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Lewis Acid Catalyzed Rearrangement of Vinylcyclopropenes for the Construction of Naphthalene and Indene Skeletons

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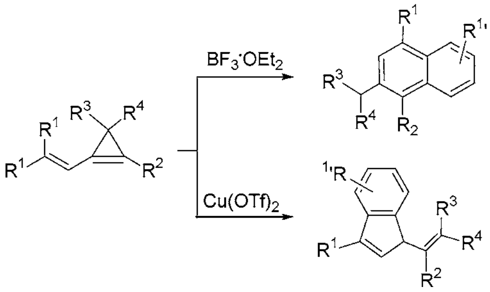
ABSTRACT



The choice of Lewis acid catalyst can result in dramatic differences in the chemoselectivity of the rearrangement reactions of vinylcyclopropenes. When BF$_3$·OEt$_2$ was used as the catalyst, naphthalenes were formed. However, when Cu(OTf)$_2$ was used as the catalyst, indenes were obtained.

Thermal and photochemical skeleton rearrangements of strained small rings with multiple bonds and functional groups have attracted much attention from both synthetic and mechanistic viewpoints. However, only a few examples of such thermal[1] and photochemical[2] skeletal conversions of vinylidenecyclopropanes **1** have been reported. Previously, we observed that naphthalene, 6a*H*-benzo[*c*]fluorine, and indene derivatives can be obtained by Lewis acid catalyzed rearrangement of arylvinylidenecyclopropanes **1** depending on the substitution pattern on the cyclopropyl ring and the electronic nature of aryl groups.[3] In this paper, we wish to report the Lewis acid catalyzed rearrangement of vinylcyclopropenes **2**, which are derived from the corresponding vinylidenecyclopropanes **1** under basic conditions, to afford naphthalene and indene skeletons in good to high yields under mild conditions.

As shown in Table 1, vinylcyclopropenes **2** are readily accessible from simple isomerization of the corresponding vinylidenecyclopropanes **1** under basic conditions. For all

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(1) (a) Paulson, D. R.; Crandall, J. K.; Bunnell, C. A. *J. Org. Chem.* **1970**, *35*, 3708. (b) Jones, M., Jr.; Hendrick, M. E.; Hardie, J. A. *J. Org. Chem.* **1971**, *36*, 3061. (c) Patrick, T. B.; Haynie, E. C.; Probst, W. J. *J. Org. Chem.* **1972**, *37*, 1553. (d) Sadler, I. H.; Stewart, J. A. G. *J. Chem. Soc., Perkin Trans. 2* **1973**, 278. (e) Sugita, H.; Mizuno, K.; Saito, T.; Isagawa, K.; Otsuji, Y. *Tetrahedron Lett.* **1992**, *33*, 2539. (f) Mizuno, K.; Sugita, H.; Kamada, T.; Otsuji, Y. *Chem. Lett.* **1994**, 449. (g) Maeda, H.; Hirai, T.; Sugimoto, A.; Mizuno, K. *J. Org. Chem.* **2003**, *68*, 7700.

(2) (a) Akasaka, T.; Misawa, Y.; Ando, W. *Tetrahedron Lett.* **1990**, *31*, 1173. (b) Mizuno, K.; Sugita, H.; Isagawa, K.; Goto, M.; Otsuji, Y. *Tetrahedron Lett.* **1993**, *34*, 5737. (c) Mizuno, K.; Nire, K.; Sugita, H.; Otsuji, Y. *Tetrahedron Lett.* **1993**, *34*, 6563. (d) Mizuno, K.; Sugita, H.; Hirai, T.; Maeda, H. *Chem. Lett.* **2000**, 1144. (e) Mizuno, K.; Nire, K.; Sugita, H.; Maeda, H. *Tetrahedron Lett.* **2001**, *42*, 2689. (f) Mizuno, K.; Maeda, H.; Sugita, H.; Nishioka, S.; Hirai, T.; Sugimoto, A. *Org. Lett.* **2001**, *3*, 581. (g) Mizuno, K.; Sugita, H.; Hirai, T.; Maeda, H.; Otsuji, Y.; Yasuda, M.; Hashiguchi, M.; Shima, K. *Tetrahedron Lett.* **2001**, *42*, 3363. (h) Maeda, H.; Zhen, L.; Hirai, T.; Mizuno, K. *ITE Lett. Batteries, New Technol. Med.* **2002**, *3*, 485.

