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Lewis-Acid-Catalyzed Rearrangement of Arylvinylidenecyclopropanes: Significant Influence of Substituents and Electronic Nature of Aryl Groups

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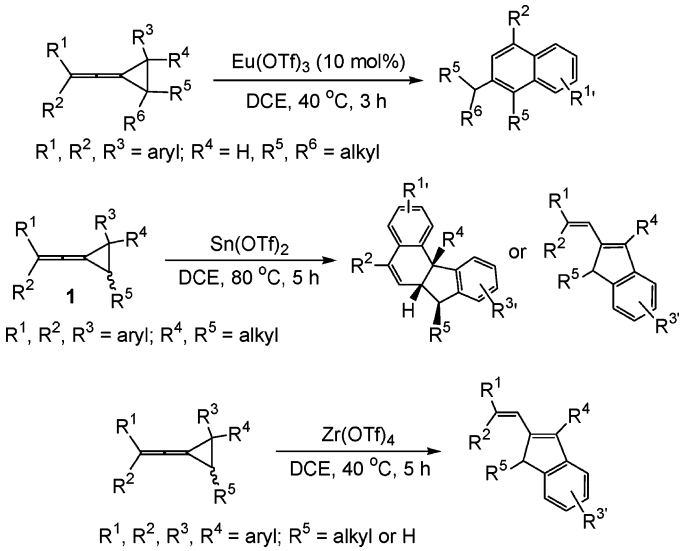

Lewis-acid-catalyzed reactions of arylvinylidenecyclopropanes having three substituents at the corresponding cyclopropyl rings have been investigated thoroughly. The reaction products are highly dependent on the substituents at the corresponding cyclopropyl rings and the electronic nature of the aryl groups. For arylvinylidenecyclopropanes bearing two alkyl groups at the C-1 position (R^1, R^2, R^3 = aryl; R^4 = H; R^5, R^6 = alkyl), naphthalene derivatives were formed in the presence of Lewis-acid $Eu(OTf)_3$ in DCE at 40 °C. For arylvinylidenecyclopropanes in which R^1, R^2, R^3 = aryl and R^4, R^5 = alkyl (syn/anti isomeric mixtures), the corresponding 6a*H*-benzo[*c*]fluorine derivatives were formed in the syn-configuration via a double intramolecular Friedel−Crafts reaction when all of the aryl groups do not have electron-withdrawing groups or the corresponding indene derivatives were obtained via an intramolecular Friedel−Crafts reaction as long as one electron-deficient aryl group was attached. For arylvinylidenecyclopropanes in which R^1, R^2, R^3, R^4 = aryl and R^5 = alkyl or H, the corresponding indene derivatives were obtained exclusively via a sterically demanding intramolecular Friedel−Crafts reaction. Lewis-acid effects and mechanistic insights have been discussed on the basis of experimental investigations.

Introduction

Vinylidenecycloproanes **1** are one of the most remarkable organic compounds known. They have an allene moiety connected by a cyclopropyl ring, and yet they are thermally stable and reactive substances. Therefore, thermal and photochemical skeletal conversions of vinylidenecyclopropanes **1** have attracted much attention from mechanistic, theoretical, spectroscopic, and synthetic viewpoints.[1,2] Recently, we have been investigating the Lewis-acid- or Brønsted-acid-catalyzed/medi-

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ated ring-opening reactions of methylenecyclopropanes (MCPs), another kind of molecule having surprising stability along with a high level of strain,[3] and found some novel reaction patterns of these substrates.[4−6] Vinylidenecyclopropanes **1**, as similar substrates with MCPs, are of synthetic interest due to the attractive feature that they have multiple possibilities for both reactions of the three strained bonds (two proximal and one distal bonds) in the cyclopropyl rings and the allene bonds.[7,8] Thus far, we found that aryl-monosubstituted vinylidenecyclopropanes **1** (R^1, R^3 = aryl; R^2 = alkyl; R^4 = H; R^5 = H or alkyl) or aryl-disubstituted ones (R^1, R^2, R^3 = aryl; R^4 = H; R^5 = H or alkyl) undergo interesting rearrangements in the presence of Lewis acids such as $Sn(OTf)_2$ to give the corresponding naphthalene derivatives **2** in good to high yields in 1,2-dichloroethane (DCE) (Scheme 1).[7a] Moreover, short thereafter, we also reported arylvinylidenecyclopropanes **1** having three substituents at the corresponding cyclopropyl rings to provide easy access to the corresponding 6a*H*-benzo[*c*]fluorine derivatives **3** (R^1, R^2, R^3 = aryl; R^4, R^5 = alkyl) via a double intramolecular Friedel−Crafts reaction or a 1-methyl-3-phenyl-1*H*-indene derivative **4a** ($R^1 = R^2 = R^3 = R^4 = C_6H_5$; R^5 = Me for **1a**) via an intramolecular Friedel−Crafts reaction in good to high yields in the presence of Lewis acids such as $Sn(OTf)_2$ under mild conditions (Scheme 1).[7b,8] These findings provide novel and alternative synthetic protocols in the preparation of a variety of aromatic compounds on the basis of the substituted manner of arylvinylidenecyclopropanes **1**. Although preliminary results on the Lewis-acid $Sn(OTf)_2$-catalyzed arylvinylidenecyclopropanes **1** have already been communicated,[7] herein we describe the full details on the scope and limitations as well as mechanistic insights of this Lewis-acid-catalyzed interesting rearrangement of multisubstituted arylvinylidenecyclopropanes **1**. In this paper, significant substituent effects on the aromatic rings and the influence of substituents on the cyclopropyl rings will be discussed in detail.

