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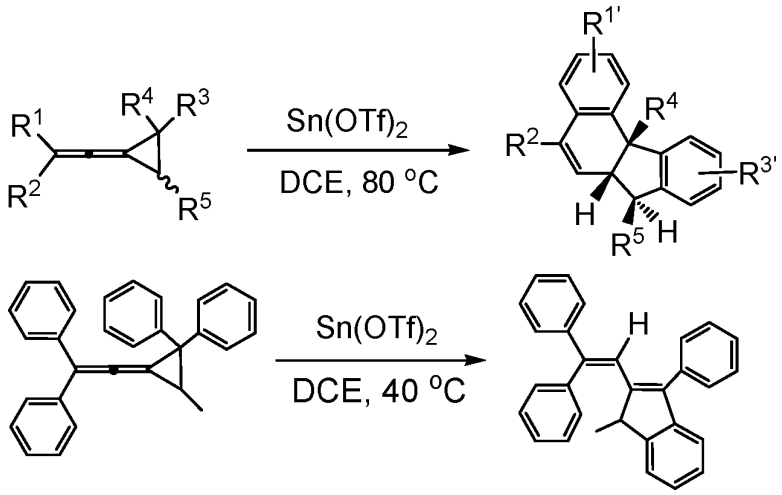

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Lewis Acid-Catalyzed Rearrangement of Multi-Substituted Arylvinylidenecyclopropanes

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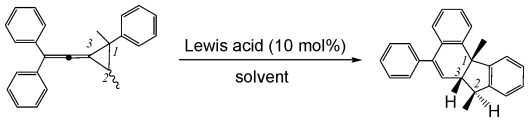
Thermal and photochemical skeletal conversions of vinylidenecyclopropanes **1** have attracted much attention from mechanistic, theoretical, spectroscopic, and synthetic viewpoints.[1,2] Recently, we have been investigating the Lewis acid-catalyzed ring-opening reactions of methylenecyclopropanes (MCPs)[3] and vinylidenecyclopropanes **1**.[4,5] Thus far, we have found that aryl-substituted derivatives of **1** undergo interesting rearrangements in the presence of Lewis or Brønsted acids to give the corresponding naphthalene derivatives in good to high yields.[4] We now wish to report the Lewis acid-catalyzed rearrangement of arylvinylidenecyclopropanes **1** having three substituents at the 1- and 2-positions of the corresponding cyclopropane to give the corresponding 6a*H*-benzo[*c*]fluorine or phenyl-1*H*-indene derivatives **2** in good to high yields under mild conditions.

An initial examination was carried out using **1a** (*Z*/*E* = 1/2 mixture determined by NOESY NMR spectroscopic analysis; see Supporting Information) as substrate in the presence of a variety of Lewis acids. We found that an interesting rearrangement took place to give 6a*H*-benzo[*c*]fluorine derivative **2a** stereoselectively with *syn*-configuration upon heating. Using $Sn(OTf)_2$ (10 mol %) as the catalyst in 1,2-dichloroethane (DCE), no reaction occurred at room temperature, and the reaction was sluggish at 40 °C. However, it proceeded smoothly under reflux (80 °C) to give **2a** in 74% yield after 6 h (Table 1, entries 2−4). Using other Lewis acids,

Table 1. Rearrangement of Diphenylvinylidenecyclopropane **1a** to (6a,7,11b)-7,11b-Dihydro-7,11b-dimethyl-5-phenyl-6a*H*-benzo[*c*]-fluorine **2a** in the Presence of a Variety of Lewis Acids (0.1 equiv)



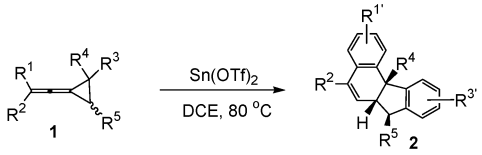
1a, (*Z*/*E* = 1:2) **2a**

entry	solvent	catalyst	temp (°C)	time (h)	yield[a] **2a** (%)
1	$ClCH_2CH_2Cl$	none	80	120	*c*
2	$ClCH_2CH_2Cl$	$Sn(OTf)_2$	25	120	*c*
3	$ClCH_2CH_2Cl$	$Sn(OTf)_2$	40	20[b]	21
4	$ClCH_2CH_2Cl$	$Sn(OTf)_2$	80	6[b]	74
5	$ClCH_2CH_2Cl$	$Zr(OTf)_4$	80	8[b]	31
6	$ClCH_2CH_2Cl$	$Zr(OTf)_4$	40	2[b]	30
7	$ClCH_2CH_2Cl$	$Cu(OTf)_2$	80	2[b]	30
8	$ClCH_2CH_2Cl$	BF_3Et_2O	80	5[b,d]	21
9	toluene	$Sn(OTf)_2$	80	6[b]	65
10	CH_3CN	$Sn(OTf)_2$	80	6	*c*
11	THF	$Sn(OTf)_2$	66	6[b]	35
12	DMF	$Sn(OTf)_2$	80	12	*c*
13	EtOH	$Sn(OTf)_2$	78	12	*c*
14	hexane	$Sn(OTf)_2$	69	6[b]	56

