promoted by the Brønsted Acid CF₃CO₂H in DCE.

action pathway. That is, the stronger Brønsted acids promoted reactions faster, whereas the weaker Brønsted acids could not promote reactions at all. Moreover, the excellent selectivity of Tf_2NH could be explained by the increased Brønsted acidity of Tf_2NH in a polar aprotic solvent, combined with the low nucleophilicity of the trifluoromethanesulfonimide anion.^[6] However, it is clear that the reaction mechanism is much more complicated to understand and that a comprehensive mechanistic explanation is difficult to achieve.

To understand the mechanism of this reaction, DFT^[7] studies have been performed with the Gaussian03 program^[8] by using the B3LYP^[9] method. The reaction pathway has been studied at the B3LYP/6-31+G^{**} level. To obtain more accurate energies, the 6-311++G^{**} basis set was used in the study of the regioselectivity. The solvent effects were estimated with the IEFPCM^[10] (UAHF atomic radii) method in DCE (dielectric constant $\varepsilon = 10.36$) based on the gasphase fully optimized structures. For each structure, harmonic-vibration-frequency calculations were carried out and thermal corrections were made. All structures were shown as transition states (with one imaginary frequency).

The reaction pathway: The reaction pathway has been explored with R, the complex of HOTf and substrate **1a** (Scheme 3). All of the optimized structures are collected in the Supporting Information, and some selected structures are shown in Figure 1. As shown in Scheme 3, the C1 or C2 atom is protonated along paths 1 and 2, which lead to product **3a** and intermediate B, respectively. The protonation steps are rate determining in paths 1 and 2. Therefore, the regioselectivity is determined by the relative free energies of TS-R-A1 and TS-R-A2. In this case, the energy difference is 2.0 kcalmol⁻¹, which is somewhat large because mixed products have been obtained in the HOTf-promoted reactions (Table 1). The regioselectivity of four kinds of acids was studied at the more accurate B3LYP/6-311++G** level and will be discussed in the next section.

In the cationic intermediate A1 (Figure 1), the C3–C5 bond is partially broken. The cationic C5 atom has a strong interaction with the electron-rich C3 atom, as indicated by the short distance of 1.810 Å between them. The C1–C4 atoms are nearly in a straight line. The angle of C3–C4–C5 is 74.8°. In TS-A1–**3a**, the angle of C3–C4–C5 increases to 94.8°; the deprotonation of the methyl group along with the



Scheme 3. Reaction pathways and the relative free energies including the solvent effects, ΔG_{sol} (in kcalmol⁻¹, 298 K). These were calculated at the B3LYP/6-31+G^{**} level of theory.

cleavage of the C3–C5 bond yields the product 3a. In 3a, the bond angle of C3–C4–C5 increases to 107.3°, and the cyclopropane is entirely opened. In TS-A2-B, the cleavage of the C4–C5 bond leads to the formation of intermediate B.

Intermediate B may be deprotonated by OTf⁻ anions to produce product **4a** (Path 3) or to form intermediate C through an intramolecular Friedel–Crafts reaction (Path 4). Partial aromatization of C over a small barrier of $0.9 \text{ kcal mol}^{-1}$ (TS-C-D) produces intermediate D, which is more stable than B by 10.4 kcal mol⁻¹. Intermediate D undergoes subsequent protonation (TS-D-E), 1,2-migration of the methyl group (TS-E-F), and release of a protonated propene (TS-F-G) to produce the aromatized naphthalene derivative **2a**. In the final step, the protonated propene releases a proton to the OTf^- anion.

The experiments show that 4a is not obtained under the conditions mediated by HOTf. In addition, 4a can be transformed into 2a in quantitative yield (see Scheme 4 below). These results are consistent with the calculation results that show 4a to be a kinetic product (Scheme 3). Low reaction temperatures and weaker Brønsted acids are beneficial for the formation of 4a. Our experiments show that 4a will be obtained when the reaction is promoted by *p*-TSA at room temperature (20°C). These facts indicate that the properties of the conjugated base of the Brønsted acid are important in the reaction.

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Figure 1. Selected optimized structures on the reaction pathway. The bond lengths are given in Ångstroms, and the bond angles are given in degrees. The relative free energies, including the solvent effects, ΔG_{sol} , (298 K) are given in kcal mol⁻¹. The geometries were fully optimized at the B3LYP/6-31+G** level.