SCHEME 1. Lewis-Acid-Catalyzed Rearrangement of Arylvinylidenecyclopropanes 1

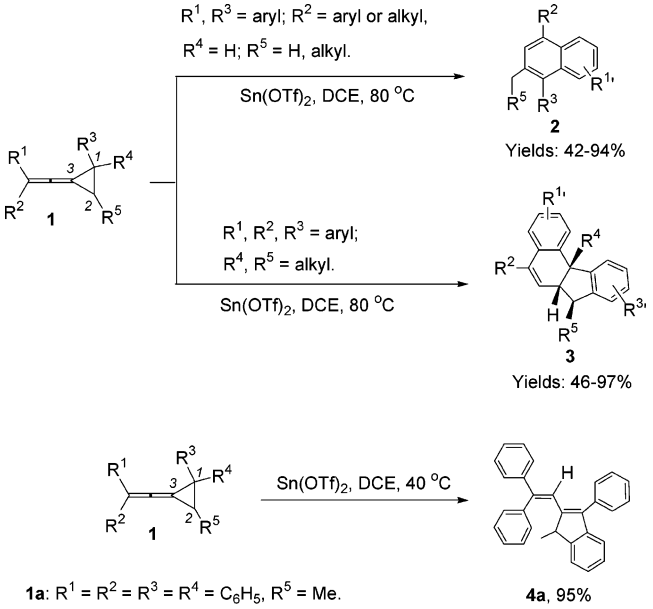

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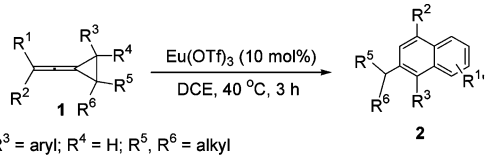
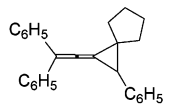
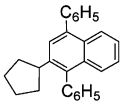
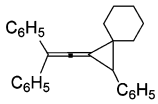
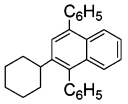
TABLE 1. Lewis-Acid Eu(OTf)$_3$-Catalyzed Rearrangement of Arylvinylidenecyclopropanes 1 in DCE at 40 °C

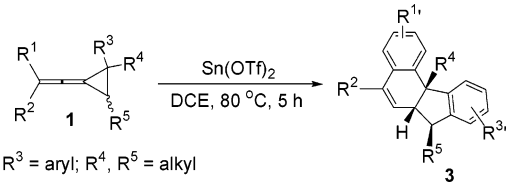


R^1, R^2, R^3 = aryl; R^4 = H; R^5, R^6 = alkyl

entry	1 ($R^1/R^2/R^3/R^5/R^6$)	yield/[%][a] 2
1	**1b** ($C_6H_5/C_6H_5/C_6H_5$/Me/Me)	**2a**, 98
2	**1c** ($C_6H_5/C_6H_5/p$-ClC_6H_4/Me/Me)	**2b**, 73
3	**1d** ($C_6H_5/C_6H_5/p$-BrC_6H_4/Me/Me)	**2c**, 86
4	**1e** ($C_6H_5/C_6H_5/p$-MeC_6H_4/Me/Me)	**2d**, 88
5	**1f** (p-MeC_6H_5/p-MeC_6H_5/C_6H_5/Me/Me)	**2e**, 64
6	**1g** 	 **2f**, 67
7	**1h** 	 **2g**, 64
8	**1i** (p-FC_6H_5/p-FC_6H_5/C_6H_5/Me/Me)	**2h**, 78
9	**1j** (p-ClC_6H_5/p-ClC_6H_5/C_6H_5/Me/Me)	**2i**, 67

[a] Isolated yields.

TABLE 2. Sn(OTf)$_2$-Catalyzed Rearrangement of Arylvinylidenecyclopropanes 1k−o in DCE at 80 °C



R^1, R^2, R^3 = aryl; R^4, R^5 = alkyl

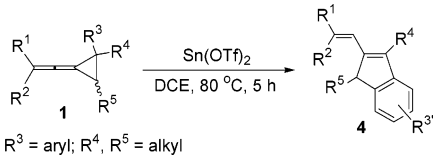
entry	1 ($R^1/R^2/R^3/R^4/R^5$)	3, yield (%)[b]
1	**1k** ($C_6H_5/C_6H_5/C_6H_5$/Me/Me) (1:2)[a]	**3a**, 74
2	**1l** ($C_6H_5/C_6H_5/p$-MeC_6H_4/Me/Me) (1:1)[a]	**3b**, 84
3	**1m** ($C_6H_5/C_6H_5/p$-$MeOC_6H_4$/Me/Me) (9:1)[a]	**3c**, 82
4	**1n** (p-MeC_6H_4/p-MeC_6H_4/C_6H_5/Me/Me) (1:3)[a]	**3d**, 47
5	**1o** ($C_6H_5/C_6H_5/C_6H_5$/Et/Me) (1:1)[a]	**3e**, 96

[a] Syn:anti. [b] Isolated yields.

Results and Discussion

Lewis-Acid-Catalyzed Rearrangement of Aryl-Disubstituted Arylvinylidenecyclopropanes 1 For Which R^1, R^2, R^3 = Aryl; R^4 = H; and R^5, R^6 = Alkyl. We first attempted to examine the Lewis-acid-catalyzed rearrangement of aryl-disubstituted arylvinylidenecyclopropanes **1b**−**j** bearing 1,1-dialkyl groups and a 2-aryl group at the corresponding cyclopropyl ring (R^1, R^2, R^3 = aryl; R^4 = H; R^5, R^6 = alkyl). An initial examination was carried out using arylvinylidenecyclopropane **1b** (R^1, R^2, R^3 = C_6H_5; R^4 = H; R^5, R^6 = Me) as substrate in the presence of a variety of Lewis acids in DCE and other solvents. The results are summarized in Table SI-1, and the corresponding naphthalene derivative **2a** was formed in moderate to good yield in the presence of a variety of Lewis acids (Supporting Information). We found that these optimized reaction conditions are to carry out the reaction in DCE at 40 °C using Eu(OTf)$_3$ (10 mol %) as a catalyst (Table SI-1, entry 7). In oxygen-atom-containing solvents such as THF, methanol, and DMF, no reaction occurred, presumably due to their coordinative nature to Lewis acids to deactivate the catalytic abilities.

