A Novel Rearrangement of Arylvinylidenecyclopropanes to Naphthalene Derivatives Catalyzed by Lewis Acids or Brønsted Acids

Guang-Cai Xu,[a] Ming Ma,[a] Le-Ping Liu,[b] Min Shi*[a]

[a] School of Chemistry & Pharmaceutics, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China
Fax +86(21)64166128; E-mail: Mshi@pub.sioc.ac.cn

[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, P. R. China

Received 4 May 2005

Abstract: Arylvinylidenecyclopropanes undergo a novel rearrangement in the presence of Lewis acids or Brønsted acids to give the corresponding naphthalene derivatives in good to high yields under mild conditions.

Key words: arylvinylidenecyclopropanes, Lewis acids, Brønsted acids, naphthalene derivatives, rearrangement

Thermal and photochemical skeletal conversions of vinylidenecyclopropanes **1** have attracted much attention from mechanistic, theoretical, spectroscopic, and synthetic viewpoints.[1,2] Vinylidenecyclopropanes **1** also undergo a variety of unique addition reactions with electrophiles to give novel products, sometimes along with the formation of cyclopropane ring-opened products.[3]

Recently, we have been investigating the Lewis acid catalyzed ring-opening reactions of methylenecyclopropanes (MCPs), another series of highly strained but readily accessible molecules. Thus far, we have found that the cyclopropane ring of MCPs can be opened by alcohols and other nucleophiles in a different, novel manner to give the corresponding homoallylic derivatives in good yields under mild conditions in the presence of Lewis acids.[4,5] Therefore, we attempted to examine the Lewis acid catalyzed reaction of **1** with a variety of nucleophiles under similar conditions. In this paper, we wish to report the Lewis acid or Brønsted acid catalyzed rearrangement of arylvinylidenecyclopropanes **1** to the corresponding naphthalene derivatives **2** in good to high yields under mild conditions.[6]

Initial examination using diphenylvinylidenecyclopropane (**1a**) as the substrate in the presence of a variety of Lewis acids or Brønsted acids, revealed that a novel rearrangement took place to give 2-methyl-1,4-diphenylnaphthalene (**2a**) under various conditions. While the reaction with $Sn(OTf)_2$ (10 mol%) as a Lewis acid in DCE, at room temperature was sluggish, the reaction proceeded smoothly under reflux (80 °C) to give **2a** in 92% yield after four hours (Table 1, entries 2 and 3). Using other Lewis acids such as $Zr(OTf)_4$, $Cu(OTf)_2$, and $BF_3 \cdot OEt_2$ under identical conditions, **2a** was obtained in lower yields (Table 1, entries 4, 7, and 8). A prolonged reaction time is required in the presence of Lewis acids $Yb(OTf)_3$ and $Sc(OTf)_3$ to give **2a** in 58% and 41% yields, respectively (Table 1, entries 5 and 6). Brønsted acid TfOH (10 mol%) is also fairly effective in this reaction giving **2a** in moderate yield (42%) at room temperature and in high yield (94%) at 80 °C (Table 1, entries 10 and 11). At 80 °C, TsOH is as effective as TfOH (Table 1, entry 9). Examination of solvent effects revealed that DCE is the best solvent for this novel rearrangement (Table 1, entries 12–18).

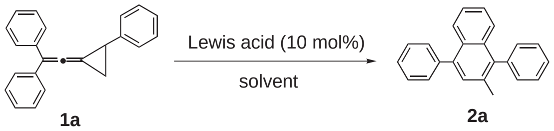
Next, we carried out the reaction with a variety of derivatives of **1** in the presence of $Sn(OTf)_2$ under the optimized conditions. As can be seen from Table 2, the corresponding rearranged products **2**, naphthalene derivatives, were obtained in good to high yields (Table 2, entries 1–8). For vinylidenecyclopropanes **1g** ($R^3 = R^4$ = aliphatic group) and **1h** (R^3 = aliphatic group, *cis*/*trans* = 1:1), **2g** and **2h** were obtained in good yields (Table 2, entries 6 and 7). For vinylidenecyclopropanes **1i** (R^2 = aliphatic group, *cis*/*trans* = 1:1), the corresponding naphthalene derivative **2i** was formed in 50% yield as the sole product (Table 2, entry 8).

Their structures were determined by ^1H and ^{13}C NMR spectroscopic data as well as HRMS or microanalyses.