(3) (a) Shi, M.; Lu, J.-M. *J. Org. Chem.* **2006**, *71*, 1920. (b) Shi, M.; Lu, J.-M. *Synlett* **2005**, 2352. (c) Shi, M.; Ma, M.; Shao, L.-X. *Tetrahedron Lett.* **2005**, *46*, 7609. (d) Shi, M.; Lu, J.-M.; Xu, G.-C. *Tetrahedron Lett.* **2005**, *46*, 4745. (e) Xu, G.-C.; Ma, M.; Liu, L.-P.; Shi, M. *Synlett* **2005**, 1869. (f) Xu, G.-C.; Liu, L.-P.; Lu, J.-M.; Shi, M. *J. Am. Chem. Soc.* **2005**, *127*, 14552.

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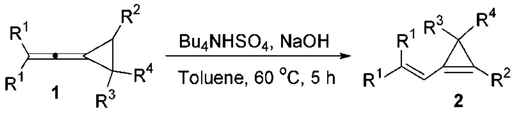
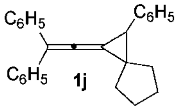
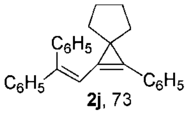
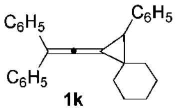
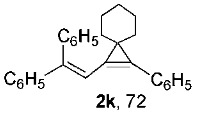
Table 1. Isomerization of Vinylidenecyclopropanes **1** to Vinylcyclopropenes **2**



entry[a]	**1** ($R^1/R^2/R^3/R^4$)	yield (%)[b]
1	**1a** (C_6H_5/C_6H_5/Me/Me)	**2a**, 92
2	**1b** (4-FC_6H_4/C_6H_5/Me/Me)	**2b**, 63
3	**1c** (4-ClC_6H_4/C_6H_5/Me/Me)	**2c**, 81
4	**1d** (4-MeC_6H_4/C_6H_5/Me/Me)	**2d**, 79
5	**1e** (C_6H_5/4-ClC_6H_4/Me/Me)	**2e**, 93
6	**1f** (C_6H_5/4-BrC_6H_4/Me/Me)	**2f**, 93
7	**1g** (C_6H_5/4-MeC_6H_4/Me/Me)	**2g**, 85
8	**1h** (C_6H_5/C_6H_5/Me/H)	**2h**, 61
9	**1i** (C_6H_5/C_6H_5/H/H)	**2i**, 68
10	 **1j**	 **2j**, 73
11	 **1k**	 **2k**, 72

[a] All reactions were carried out using **1** (0.2 mmol), NaOH (20.0 equiv), and Bu_4NHSO_4 (2.0 equiv) in toluene (5.0 mL) at 60 °C for 5 h. [b] Isolated yields.

vinylidenecyclopropanes **1** examined, the isomerization reaction proceeded smoothly to give vinylcyclopropenes **2** in good to high yields within 5 h under mild conditions (Table 1). Compound **2b** was unambiguously determined by an X-ray diffraction (Figure 1).[4]

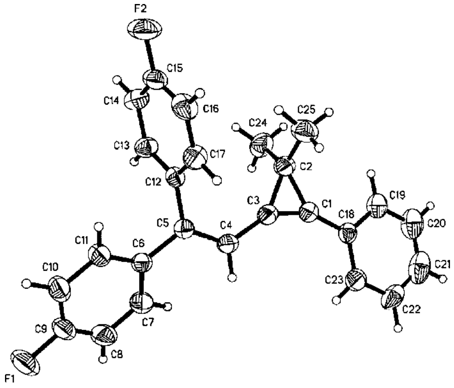
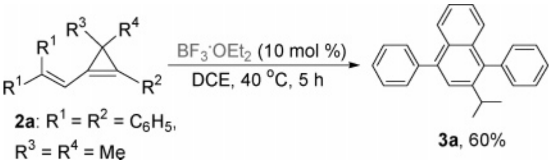


Figure 1. ORTEP drawing of compound **2b**.