TABLE 3. Sn(OTf)$_2$-Catalyzed Rearrangement of Arylvinylidenecyclopropanes 1p−v in DCE at 80 °C



R^1, R^2, R^3 = aryl; R^4, R^5 = alkyl

entry	1 ($R^1/R^2/R^3/R^4/R^5$)	4, yield (%)[b]
1	**1p** ($C_6H_5/C_6H_5/p$-ClC_6H_4/Me/Me) (1:2)[a]	**4b**, 91
2	**1q** ($C_6H_5/C_6H_5/p$-BrC_6H_4/Me/Me) (1:2)[a]	**4c**, 97
3	**1r** (p-FC_6H_4/p-FC_6H_4/p-ClC_6H_4/Me/Me) (2:1)[a]	**4d**, 95
4	**1s** (p-FC_6H_4/p-FC_6H_4/p-MeC_6H_4/Me/Me) (*syn*)	**4e**, 88
5	**1t** (p-FC_6H_4/p-FC_6H_4/C_6H_5/Me/Me) (1:3)[a]	**4f**, 97
6	**1u** (p-ClC_6H_4/p-ClC_6H_4/C_6H_5/Me/Me) (3:2)[a]	**4g**, 96
7	**1v** ($C_6H_5/C_6H_5/p$-FC_6H_4/Me/Me) (1:1)[a]	**4h**, 91

[a] Syn:anti. [b] Isolated yields.

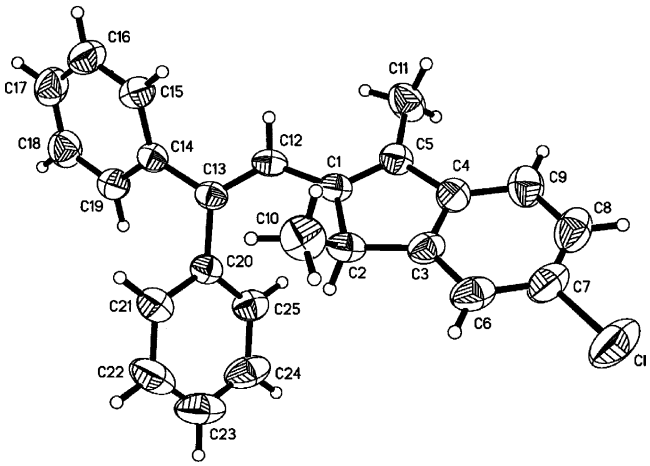


FIGURE 1. ORTEP drawing of **4b**.

Next, we carried out the reaction of a variety of arylvinylidenecyclopropane derivatives **1c**−**j** in the presence of Eu(OTf)$_3$ under these optimized conditions. The results including arylvinylidenecyclopropane **1b** are summarized in Table 1. As can be seen from Table 1, the corresponding rearranged products **2b**−**i**, naphthalene derivatives, were obtained in moderate to good yields within 3 h (Table 1, entries 1−9). For spiro-type arylvinylidenecyclopropane derivatives **1g** and **1h**, the corresponding naphthalene derivatives **2f** and **2g** were obtained in 67% and 64% yields, respectively (Table 1, entries 6 and 7). For arylvinylidenecyclopropane derivatives **1i** and **1j** bearing electron-withdrawing groups on the benzene rings of R^1 and R^2, similar rearrangements also took place to give the corresponding naphthalene derivatives **2h** and **2i** in moderate yields (Table 1, entries 8 and 9).

A plausible mechanism for rearrangement of arylvinylidenecyclopropanes **1b**−**j** in the presence of Lewis acid has been described in the previous communication via a vinyl-group-

SCHEME 2. Lewis-Acid-Catalyzed Rearrangement of Arylvinylidenecyclopropanes 1p−v

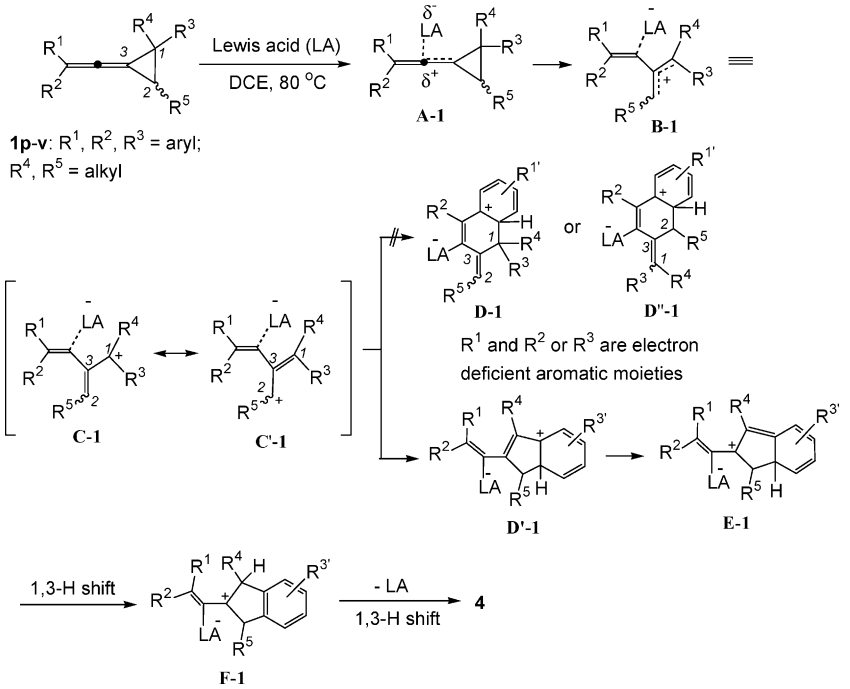
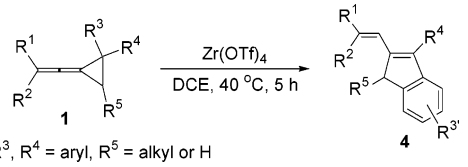