Based on the above results and our previous investigations on the Lewis acid catalyzed ring-opening reaction of MCPs,[4,5] a plausible mechanism for the rearrangement of arylvinylidenecyclopropanes **1** in the presence of either Lewis acids or Brønsted acids is outlined in Scheme 1. The coordination of **1** to the Lewis acid[6] or the addition of **1** with a Brønsted acid initially gave 1-cyclopropylvinyl cation **A**, a vinyl group stabilized cyclopropyl cation,[8] which results in the formation of cyclopropane ring-opened cationic intermediate **B**, which is stabilized by the aromatic R^3 group in most cases.[3l] The intramolecular Friedel–Crafts reaction produces the cyclized intermediate **C**. The rearrangement of **C** affords the intermediate **D**. The 1,4-proton shift along with release of Lewis acid or deprotonation gives the corresponding intermediate **E**. The 1,3-proton shift produces the thermodynamically favored naphthalene derivatives **2**;[9] this is the driving force in this reaction moving the equilibrium towards the formation of the naphthalene derivatives **2** (Scheme 1).

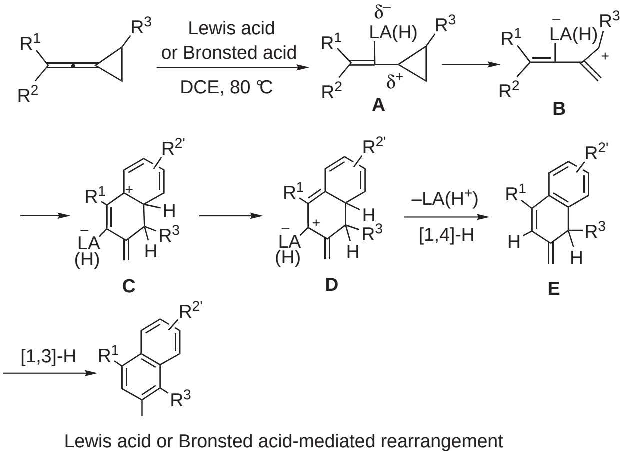
SYNLETT 2005, No. 12, pp 1869–1872
Advanced online publication: 22.06.2005
DOI: 10.1055/s-2005-871565; Art ID: U13305ST

Table 1 Rearrangement of Diphenylvinylidenecyclopropane (**1a**) to 2-Methyl-1,4-diphenylnaphthalene (**2a**) in the Presence of a Variety of Lewis Acids or Brønsted Acids[7]



Entry	Solvent	Lewis acid (0.1 equiv)	Temperature (°C)	Time (h)[b]	Yield (%)[a] **2a**
1	$ClCH_2CH_2Cl$	none	80	120	–[c]
2	$ClCH_2CH_2Cl$	$Sn(OTf)_2$	25	120	51
3	$ClCH_2CH_2Cl$	$Sn(OTf)_2$	80	4	92
4	$ClCH_2CH_2Cl$	$Zr(OTf)_4$	80	4	81
5	$ClCH_2CH_2Cl$	$Yb(OTf)_3$	80	9	58
6	$ClCH_2CH_2Cl$	$Sc(OTf)_3$	80	50	41
7	$ClCH_2CH_2Cl$	$Cu(OTf)_2$	80	4	41
8	$ClCH_2CH_2Cl$	$BF_3 \cdot OEt_2$	80	4	71
9	$ClCH_2CH_2Cl$	TsOH	80	4	92
10	$ClCH_2CH_2Cl$	TfOH	80	4	94
11	$ClCH_2CH_2Cl$	TfOH	25	10	42
12	CH_3CH_2OH	$Sn(OTf)_2$	78	10	34
13	THF	$Sn(OTf)_2$	66	25	83
14	Toluene	$Sn(OTf)_2$	80	4	87
15	CH_3CN	$Sn(OTf)_2$	80	4	65
16	CH_3CN	$Zr(OTf)_4$	80	4	63
17	CH_3CN	$Yb(OTf)_3$	80	50	–[c]
18	Toluene	$Zr(OTf)_4$	80	4	68

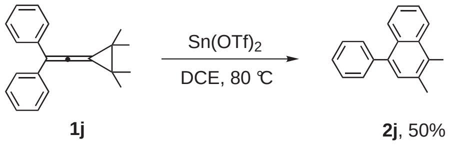
[a] Isolated yields.
[b] Until all of the starting material **1** was consumed.
[c] No reaction occurred.



Scheme 1 Plausible mechanism for the rearrangement of arylvinylidenecyclopropanes **1** in the presence of Lewis acid or Brønsted acid.