Initial examinations using vinylcyclopropene **2a** ($R^1 = R^2 = C_6H_5$; $R^3 = R^4 =$ Me) as the substrate in the presence of various Brønsted acids, such as trifluoromethanesulfonic acid (TfOH), CF_3CO_2H, CH_3CO_2H, and the Lewis acid $BF_3{\cdot}OEt_2$, were aimed at determining the optimal conditions for rearrangement to **3a**. The results are summarized in the Supporting Information. It was found that $BF_3{\cdot}OEt_2$ was the best catalyst and that 1,2-dichloroethane (DCE) was the solvent of choice, and **3a** was produced in 60% yield at 40 °C (Scheme 1) (see the Supporting Information for details). The generality of this transformation was examined, and we found that for all of the employed substrates (**2**) the corresponding rearranged product **3** could be obtained in good yield (Table 2).

Scheme 1. Optimal Conditions for the Formation of Naphthalene **3a**



A plausible mechanism for the $BF_3{\cdot}OEt_2$-catalyzed rearrangement of vinylcyclopropenes **2** to naphthalenes **3** is outlined in Scheme 1. Initially, reaction of $BF_3{\cdot}OEt_2$ with trace amounts of water in the system generates the Brønsted acid catalyst **A**,[5] which is similar to the Brønsted acid TfOH. The reaction of catalyst **A** with **2** produces cationic intermediate **B** (the corresponding counteranion in all of the intermediates has been omitted for convenience), which will rearrange to either ring-opened cationic intermediate **C** or resonance-stabilized intermediate **C'** via σ-bond *b* cleavage.[6] Subsequent intramolecular Friedel−Crafts reaction of **C'** with the aromatic group R^1 gives the cyclized intermediate **D**, which affords intermediate **E** via deprotonation. Finally, aromatization of intermediate **E** furnishes the corresponding naphthalene **3** (Scheme 2).

Interestingly, we found that vinylcyclopropenes **2** can rearrange to the corresponding indene derivatives **4** in the

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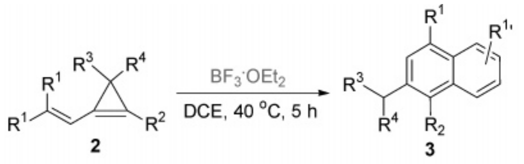
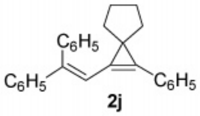
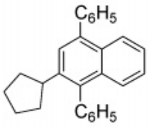
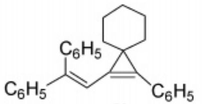
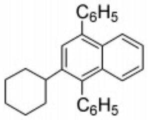
[4] The crystal data of **2b** have been deposited in the CCDC with number 602862. Empirical formula: $C_{25}H_{20}F_2$. Formula weight: 358.41. Crystal color, habit: colorless, prismatic. Crystal system: monoclinic. Lattice type: primitive. Lattice parameters: $a = 12.5896(12)$ Å, $b = 9.1294(8)$ Å, $c = 17.6833(16)$ Å, $\alpha = 90°$, $\beta = 102.192(2)°$, $\gamma = 90°$, $V = 1986.6(3)$ Å^3. Space group: $P2(1)/n$. $Z = 4$; $D_c = 1.198$ g/cm^3; $F_{000} = 752$. Diffractometer: Rigaku AFC7R. Residuals: R. R_w: 0.0431, 0.1098.