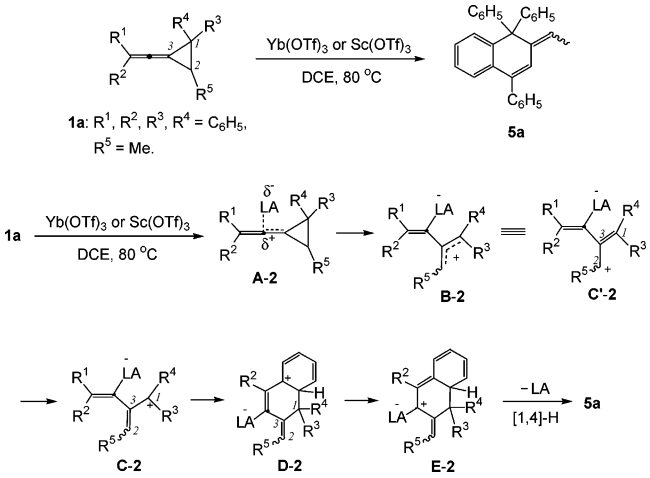
TABLE 4. $Zr(OTf)_4$-Catalyzed Rearrangement of Arylvinylidenecyclopropanes 1 in DCE at 40 °C



entry	**1** ($R^1/R^2/R^3/R^4/R^5$)	**4**, yield (%)[a]
1	**1a** ($C_6H_5/C_6H_5/C_6H_5/C_6H_5$/Me)	**4a**, 98
2	**1w** ($C_6H_5/C_6H_5/p$-ClC_6H_4/p-ClC_6H_4/Me)	**4i**, 95
3	**1x** ($C_6H_5/C_6H_5/p$-FC_6H_4/p-FC_6H_4/Me)	**4j**, 97
4	**1y** ($C_6H_5/C_6H_5/p$-MeC_6H_4/p-MeC_6H_4/Me)	**4k**, 90
5	**1z** ($C_6H_5/C_6H_5/p$-$MeOC_6H_4/p$-$MeOC_6H_4$/Me)	**4l**, 94
6	**1aa** (p-FC_6H_4/p-$FC_6H_4/C_6H_5/C_6H_5$/Me)	**4m**, 91
7	**1ab** (p-MeC_6H_4/p-$MeC_6H_4/C_6H_5/C_6H_5$/Me)	**4n**, 96
8	**1ac** ($C_6H_5/C_6H_5/C_6H_5/C_6H_5$/H)	**4o**, 95
9	**1ad** ($C_6H_5/C_6H_5/p$-ClC_6H_4/p-ClC_6H_4/H)	**4p**, 76
10	**1ae** ($C_6H_5/C_6H_5/p$-MeC_6H_4/p-MeC_6H_4/H)	**4q**, 83

[a] Isolated yields.

SCHEME 3. Lewis-Acid $Yb(OTf)_3$- or $Sc(OTf)_3$-Catalyzed Rearrangement of Arylvinylidenecyclopropane 1a



stabilized zwitterionic intermediate,[9,10] intramolecular Friedel−Crafts reaction, 1,3-proton shift, and aromatization.[7a]

Lewis-Acid-Catalyzed Rearrangement of Arylvinylidenecyclopropanes 1 For Which R^1, R^2, R^3 = Aryl and R^4, R^5 = Alkyl. Previously, we reported that using arylvinylidenecyclopropanes **1** having three substituents at the C-1 and C-2 positions (R^1, R^2, R^3 = aryl; R^4, R^5 = alkyl) (syn/anti isomeric mixtures) as substrates, an interesting rearrangement took place to give 6a*H*-benzo[*c*]fluorine derivatives **3** stereoselectively with syn-configuration in DCE in the presence of $Sn(OTf)_2$ upon heating at 80 °C.[7b] Further studies revealed that the electronic nature of aryl groups of this kind of substrates dramatically affects the reaction pattern. In this full paper we attempted to correct our conclusion because the structures of the products derived from arylvinylidenecyclopropanes having electron-deficient aromatic group were misassigned.[12] For example, we found that for arylvinylidenecyclopropanes **1k−o** in which aromatic groups of R^1, R^2, and R^3 have no electron-deficient substituents on the benzene ring and the cyclopropyl ring, the corresponding 6a*H*-benzo[*c*]fluorine derivatives **3a−e** can be obtained in moderate

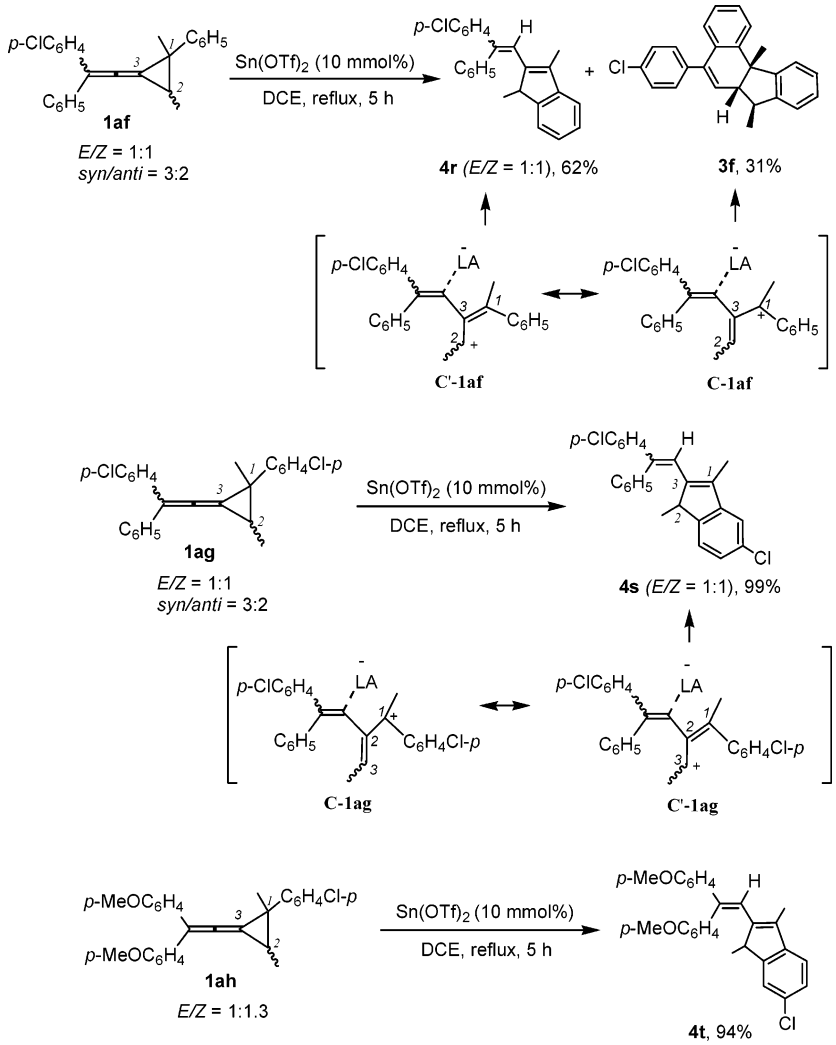
(9) (a) In *Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; John Wiley & Sons: New York, 1997; pp 137−138. (b) Olah, G. A.; Reddy, V. P.; Prakash, G. K. S. *Chem. Rev.* **1992**, *92*, 69−95.