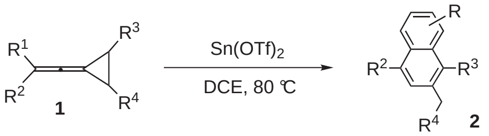
Interestingly, for diphenylvinylidenecyclopropane (**1j**), naphthalene derivative **2j** was formed in good yield under identical conditions by eliminating one propene molecule (Scheme 2); currently, its reaction mechanism remains obscure.

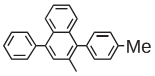
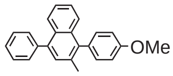
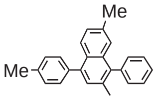
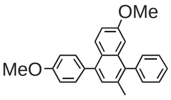
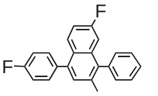
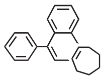
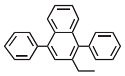
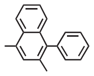
In conclusion, we have found a novel rearrangement of arylvinylidenecyclopropanes **1** to the corresponding naphthalene derivatives **2**, in the presence of Lewis acids



Scheme 2 Rearrangement of diphenylvinylidenecyclopropane (**1j**) in the presence of Lewis acid $Sn(OTf)_2$ in DCE at 80 °C.[7]

Table 2 Lewis Acid $Sn(OTf)_2$-Catalyzed Rearrangement of a Variety of Arylvinylidenecyclopropanes **1** in DCE at 80 °C[7]



Entry	R^1, R^2	R^3, R^4	Time (h)	Yield (%)[a] **2**
1	C_6H_5, C_6H_5	*p*-MeC_6H_4, H **1b**	10	 **2b,** 80
2	C_6H_5, C_6H_5	*p*-$MeOC_6H_4$, H **1c**	10	 **2c**, 61
3	*p*-MeC_6H_4, *p*-MeC_6H_4	C_6H_5, H **1d**	10	 **2d**, 91
4	*p*-$MeOC_6H_4$, *p*-$MeOC_6H_4$	C_6H_5, H **1e**	10	 **2e**, 70
5	*p*-FC_6H_4, *p*-FC_6H_4	C_6H_5, H **1f**	10	 **2f**, 80
6	C_6H_5, C_6H_5	$–(CH_2)_4–$ **1g**	10	 **2g**, 42
7	C_6H_5, C_6H_5	C_6H_5, Me (*cis*/*trans* = 1:1) **1h**	10	 **2h**, 85
8	Me, C_6H_5 (*cis*/*trans* = 1:1)	C_6H_5, H **1i**	10	 **2i**, 50

[a] Isolated yields.

or Brønsted acids, in good to high yields.[10] A plausible reaction mechanism has been discussed. The novelty in this paper is the efficient and cascade formation of naphthalene derivatives **2** catalyzed by Lewis acids or Brønsted acids under mild conditions. Efforts are underway to elucidate the mechanistic details of this reaction and to disclose the scope and limitations of this transformation.

Acknowledgment

We thank the State Key Project of Basic Research (Project 973) (No. G2000048007), Shanghai Municipal Committee of Science and Technology, Chinese Academy of Sciences (KGCX2-210-01), and the National Natural Science Foundation of China for financial support (20472096, 203900502, and 20272069).