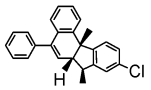
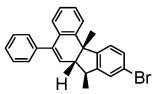
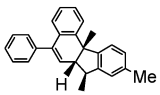
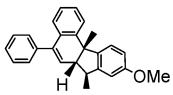
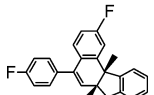
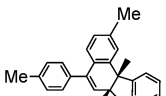
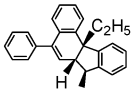
[a] Isolated yield. [b] Until all of the starting material **1a** was consumed. [c] No reaction occurred. [d] At room temperature, **2a** was obtained in 52% in DCE with 10 mol % of BF_3OEt_2.

such as $Zr(OTf)_4$, $Cu(OTf)_2$, and BF_3·OEt_2, under identical conditions, **2a** was obtained in lower yields (Table 1, entries 5−8). In the presence of lanthanide Lewis acids $Yb(OTf)_3$ and $Sc(OTf)_3$, no reaction occurred. Solvent effects have been examined with $Sn(OTf)_2$ (10 mol %) at 80 °C. DCE is the solvent of choice (Table 1, entries 9−14). Therefore, these optimized reaction conditions are to carry out the reaction in DCE at 80 °C using $Sn(OTf)_2$ (10 mol %) as a catalyst.

Table 2. Lewis Acid $Sn(OTf)_2$-Catalyzed Rearrangement of a Variety of Arylvinylidenecyclopropanes **1** in DCE at 80 °C



1 **2**

entry	R^1, R^2	R^3, R^4, R^5	time/h	yield/[%][a] **2**
1	C_6H_5, C_6H_5	*p*-ClC_6H_4, Me, Me **1b**, (*Z*/*E* = 1:2)	5	 **2b**, 91
2	C_6H_5, C_6H_5	*p*-BrC_6H_4, Me, Me **1c**, (*Z*/*E* = 1:2)	5	 **2c**, 97
3	C_6H_5, C_6H_5	*p*-MeC_6H_4, Me, Me **1d**, (*Z*/*E* = 1:1)	5	 **2d**, 84
4	C_6H_5, C_6H_5	*p*-$MeOC_6H_4$, Me, Me **1e**, (*Z*/*E* = 9:1)	5	 **2e**, 82
5	*p*-FC_6H_4, *p*-FC_6H_4	C_6H_5, Me, Me **1f**, (*Z*/*E* = 1:3)	5	 **2f**, 97
6	*p*-MeC_6H_5, *p*-MeC_6H_5	C_6H_5, Me, Me **1g**, (*Z*/*E* = 1:3)	5	 **2g**, 47
7	C_6H_5, C_6H_5	C_6H_5, Et, Me **1h**, (*Z*/*E* = 2:3)	5	 **2h**, 96

[a] Isolated yield.

Next, we carried out the reaction of a variety of arylvinylidenecyclopropane derivatives **1** (*Z*/*E* isomeric mixtures) in the presence of $Sn(OTf)_2$ under these optimized conditions. The results are sum-

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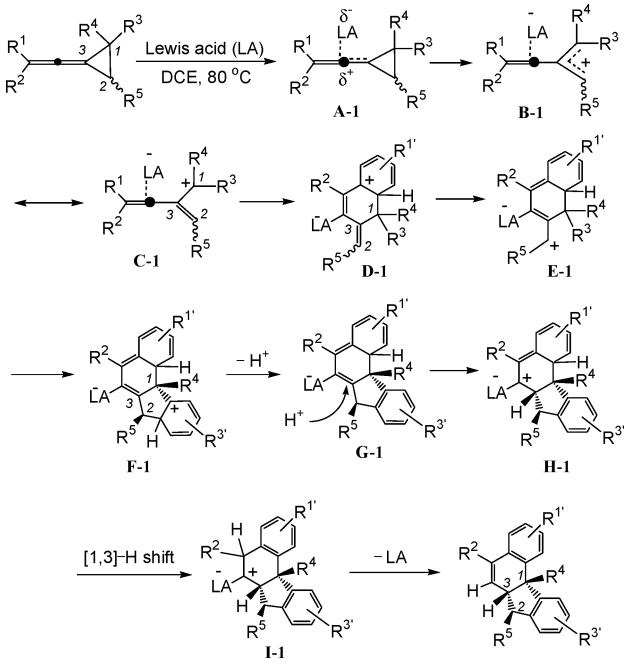
Scheme 1. A Plausible Mechanism for the Rearrangement of Arylvinylidenecyclopropanes **1** and **2** in the Presence of Lewis Acid