[5] For related papers, which report that trace amounts of water are required to trigger the formation of cation **B** with BF_3 ($BF_3 + H_2O + Me_2CH{=}CH_2 \rightarrow Me_3CH^+BF_3OH^-$), see: (a) Evans, A. G.; Holden, D.; Plesch, P.; Polanyi, M.; Skinner, H. A.; Weinberger, M. A. *Nature* **1946**, *157*, 102. (b) Evans, A. G.; Meadows, G. W.; Polanyi, M.; Skinner, H. A.; Weinberger, M. A. *Nature* **1946**, *158*, 94. (c) Evans, A. G.; Polanyi, M. *J. Chem. Soc.* **1947**, 252. (d) Prakash, G. K. S.; Mathew, T.; Hoole, D.; Esteves, P. M.; Wang, Q.; Rasul, G.; Olah, G. A. *J. Am. Chem. Soc.* **2004**, *126*, 15770. The rearrangement of **2a** in anhydrous DCE was also studied by bubbling BF_3 gas into the reaction solution by means of a Schlenk tube, under an argon atmosphere. The reaction proceeded slowly under these conditions. However, when the solution was exposed to the ambient atmosphere for several minutes, the reaction proceeded smoothly to give product **3a** in good yield.

[6] Reaction of electrophilic reagents with strained bonds has been extensively studied. See: (a) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461. (b) Leftin, J. H.; Gil-Av, G. *Tetrahedron Lett.* **1972**, *13*, 3368. (c) Padwa, A.; Rieker, W. F.; Rosenthal, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1710. (d) Padwa, A.; Blacklock, T. J.; Loza, R. *J. Am. Chem. Soc.* **1981**, *103*, 2404.

Table 2. $BF_3 \cdot OEt_2$-Catalyzed Rearrangement of **2** for the Formation of Naphthalenes **3**

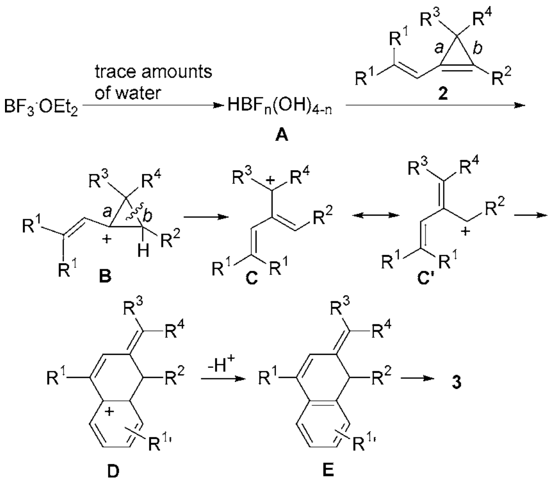


entry[a]	**2** ($R^1/R^2/R^3/R^4$)	yield (%)[b]
1	**2a** (C_6H_5/C_6H_5/Me/Me)	**3a**, 60
2	**2b** ($4\text{-}FC_6H_4/C_6H_5$/Me/Me)	**3b**, 55
3	**2c** ($4\text{-}ClC_6H_4/C_6H_5$/Me/Me)	**3c**, 65
4	**2d** ($4\text{-}MeC_6H_4/C_6H_5$/Me/Me)	**3d**, 70
5	**2e** ($C_6H_5/4\text{-}ClC_6H_4$/Me/Me)	**3e**, 63
6	**2f** ($C_6H_5/4\text{-}BrC_6H_4$/Me/Me)	**3f**, 65
7	**2g** ($C_6H_5/4\text{-}MeC_6H_4$/Me/Me)	**3g**, 68
8	**2h** (C_6H_5/C_6H_5/Me/H)	**3h**, 63
9	**2i** (C_6H_5/C_6H_5/H/H)	**3i**, 60
10	 **2j**	 **3j**, 66
11	 **2k**	 **3k**, 65