(10) Bollinger, J. M.; Brinich, J. M.; Olah, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 4025−4033.

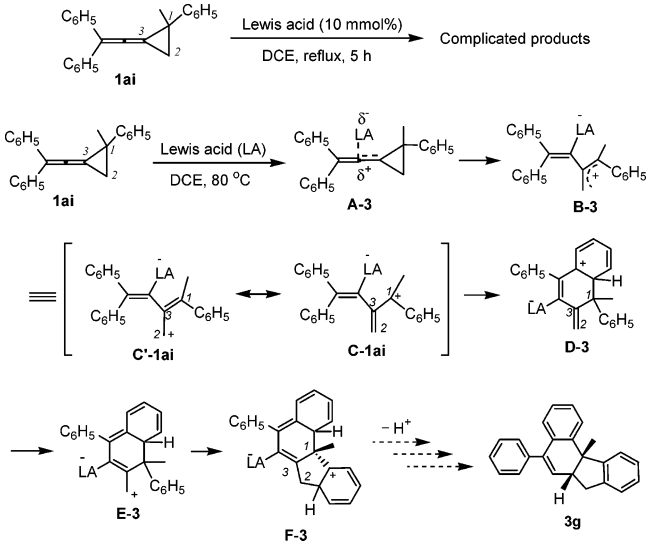
(11) For the mechanism of the 1,3-proton shift, see: Carey, F. A.; Sundburg, R. J. *Advanced Organic Chemistry*, 3rd ed.; Plenum Press: New York, 1990; pp 609−613.

(12) In our previous communication, the structures of products **2b**, **2c**, and **2f** have been misassigned. This misassignment is simply due to our carelessness. Since the structures of 6a*H*-benzo[*c*]fluorine derivative **3a** and 1-methyl-3-phenyl-1*H*-indene derivative **4a** have been determined by X-ray diffraction, we overlooked the NMR spectroscopic data of the products derived from arylvinylidenecyclopropanes **1b**, **1c**, and **1f**, which have electron-deficient aromatic moieties.

SCHEME 4. Sn(OTf)$_2$-Catalyzed Rearrangement of Unsymmetric Arylvinylidenecyclopropanes 1af, 1ag, and 1ah



SCHEME 5. Lewis-Acid-Catalyzed Rearrangement of Arylvinylidenecyclopropane 1ai



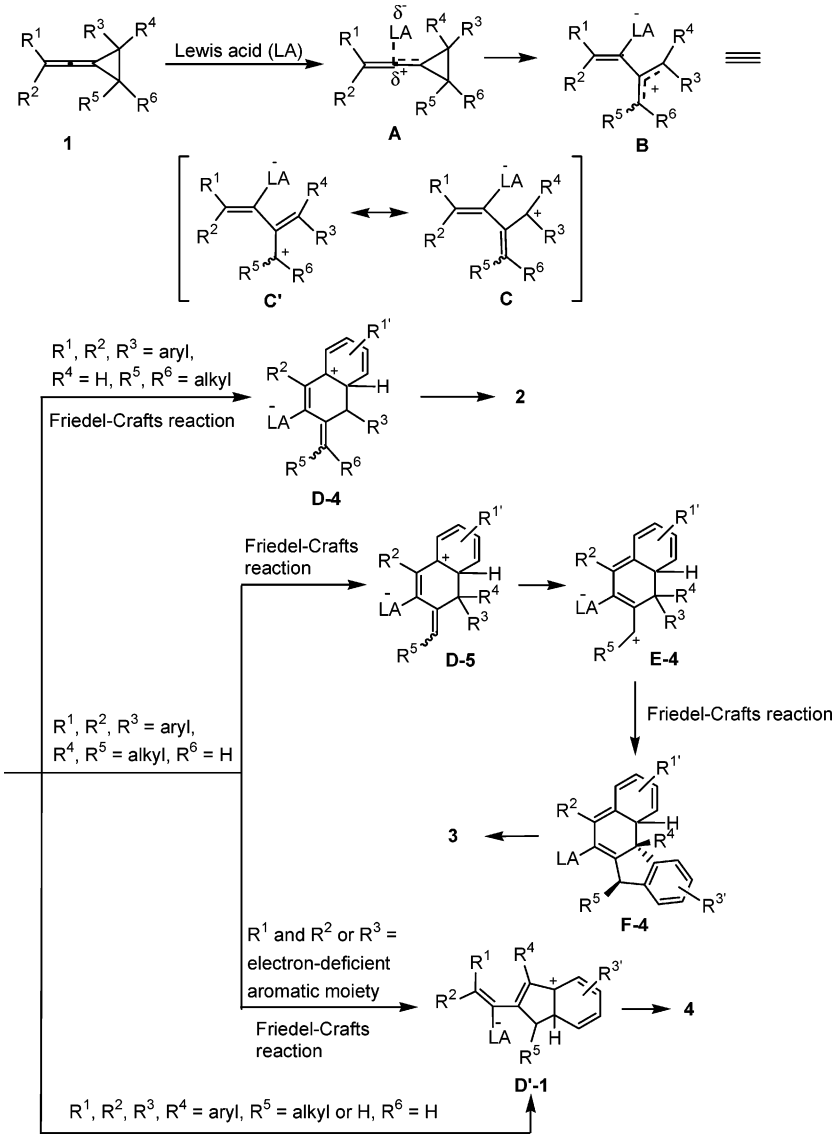
to good yields via a double intramolecular Friedel−Crafts reaction as those described in the previous paper (Table 2).[7b] However, for arylvinylidenecyclopropanes **1p**−**v**, as long as one of the aromatic groups of R^1, R^2, or R^3 has electron-withdrawing substituents on the benzene ring or cyclopropyl ring, we found that the rearranged products were indene derivatives **4b**−**h** obtained via an intramolecular Friedel−Crafts reaction under standard conditions (Table 3). In order to unambiguously confirm this drastic difference on the reaction product due to the electronic nature on the aromatic rings of arylvinylidenecyclopropanes, X-ray diffraction of **4b** was carried out. The ORTEP drawing of **4b** is shown in Figure 1.[13]