The reactivity and the regioselectivity: The optimized reactants and the transition states of the two protonation transition states (TS-R-A1 and TS-R-A2) for Tf₂NH, HOTf, MeSO₃H, and *p*-TSA are shown in Figure 2, and the corresponding data are listed in Table 7. The reaction barriers show that the sequence of reactivity is almost the same as that of the acidity of the employed acids: HOTf (9.4 kcal mol⁻¹) > *p*-TSA (13.8 kcalmol⁻¹) > Tf₂NH (14.5 kcalmol⁻¹) > MeSO₃H (17.0 kcalmol⁻¹). The Tf₂NH acid shows stronger acidity than MeSO₃H in this reaction.

As shown in Table 7, the difference in the relative free energies, ΔG_{sol} , between HOTf-TS-R-A1 and HOTf-TS-R-A2 is only 0.4 kcalmol⁻¹, whereas for other acids, the energy differences are larger than 2.6 kcalmol⁻¹. These results are consistent with the experimental observation that the use of HOTf as the promoter always leads to mixed reaction products.

It is very notable that, despite similar structures, HOTf and MeSO₃H have very different behaviors in this reaction. The data shown in Table 7 indicate that the difference in the relative electronic energies, ΔE , between MeSO₃H-TS-R-A1 and MeSO₃H-TS-R-A2 is 2.2 kcal mol⁻¹. MeSO₃H-TS-R-A2 has larger entropy, and the difference in the ΔG_{gas} values is increased to 3.8 kcal mol⁻¹. The difference in the solvation effects of MeSO₃H-TS-R-A1 and MeSO₃H-TS-R-A2 is 0.4 kcal mol⁻¹. Thus, the difference in the ΔG_{sol} values is 3.4 kcalmol⁻¹ (Table 7, entries 1–3). For HOTf, the difference in the ΔE values between HOTf-TS-R-A1 and HOTf-TS-R-A2 is also 2.2 kcalmol⁻¹. The relative entropy of HOTf-TS-R-A2 decreased by –2.607 units, and the difference in the ΔG_{gas} values decreased to 1.9 kcalmol⁻¹. HOTf-TS-R-A1 has a relatively larger solvation effect. Subsequently, the difference in the ΔG_{sol} values decreased to 0.4 kcalmol⁻¹ (Table 7, entries 7–9). Therefore, the entropy effect and the solvation effect are important for the selectivity.

In order to confirm that both path 3 and path 4 are involved in the reaction, the control experiment shown in Scheme 4 was carried out. We found that, under the standard conditions, triene product **4a** can be smoothly transformed into the corresponding naphthalene derivative **2a** in quantitative yield (Scheme 4). This result suggests that **2a** could indeed be formed from protonation of **4a** through the mechanism shown as path 4 in Scheme 3.

To identify the released propene, we used GC–MS to detect this small molecule in the reaction system of the Tf_2NH -promoted rearrangement of **1a** in DCE. On the basis of the mass spectrum, propene was indeed detected (see spectrum in the Supporting Information). Therefore, we can confirm that, in the Tf_2NH -promoted rearrangement of diarylvinylidenecyclopropanes **1** bearing four methyl groups at the cyclopropane ring, the corresponding naphtha-



Figure 2. The optimized reactants and transition states of the two protonation steps for the Tf₂NH, HOTf, MeSO₃H, and *p*-TSA acids. The geometries were fully optimized at the B3LYP/6-311++G^{**} level. The relative free energies, including the ΔG_{sol} values, are given in kcal mol⁻¹.

Table 7. The relative electronic energies (ΔE , in kcal mol⁻¹), relative free energies in the gas phase ($\Delta G_{\rm gas}$, in kcal mol⁻¹), relative free energies in solvation ($\Delta G_{\rm sol}$, in kcal mol⁻¹), and relative entropies (ΔS , in cal mol K⁻¹) of TS-R-A2 and TS-R-A1 for the Tf₂NH, HOTf, MeSO₃H, and *p*-TSA acids.