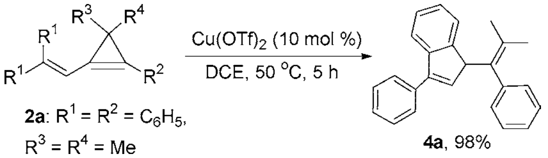
[a] All reactions were carried out using **2** (0.2 mmol) in the presence of $BF_3 \cdot OEt_2$ (10 mol %) and DCE (5.0 mL) at 40 °C for 5 h. [b] Isolated yields.

presence of the Lewis acid $Cu(OTf)_2$ in DCE at 50 °C. The optimization of the reaction conditions for this process is summarized in the Supporting Information in the presence of various Lewis acids, such as $Sc(OTf)_3$, $Sn(OTf)_2$, $Eu(OTf)_3$, and $Zr(OTf)_4$. It was found that $Cu(OTf)_2$ was the best catalyst and that 1,2-dichloroethane (DCE) was the solvent of choice, and **4a** was produced in 98% yield at 50 °C (Scheme 3) (see the Supporting Information for details).

Scheme 2. Plausible Mechanism for the Formation of Naphthalenes **3**



Scheme 3. Optimal Conditions for the Formation of Indene **4a**



It should be emphasized here that, using Brønsted acid CF_3CO_2H as a catalyst, both indene and naphthalene products can be obtained as a mixture. Compound **4a** was unambiguously determined by an X-ray diffraction (Figure 2).[7] The generality of this $Cu(OTf)_2$-catalyzed rearrangement reaction is satisfactory, and the reaction can tolerate various substituents, whether they are electron-rich or -poor aryl groups (R^1 and R^2) or methyl groups or hydrogen atoms (R^3 and R^4). All reactions proceeded smoothly to give the corresponding indene derivative **4** in good to high yields under the optimal conditions (Table 3).

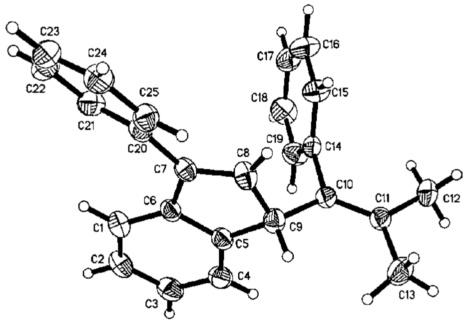


Figure 2. ORTEP drawing of compound **4a**.

A plausible mechanism for the formation of indenes **4** is illustrated in Scheme 4. The coordination of **2** to the Lewis acid initially gives zwitterionic intermediate **F**, which results in the formation of cyclopropyl ring-opened zwitterionic intermediate **G** via σ-bond *a*-cleavage. Intermediate **G** also can be drawn as its delocalized representations as intermediate **H** or intermediate **H’**.[6,8] Subsequent intramolecular Friedel−Crafts reaction of intermediate **H’** with aromatic group R^1 affords intermediate **I**. Elimination of Lewis acid and deprotonation from intermediate **I** furnish **4**.

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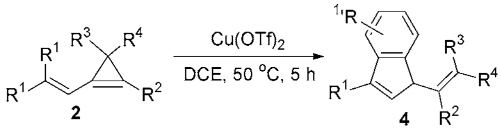
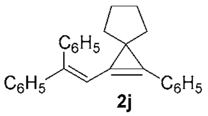
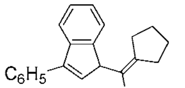
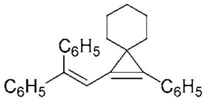
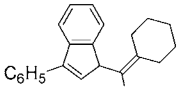
(7) The crystal data of **4a** have been deposited in the CCDC with number 615026. Empirical formula: $C_{25}H_{22}$. Formula weight: 322.43. Crystal color, habit: colorless, prismatic. Crystal system: Triclinic. Lattice type: primitive. Lattice parameters: $a = 8.1168(19)$ Å, $b = 10.068(2)$ Å, $c = 11.493(16)$ Å, $\alpha = 93.001(4)°$, $\beta = 98.563(4)°$, $\gamma = 98.080(4)°$, $V = 917.0(4)$ Å^3. Space group: $P\bar{1}$. $Z = 2$; $D_c = 1.168$ g/cm^3; $F_{000} = 344$. Diffractometer: Rigaku AFC7R. Residuals: R. R_w: 0.0655, 0.1722.