A rational explanation of this drastic difference can be attributed to the nature of Friedel−Crafts reaction.[14] For arylvinylidenecyclopropanes **1k**−**o** having no electron-deficient aromatic substituents, the corresponding 6a*H*-benzo[*c*]fluorine derivatives **3** were formed with a syn-configuration via a double intramolecular Friedel−Crafts reaction as described in the previous communication.[7b]

(13) The crystal data of **4b** has been deposited in CCDC with number 295457. Empirical formula: C25H21Cl. Formula weight: 356.87. Crystal color, habit: colorless, prismatic. Crystal dimensions: 0.423 × 0.270 × 0.201 mm. Crystal system: monoclinic. Lattice type: primitive. Lattice parameters: a = 11.0128(11) Å, b = 9.9609(10) Å, c = 18.4801(18) Å, α = 90°o, β = 102.407(2)°, γ = 90°, V = 1979.9(3) Å^3. Space group: $P2_1/c$. Z = 4. D_{calcd} = 1.197 g/cm^3. F_{000} = 752. Diffractometer: Rigaku AFC7R. Residuals: R, Rw: 0.0456, 0.0972. The crystal data of **3a** and **4a** can be found in the Supporting Information of the previous communication (ref 7b).

(14) (a) Fleming, I. *Chemtracts: Org. Chem.* **2001**, *14*, 405−406. (b) Chevrier, B.; Weis, R. *Angew. Chem.* **1974**, *86*, 12−21.

SCHEME 6. Summary of Lewis-Acid-Catalyzed Rearrangement of Arylvinylidenecyclopropanes 1



For arylvinylidenecyclopropanes **1p**−**v** having at least one electron-deficient aromatic compound, similar to the previous examples,[7] the corresponding cyclopropyl ring-opened zwitterionic intermediate **B-1** or the resonance-stabilized zwitterionic intermediates **C′-1** and **C-1** are formed from the initial zwitterionic intermediate **A-1**. Intramolecular Friedel−Crafts reaction with the aromatic R^3 group at the **C-1** position takes place to produce zwitterionic intermediate **D′-1**, which affords the corresponding zwitterionic intermediate **E-1** via an allylic rearrangement. Subsequent 1,3-proton shift along with release of the Lewis acid via zwitterionic intermediate **F-1** produces the corresponding indene derivative **4** (Scheme 2). When R^3 is an electron-deficient aromatic moiety and R^1 and R^2 are electron-neutral aromatic moieties (phenyl groups) or electron-rich aromatic moieties (4-methylphenyl groups), the corresponding zwitterionic intermediate **C-1** is not as stable as that when R^3 is an electron-neutral aromatic moiety (phenyl group) or electron-rich aromatic moiety (4-methylphenyl group) since in this case the corresponding zwitterionic intermediate **C-1** is more stabilized by the electron-rich aromatic moiety from the point of view of the stabilization of cationic intermediate. Sterically, intramolecular Friedel−Crafts reaction can more easily take place with the aromatic R^3 group at the C-1 position than that with the aromatic R^1 or R^2 group in zwitterionic intermediate **C′-1**. Therefore, intramolecular Friedel−Crafts reaction takes place from zwitterionic intermediate **C′-1** with the aromatic R^3 group at the C-1 position to give the corresponding indene derivative **4** (Scheme 2). When R^3 is an electron-neutral or electron-rich aromatic moiety and R^1 and/or R^2 are electron-deficient aromatic moieties/moiety, the subsequent intramolecular Friedel−Crafts reaction cannot easily take place from zwitterionic intermediate **C-1** to provide the corresponding zwitterionic intermediates **D-1** and **D″-1** because intramolecular Friedel−Crafts reaction takes place more easily for electron-rich aromatic moiety,[14] although the corresponding zwitterionic intermediate **C-1** is more stabilized by the electron-rich aromatic moiety of R^3 group. This is why in the case of arylvinylidenecyclopropanes **1p**−**v** having electron-deficient aromatic moieties (R^1 and R^2 or R^3), the corresponding indene derivatives **4** are exclusively formed.

Lewis-Acid-Catalyzed Rearrangement of Arylvinylidenecyclopropanes 1 For Which R^1, R^2, R^3, R^4 = Aryl and R^5 = Alkyl or H. In addition, for arylvinylidenecyclopropanes **1** bearing two aromatic groups at the C-1 position, only one case

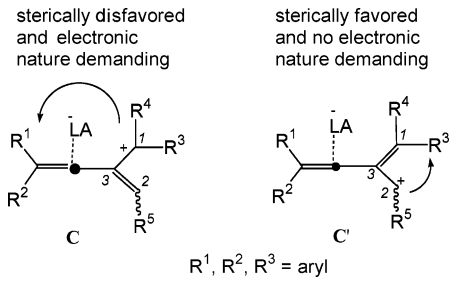


FIGURE 2. Difference in two kinds of intramolecular Friedel−Crafts reactions.

has been reported using **1a** ($R^1 = R^2 = R^3 = R^4 = C_6H_5$; R^5 = Me) as substrate to give the corresponding 1-methyl-3-phenyl-1*H*-indene derivative **4a** in good yield in DCE in the presence of $Sn(OTf)_2$ in our previous short communication.[7b] Therefore, we further optimized these reaction conditions and synthesized a variety of arylvinylidenecyclopropanes **1w**−**ae** bearing two aromatic groups at the C-1 position for this reaction. These reaction conditions were optimized in a similar manner as those described above. The results are summarized in Table SI-2 (Supporting Information). $Zr(OTf)_4$ is the most effective catalyst to give **4a** in 98% yield at 40 or 80 °C within 5 h (Table SI-2, entries 7 and 8). Solvent effects have also been examined with $Zr(OTf)_4$ (10 mol %) at 40 °C in toluene, MeCN, THF, ethanol, DMF, and hexane. We found that the best reaction conditions are to carry out the reaction in DCE at 40 °C using $Zr(OTf)_4$ (10 mol %) as a catalyst (Table SI-2, Supporting Information).