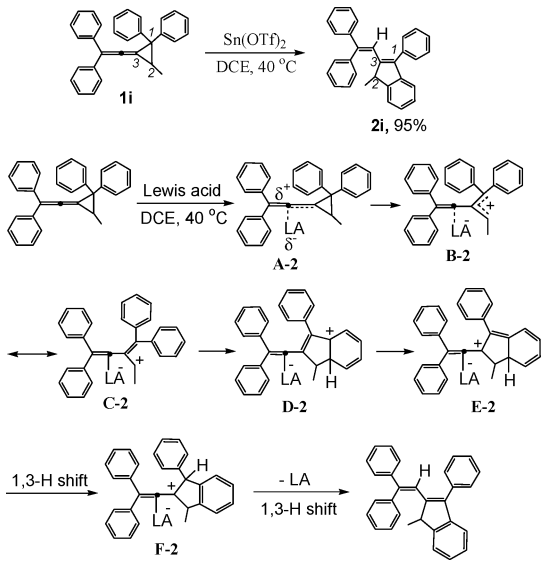
marized in Table 2. As can be seen from Table 2, the corresponding rearranged products **2**, 6a*H*-benzo[*c*]fluorine derivatives, were obtained in good to high yields within 5 h with *syn*-configuration (Table 2, entries 1−7).

The product structures were determined by ^{1}H and ^{13}C NMR spectroscopic data and HRMS or microanalyses (Supporting Information). The structure of **2a** was further confirmed by X-ray diffraction analysis (Supporting Information).

A plausible mechanism for the observed rearrangements of **1** in the presence of Lewis acids is outlined in Scheme 1. The coordination of **1** to the Lewis acid[5] initially gives zwitterionic intermediate **A-1**, a vinyl group stabilized cyclopropyl cationic intermediate,[6] which results in the formation of cyclopropane ring-opened zwitterionic intermediate **B-1** or the resonance-stabilized zwitterionic intermediate **C-1** by the aromatic R^3 group. Subsequently, intramolecular Friedel−Crafts reaction with either the aromatic R^1 or R^2 group produces the cyclized zwitterionic intermediate **D-1**, which affords the zwitterionic intermediate **E-1** via an allylic rearrangement. This is followed by another sterically demanding intramolecular Friedel−Crafts reaction with the aromatic R^3 group to produce the cyclized zwitterionic intermediate **F-1** with *syn*-configuration. Deprotonation of **F-1** affords the corresponding intermediate **G-1**, and the addition of the corresponding released proton produces zwitterionic intermediate **H-1**. The 1,3-proton shift along with the release of Lewis acid produces the corresponding thermodynamically favored 6a*H*-benzo[*c*]fluorine derivatives **2**.[7] This appears to be the driving force in these reactions to move the reaction forward and to allow for the formation of 6a*H*-benzo[*c*]fluorine derivatives **2** (Scheme 1).

Interestingly, with diphenylvinylidenecyclopropane **1i**, which has two phenyl groups at the C-1 position of the cyclopropane, as the substrate under the similar conditions, we found that 2-(2,2-diphenylvinyl)-1-methyl-3-phenyl-1*H*-indene **2i** was formed in 95% yield (Scheme 2). A plausible mechanism is shown in Scheme 2. Similar to the previous examples, the corresponding cyclopropane ring-opened zwitterionic intermediate **B-2** or the resonance-stabilized zwitterionic intermediate **C-2** is formed from the initial zwitterionic intermediate **A-2**. Intramolecular Friedel−Crafts reaction with the phenyl group at the C-1 position produces zwitterionic intermediate **D-2**, which affords the corresponding zwitterionic intermediate **E-1** via an allylic rearrangement. Subsequent 1,3-proton

Scheme 2. Rearrangement of Diphenylvinylidenecyclopropane **1i** in the Presence of $Sn(OTf)_2$ in DCE at 40 °C and a Plausible Mechanism



shift along with the release of Lewis acid produces the corresponding indene derivative **2i**. Its structure was determined by spectroscopic data and X-ray diffraction analysis (Supporting Information). Further details regarding this reaction will be reported in due course.

In conclusion, we have identified an efficient Lewis acid-catalyzed rearrangement of arylvinylidenecyclopropanes **1** having three substituents at the 1,2-positions of the cyclopropane to provide easy access to 6a*H*-benzo[*c*]fluorine derivatives via a double intramolecular Friedel−Crafts reaction or a 1-methyl-3-phenyl-1*H*-indene derivative via an intramolecular Friedel−Crafts reaction under mild reaction conditions in good to excellent yields. Efforts are in progress to elucidate further mechanistic details of these reactions and to understand their scopes and limitations.

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

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