Entry	Acid	ΔE	$\Delta G_{ m gas}$	$\Delta G_{ m sol}$	ΔS
1	MeSO ₃ H-TS-R-A1	24.2	25.4	20.4	-10.671
2	MeSO ₃ H-TS-R-A2	22.0	21.6	17.0	-10.276
3	MeSO ₃ H-R	0.0	0.0	0.0	0.0
4	Tf ₂ NH-TS-R-A1	22.0	22.4	17.7	-14.034
5	Tf ₂ NH-TS-R-A2	16.9	17.2	14.5	-13.122
6	Tf ₂ NH-R	0.0	0.0	0.0	0.0
7	HOTf-TS-R-A1	17.8	15.9	9.8	-3.803
8	HOTf-TS-R-A2	15.6	14.0	9.4	-6.410
9	HOTf-R	0.0	0.0	0.0	0.0
10	p-TSA-TS-R-A1	24.8	22.7	16.5	5.456
11	p-TSA-TS-R-A2	22.2	18.1	13.8	4.451
12	p-TSA-R	0.0	0.0	0.0	0.0



Scheme 4. Transformation of 4a into 2a promoted by Tf₂NH.

lene derivatives **2** were produced, along with the release of a propene molecule.

We also investigated the rearrangement reaction of butatrienecyclopane $6^{[11]}$ catalyzed by a variety of Brønsted or Lewis acids. However, it was found that compound **6** was extremely labile and underwent a polymerization reaction in

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the presence of Brønsted acids; Lewis acids were suitable catalysts in this case. The results of the Lewis acid catalyzed rearrangement are shown in Table 8. With $Zr(OTf)_4$ as the

Table 8. Lewis acid catalyzed rearrangement of butatrienecycloproane $\boldsymbol{6}$ in DCE.



[a] All reactions were carried out at room temperature with 10 mol% of catalyst. [b] Yield of isolated product. [c] The reaction was carried out at room temperature for 18 h, then at 50 °C for 6 h.

catalyst at room temperature, the rearrangement proceeded rapidly in DCE to give the ring-opened products **7a** and **7b** in 29 and 11 % yields, respectively, along with some polymerized byproducts (Table 8, entry 1). After screening various Lewis acids, we found that $Sn(OTf)_2$ is the best catalyst for this reaction; it gave **7a** and **7b** in 54 and 12 % yields under similar conditions (Table 8, entry 2). La(OTf)₃ and Yb(OTf)₃ are less effective in this reaction under the standard conditions (Table 8, entries 5 and 6). The structures of **7a** and **7b** were determined by ¹H NMR, ¹³C NMR, DEPT, ¹H–¹H NOESY (Scheme 5), HMQC, HMBC, MS–HRMS,



Scheme 5. ¹H–¹H NOE interactions of **7a** and **7b**.

and IR spectroscopic data. Furthermore, the structure of 7a was also confirmed on the basis of computational calculations of the ¹³C NMR chemical shifts by the gauge including atomic orbital (GIAO)^[12] method at the B3LYP/6-31G* level by using the Gaussian03 program (see the Supporting Information). Although the reaction outcomes are quite different from those of diarylvinylidenecyclopropanes **1** under similar reaction conditions, this result suggests that 1,2,3-butatriene and allene moieties connected with cyclopropane rings can significantly affect the rearrangement pathway in the presence of Brønsted or Lewis acid.

Conclusions

In this paper, we have disclosed the transformations of diarylvinylidenecyclopropanes 1 in the presence of Brønsted acids Tf₂NH or *p*-TSA. In these transformations, the corresponding naphthalene derivatives 2 or trienes 4, respectively, can be obtained in moderate to good yields. A wide range of substitutent aromatic groups on diarylvinylidenecyclopropanes 1 have been examined in both reactions. A plausible reaction mechanism has been discussed on the basis of the capture of the propene by GC-MS and the transformation of 4a into 2a. More importantly, a mechanistic study has been performed with DFT calculations. It was found that the p K_a value of the Brønsted acid, as well as the entropy and solvent effects, played a significant role in this reaction; these factors can discriminate the differences in the reactivity and regioselectivity among the Brønsted acids used in this reaction. These processes provide an efficient route to the synthesis of naphthalene derivatives and trienes. In addition, the investigation of the reaction mechanism has proven our hypothesis to a certain extent. Furthermore, we have also disclosed the rearrangement reaction of butatrienecyclopane 6 catalyzed by Lewis acids, to provide ring-opened products in moderate yields. Efforts are in progress to further elucidate the mechanistic details of this reaction and to disclose its scope and limitations.