Next, we carried out reaction of a variety of arylvinylidenecyclopropanes **1w**−**ae** (R^1, R^2, R^3, R^4 = aryl; R^5 = alkyl or H) under these optimized conditions. The results including arylvinylidenecyclopropane **1a** are summarized in Table 4. As can be seen from Table 4, the corresponding rearranged products indene derivatives, **4a** and **4i**−**q**, were obtained in good to high yields within 5 h in DCE at 40 °C for arylvinylidenecyclopropanes **1w**−**ae** having either electron-rich or electron-deficient aromatic moieties (Table 4). In this case, when R^5 does not have a substituent (R^5 = H for **1ac**−**ae**), the corresponding indene derivatives **4o**−**q** were also obtained in 76−95% yields under standard conditions (Table 4, entries 8−10).

In this case, sterically, the subsequent intramolecular Friedel−Crafts reaction with the aromatic R^3 or R^4 group at the C-1 position can easily take place to produce the corresponding indene derivative **4** as described in the previous communication.[7b]

Lewis-Acid Effects on the Rearrangement of Arylvinylidenecyclopropanes 1 For Which R^1, R^2, R^3, R^4 = aryl and R^5 = alkyl. Interestingly, we found that when $Yb(OTf)_3$ or $Sc(OTf)_3$ was used in the rearrangement of arylvinylidenecyclopropane **1a**, the rearranged product **5a**, 2-ethylidene-1,1,4-triphenyl-1,2-dihydro-naphthalene, was formed as a mixture of *Z*:*E* isomers in higher yields rather than the indene derivative in DCE at 40 or 80 °C (Scheme 3). The structure of **5a** was determined by spectroscopic data (Supporting Information). The reaction conditions were examined in a similar manner as that described above. The results are summarized in Table SI-3 (Supporting Information). The best reaction conditions are found when the reaction is carried out in DCE using $Yb(OTf)_3$ as a catalyst at 80 °C (Table SI-3, entry 4). The reaction mechanism is also shown in Scheme 3. The corresponding cyclopropyl ring-opened zwitterionic intermediate **B-2** or the resonance-stabilized zwitterionic intermediates **C′-2** and **C-2** are formed similarly from the initial zwitterionic intermediate **A-2** in the presence of Lewis-acid $Yb(OTf)_3$ or $Sc(OTf)_3$. Subsequently, intramolecular Friedel−Crafts reaction of intermediate **C-2** stabilized by two aromatic R^3 and R^4 groups with the aromatic R^1 or R^2 group produces the cyclized zwitterionic intermediate **D-2**, which affords the corresponding zwitterionic intermediate **E-2** via an allylic rearrangement. In the presence of Lewis-acid $Yb(OTf)_3$ or $Sc(OTf)_3$, the second sterically demanding intramolecular Friedel−Crafts reaction of intermediate **E-2** with the aromatic R^3 group does not take place to give the corresponding 6a*H*-benzo[*c*]fluorine derivative. Alternatively, the 1,4-proton shift along with the release of Lewis acid takes place to produce the corresponding 1,2-dihydro-naphthalene derivative **5a**.[15] Since R^3 and R^4 are not hydrogen atoms, it is impossible to give the corresponding naphthalene derivative via aromatization from zwitterionic intermediate **E-2**. Therefore, 1,2-dihydro-naphthalene derivative **5a** becomes the corresponding thermodynamically favored product in this case. This result suggests that the employed Lewis acids also play an important role in this reaction. For the same arylvinylidenecyclopropane substrate, different Lewis acid can produce different products even under similar reaction conditions.

Mechanistic Discussion. In order to clarify the significant substituent effects on the rearrangement of arylvinylidenecyclopropanes catalyzed by Lewis acid, we attempted to synthesize unsymmetric arylvinylidenecyclopropanes **1af** and **1ag** bearing electron-deficient aromatic moieties to examine their rearrangement under our standard conditions. With unsymmetrical arylvinylidenecyclopropane **1af** as the substrate under these optimized conditions, we found that 2-(2,2-diarylvinyl)-1-methyl-3-methyl-1*H*-indene derivative **4r** can be obtained in 62% yield as a mixture of *E*- and *Z*-isomers along with 6a*H*-benzo[*c*]fluorine derivative **3f** in 31% yield (Scheme 4). For unsymmetrical arylvinylidenecyclopropane **1ag**, which has a *p*-chlorophenyl group at the C-1 position of the cyclopropyl ring, 2-(2,2-diarylvinyl)-1-methyl-3-methyl-1*H*-indene derivative **4s** was obtained in 99% yield exclusively as a mixture of *E*- and *Z*-isomers (Scheme 4). These results suggest that the double intramolecular Friedel−Crafts reaction from zwitterionic intermediate **C-1af** indeed selectively takes place with the phenyl group to give the corresponding 6a*H*-benzo[*c*]fluorine derivative **3f** along with another sterically favored intramolecular Friedel−Crafts reaction with the phenyl group at the C-1 position from zwitterionic intermediate **C′-1af** to produce the corresponding indene derivative **4r**. In the case of arylvinylidenecyclopropane **1ag**, the corresponding zwitterionic intermediate **C-1ag** is not as stable due to the electron-deficient *p*-chlorophenyl group, and therefore, the sterically favored intramolecular Friedel−Crafts reaction with the *p*-chlorophenyl group at the C-1 position from zwitterionic intermediate **C′-1ag** exclusively takes place to produce the corresponding indene derivative **4s** in high yield (Scheme 4). For arylvinylidenecyclopropane **1ah** bearing two strongly electron-donating methoxy groups on the benzene rings and an electron-deficient *p*-chlorophenyl group at the C-1 position of the cyclopropyl ring, the subsequent intramolecular Friedel−Crafts reaction still exclusively proceeds through the sterically favored way to give the corresponding indene derivative **4t** in 94% yield under standard conditions (Scheme 4).