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

Table 3. Cu(OTf)$_2$-Catalyzed Rearrangement of Vinylcyclopropenes **2** for the Formation of Indenes **4**

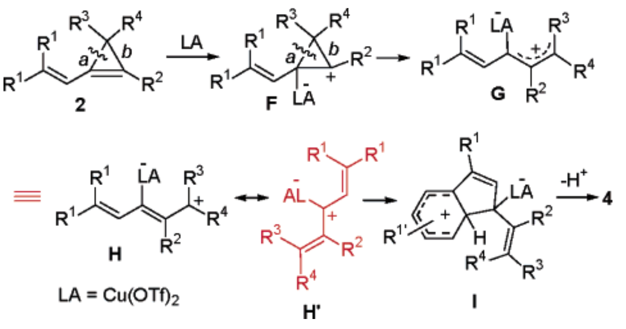


entry[a]	**2** ($R^1/R^2/R^3/R^4$)	yield (%)[b]
1	**2a** (C_6H_5/C_6H_5/Me/Me)	**4a**, 98
2	**2b** (4-FC_6H_4/C_6H_5/Me/Me)	**4b**, 68
3	**2c** (4-ClC_6H_4/C_6H_5/Me/Me)	**4c**, 78
4	**2d** (4-MeC_6H_4/C_6H_5/Me/Me)	**4d**, 94
5	**2e** (C_6H_5/4-ClC_6H_4/Me/Me)	**4e**, 87
6	**2f** (C_6H_5/4-BrC_6H_4/Me/Me)	**4f**, 80
7	**2g** (C_6H_5/4-MeC_6H_4/Me/Me)	**4g**, 98
8	**2h** (C_6H_5/C_6H_5/Me/H)	**4h**, 84
9	 **2j**	 **4i**, 78
10	 **2k**	 **4j**, 75

[a] All reactions were carried out using **2** (0.2 mmol) in the presence of Cu(OTf)$_2$ (10 mol %) and DCE (5.0 mL) at 50 °C for 5 h. [b] Isolated yields.

At the present stage, we believe that the coordination of sterically bulky LA to the cyclopropene moiety of **2** exclusively produces intermediate **F** due to the steric repulsion of LA and the aromatic R^2 group. However, the coordination of a proton to the cyclopropene moiety of **2** gives a more stabilized intermediate **B**. The different coordination place in the cyclopropene moiety of **2** causes the different reaction products.

Scheme 4. Plausible Mechanism for the Formation of Indenes **4**



In conclusion, we have discovered efficient and mild Lewis acid catalyzed rearrangement reactions of vinylcyclopropenes **2**. In these reactions, the choice of Lewis acid catalyst is important and naphthalenes **3** or indenes **4** can be obtained in good to high yields. Stronger Lewis acid catalysts (or Brϕnsted acid in this case) and somewhat weak Lewis acid catalysts will result in the different σ-bond cleavage of **2**, which directly affects the subsequent Friedel−Crafts reaction and determines the product structure. Efforts are underway in the laboratory to further elucidate the mechanistic details of these reactions and to understand their scope and limitations.

Acknowledgment. Financial support from the Shanghai Municipal Committee of Science and Technology (04JC14083, 06XD14005), the National Natural Science Foundation of China (203900502, 20472096, and 20672127), and the Cheung Kong Scholar Program is greatly appreciated.

Supporting Information Available: Spectroscopic data of all the new compounds, detailed experimental procedures, and X-ray data for compounds **2b** and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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