Experimental Section

General remarks: ¹H NMR spectra were recorded on a 300 MHz or 400 MHz spectrometer in CDCl₃ by using tetramethylsilane (TMS) as the internal standard. Infrared spectra were measured on a Perkin–Elmer 983 spectrometer. Mass spectra were recorded with a HP-5989 instrument, and HRMS (EI) was performed with a Finnigan MA⁺ mass spectrometer. Satisfactory CHN microanalyses were obtained with a Carlo–Erba 1106 analyzer. Melting points are uncorrected. All reactions were monitored by TLC with Huanghai GF₂₅₄ silica gel coated plates. Flash column chromatography was carried out with 300–400 mesh silica gel.

General procedure for the reactions of diarylvinylidenecyclopropanes in the presence of $(CF_3SO_2)_2NH$: Under an argon atmosphere, diarylvinylidenecyclopropanes (0.18 mmol) and DCE (3.0 mL) were added into a Schlenk tube. The mixture was heated under reflux, and then $(CF_3SO_2)_2NH$ (51 mg, 1.0 equiv) was added. The reaction was quenched by addition of anhydrous NaHCO₃, and then the product mixture was purified by flash column chromatography.

Compound 2b: A white solid; m.p. 64–66 °C; ¹H NMR (CDCl₃, 300 MHz, TMS): δ = 2.43 (s, 3 H, CH₃), 2.48 (s, 3 H, CH₃), 2.52 (s, 3 H, CH₃), 2.60 (s, 3 H, CH₃), 7.16–7.37 (m, 6 H, Ar), 7.77–7.84 ppm (m, 2 H, Ar); ¹³C NMR (CDCl₃, 75 MHz, TMS): δ = 14.6, 20.8, 21.2, 22.0, 123.1, 226.4, 126.6, 128.5, 128.8, 129.2, 129.8, 130.0, 132.6, 133.2, 135.1, 136.5, 137.6, 138.1 ppm; IR (CH₂Cl₂): $\tilde{\nu}$ = 3020, 2920, 2864, 2725, 1903, 1695, 1623, 1599, 1517, 1507, 1440, 1380, 1358, 1182, 1109, 1037, 1022, 933, 883, 821, 774, 728, 577, 538 cm⁻¹; MS: *m/z* (%): 260 [*M*⁺] (100), 259 (5.42), 245 (30.34), 243 (3.63), 230 (11.30), 229 (12.43), 228 (4.80), 215 (9.42), 202 (3.03); HRMS (EI): calcd for C₂₀H₂₀: 260.1565; found: 260.1551.

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General procedure for the reactions of diarylvinylidenecyclopropanes in the presence of *p*-TSA: Under an argon atmosphere, diarylvinylidenecyclopropanes **1a–g** (0.18 mmol), DCE (3.0 mL), and *p*-TSA (1.0 equiv) were added into a Schlenk tube. The resultant reaction mixture was stirred for different times at room temperature. The reaction was quenched by addition of anhydrous NaHCO₃, and then the product mixture was purified by flash column chromatography.

Compound 4a: A colorless liquid; ¹H NMR (CDCl₃, 300 MHz, TMS): $\delta = 1.58$ (s, 3H, CH₃), 1.66 (s, 3H, CH₃), 1.69 (s, 3H, CH₃), 4.43 (d, J = 1.5 Hz, 1H), 4.48 (d, J = 1.5 Hz, 1H), 6.54 (s, 1H), 7.17–7.27 ppm (m, 10H, Ar); ¹³C NMR (CDCl₃, 75 MHz, TMS): $\delta = 21.7$, 21.8, 23.0, 115.3, 126.8, 127.1, 127.5, 127.9, 128.0, 128.2, 130.4, 131.1, 134.9, 140.9, 142.8, 143.7, 144.1 ppm; IR (CH₂Cl₂): $\bar{v} = 3444$, 3058, 3026, 2974, 2926, 2853, 1950, 1731, 1660, 1598, 1578, 1491, 1446, 1369, 1318, 1278, 1158, 1073, 1032, 1001, 942, 922, 901, 841, 757, 699, 573 cm⁻¹; MS: *m/z* (%): 274 [*M*⁺] (59), 259 (100), 215 (45), 115 (69), 105 (51), 91 (85), 77 (47), 41 (50); HRMS (EI): calcd for C₂₁H₂₂: 274.1722; found: 274.1721.

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