These results obtained in the above control experiments can explain the subtle substituent effects in this interesting Lewis-

(15) For arylvinylidenecyclopropanes **1w**, **1x**, **1z**, and **1aa**, similar products can be isolated in moderate yields along with some unidentified byproducts (Table SI-4 in the Supporting Information).

acid-catalyzed rearrangement of arylvinylidenecyclopropanes **1**. The stability of zwitterionic intermediate, electronic nature of aromatic group, and sterically demanding intramolecular Friedel−Crafts reaction play key roles in this reaction.

Moreover, when using arylvinylidenecyclopropane **1ai** as the substrate under standard conditions, complicated products were formed from which none of the identified compound can be cleanly isolated (Scheme 5). This may be due to the fact that the corresponding zwitterionic intermediate **C′-1ai**, derived from the initial zwitterionic intermediates **A-3** and **B-3**, is not as stable as the corresponding zwitterionic intermediate bearing an alkyl group at the C-2 position. In addition, only one phenyl group is at the C-1 position of the cyclopropyl ring. Therefore, the sterically demanding intramolecular Friedel−Crafts reaction does not have enough room to take place to give the corresponding indene derivative as a major product, although for arylvinylidenecyclopropanes **1ac**−**ae** bearing two aromatic groups at the C-1 position this type of intramolecular Friedel−Crafts reaction can easily take place to produce the corresponding indene derivatives in good yields. Moreover, in the course of the formation of the corresponding 6a*H*-benzo[*c*]fluorine derivative **3g** from zwitterionic intermediate **C-1ai**, the related zwitterionic intermediate **D-3** or **E-3** is not as stable as the corresponding zwitterionic intermediate bearing an alkyl group at the C-2 position. Therefore, the second intramolecular Friedel−Crafts reaction cannot easily take place to give the corresponding 6a*H*-benzo[*c*]fluorine derivative **3g** as a major product via the corresponding zwitterionic intermediate **F-3**. In any sense, there is no major reaction pathway in the rearrangement of arylvinylidenecyclopropane **1ai** catalyzed by Lewis acid. Many products would be produced in small amounts due to the fact that there is no major reaction course under our standard conditions. This result suggests that the structure and stability of the cationic intermediate in the corresponding zwitterionic intermediate are important in this reaction.

In conclusion, we identified an efficient Lewis-acid-catalyzed rearrangement of arylvinylidenecyclopropanes **1** having three substituents at the cyclopropyl ring to provide easy access to naphthalene derivatives **2** through an intramolecular Friedel−Crafts reaction, or 6a*H*-benzo[*c*]fluorine derivatives **3** via a double intramolecular Friedel−Crafts reaction, or the corresponding indene derivative **4** via a sterically favored intramolecular Friedel−Crafts reaction under mild reaction conditions in good to excellent yields depending on the substituents at the cyclopropyl ring and the electronic nature of the aryl groups. The corresponding reaction mechanisms have been discussed on the basis of the control experiments and related investigations. In addition, the scope and limitations have been disclosed in this paper. Since the reaction pattern of the present reactions is complicated, the corresponding simply summarized reaction mechanism and reaction pathways are shown in Scheme 6. Intramolecular Friedel−Crafts reaction of carbocation in zwitterionic intermediate **C** with an aromatic R^1 or R^2 group is a sterically disfavored and electronic nature demanding process. Therefore, for an electron-deficient aromatic moiety, this kind of intramolecular Friedel−Crafts reaction will not take place (Figure 2). However, intramolecular Friedel−Crafts reaction of carbocation in zwitterionic intermediate **C′** with an aromatic R^3 group is a sterically favored and no electronic nature demanding process. Therefore, even for an electron-deficient aromatic moiety this kind of intramolecular Friedel−Crafts reaction can easily take place (Figure 2). The difference in the electronic nature and steric requirement of the two kinds of intramolecular Friedel−Crafts reactions produces different products. In addition, for the same arylvinylidenecyclopropane substrate, different Lewis acid can produce different products even under similar reaction conditions. At the present stage, the influence of the metal nature in the Lewis acids is not understood very well. Efforts are in progress to elucidate further mechanistic details of these reactions and understand their scopes and limitations. Work along this line is currently in progress.

Experimental Section

General Remarks. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass spectra were recorded by EI, MALDI, and ESI methods, and HRMS was measured by EI method. CHN microanalyses were recorded on an analyzer. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC plates. Flash column chromatography was carried out using 300−400 mesh silica gel at increased pressure.

Typical Reaction Procedure for the Preparation of Diarylvinylidenecyclopropanes. A mixture of Bu_4NHSO_4 (10 mmol) and powdered NaOH (80 g) was added to a tetrahydrofuran (THF, 50 mL) solution containing 1,1-dibromo-2,2-diphenylcyclopropane (10 mmol) and an excess of 1,1-diphenylprop-1-ene (12 mmol). The mixture was vigorously stirred at room temperature for 24 h. Flash column chromatography of the resulting mixture on silica gel gave product **1a** (31%) as a white solid.

Typical Reaction Procedure for the Rearrangement of Diarylvinylidenecyclopropanes to 4. To a solution of diarylvinylidenecyclopropane **1a** (76.8 mg, 0.2 mmol) in 1,2-dichloroethane (DCE) (2.0 mL) was added $Zr(OTf)_4$ (13.7 mg, 0.02 mmol), and the reaction mixture was stirred for 5 h at 40 °C (monitored by TLC). After the starting material diarylvinylidenecyclopropane **1a** was consumed, the solvent was removed under reduced pressure and the residue subjected to a flash column chromatography to give the desired product **4a** (75.3 mg, 98%) as a white solid.

Acknowledgment. We thank the Shanghai Municipal Committee of Science and Technology (04JC14083, 06XD14005), Chinese Academy of Sciences (KGCX2-210-01), East China University of Science and Technology of Changjiang Scholarship, and National Natural Science Foundation of China for financial support (20472096, 203900502, and 20672127).

Supporting Information Available: Experimental details, IR, ^{13}C and ^{1}H NMR spectroscopic and analytic data for **2**−**5**, and X-ray crystal data of **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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