References

(1) (a) Poutsma, M. L.; Ibarbia, P. A. *J. Am. Chem. Soc.* **1971**, *93*, 440. (b) Smadja, W. *Chem. Rev.* **1983**, *83*, 263. (c) Paulson, D. R.; Crandall, J. K.; Bunnell, C. A. *J. Org. Chem.* **1970**, *35*, 3708. (d) Hendrick, M. E.; Hardie, J. A.; Jones, M. Jr. *J. Org. Chem.* **1971**, *36*, 3061. (e) Patrick, T. B.; Haynie, E. C.; Probst, W. J. *J. Org. Chem.* **1972**, *37*, 1553. (f) Aue, D. H.; Meshishnek, M. H. *J. Am. Chem. Soc.* **1977**, *99*, 223. (g) Sasaki, T.; Eguchi, S.; Ogawa, T. *J. Am. Chem. Soc.* **1975**, *97*, 4413. (h) Sadler, I. H.; Stewart, J. A. G. *J. Chem. Soc., Perkin Trans. 2* **1973**, 278. (i) Sugita, H.; Mizuno, K.; Saito, T.; Isagawa, K.; Otsuji, Y. *Tetrahedron Lett.* **1992**, *33*, 2539. (j) Mizuno, K.; Sugita, H.; Kamada, T.; Otsuji, Y. *Chem. Lett.* **1994**, 449. (k) Akasaka, T.; Misawa, Y.; Ando, W. *Tetrahedron Lett.* **1990**, *31*, 1173. (l) Mizuno, K.; Sugita, H.; Isagawa, K.; Goto, M.; Otsuji, Y. *Tetrahedron Lett.* **1993**, *34*, 5737. (m) Mizuno, K.; Nire, K.; Sugita, H.; Otsuji, Y. *Tetrahedron Lett.* **1993**, *34*, 6563. (n) Mizuno, K.; Sugita, H.; Hirai, T.; Maeda, H. *Chem. Lett.* **2000**, 1144. (o) Mizuno, K.; Nire, K.; Sugita, H.; Maeda, H. *Tetrahedron Lett.* **2001**, *42*, 2689. (p) Mizuno, K.; Maeda, H.; Sugita, H.; Nishioka, S.; Hirai, T.; Sugimoto, A. *Org. Lett.* **2001**, *3*, 581. (q) Mizuno, K.; Sugita, H.; Hirai, T.; Maeda, H.; Otsuji, Y.; Yasuda, M.; Hashiguchi, M.; Shima, K. *Tetrahedron Lett.* **2001**, *42*, 3363. (r) Maeda, H.; Zhen, L.; Hirai, T.; Mizuno, K. *ITE Lett. Batteries, New Technol. Med.* **2002**, *3*, 485. (s) Sydnes, L. K. *Chem. Rev.* **2003**, *103*, 1133.

(2) For the synthesis of vinylidenecyclopropanes, see: (a) Isagawa, K.; Mizuno, K.; Sugita, H.; Otsuji, Y. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2283; and references cited therein. (b) Sasaki, T.; Eguchi, S.; Ohno, M.; Nakata, F. *J. Org. Chem.* **1976**, *41*, 2408. (c) Sasaki, T.; Eguchi, S.; Ogawa, T. *J. Org. Chem.* **1974**, *39*, 1927. (d) Sasaki, T.; Eguchi, S.; Ogawa, T. *Heterocycles* **1975**, *3*, 193. (e) Eguchi, S.; Arasaki, M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1047. (f) Sugita, H.; Mizuno, K.; Mori, T.; Isagawa, K.; Otsuji, Y. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 984. (g) Patrick, T. B. *Tetrahedron Lett.* **1974**, *15*, 1407. (h) Al-Dulayymi, J. R.; Baird, M. S. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1547. (i) Patrick, T. B. *J. Org. Chem.* **1977**, *42*, 3354. (j) Hartzler, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 4527.

(3) For the reactions of vinylidenecyclopropanes with carbenes and carbene complexes, see: (a) Crandall, J. K.; Paulson, D. R.; Bunnell, C. A. *Tetrahedron Lett.* **1969**, 4217. (b) Hwu, C.-C.; Wang, F.-C.; Yeh, M.-C. P. *J. Organomet. Chem.* **1994**, *474*, 123. (c) Billups, W. E.; Haley, M. M.; Boese, R.; Blaser, D. *Tetrahedron* **1994**, *50*, 10693. (d) Maeda, H.; Hirai, T.; Sugimoto, A.; Mizuno, K. *J. Org. Chem.* **2003**, *68*, 7700. (e) Bloch, R.; Perchec, P. L.; Conia, J.-M. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 798. (f) Pasto, D. J.; Yang, S. H. *J. Org. Chem.* **1986**, *51*, 1676. (g) Pasto, D. J.; Miles, M. F. *J. Org. Chem.* **1976**, *41*, 2608. (h) Pasto, D. J.; Chen, A. F.-T.; Binsch, G. *J. Am. Chem. Soc.* **1973**, *95*, 1553. (i) Pasto, D. J.; Chen, A. F.-T. *J. Am. Chem. Soc.* **1971**, *93*, 2562. (j) Pasto, D. J.; B orchardt, J. K.; Fehlner, T. P.; Baney, H. F.; Schwartz, M. E. *J. Am. Chem. Soc.* **1976**, *98*, 526. (k) Pasto, D. J.; Fehlner, T. P.; Schwartz, M. E.; Baney, H. F. *J. Am. Chem. Soc.* **1976**, *98*, 530. (l) Pasto, D. J.; Miles, M. F. *J. Org. Chem.* **1976**, *41*, 425. (m) Pasto, D. J.; Chen, A. F.-T.; Cuirdaru, G.; Paquette, L. A. *J. Org. Chem.* **1973**, *38*, 1015. (n) Gompper, R.; Lach, D. *Tetrahedron Lett.* **1973**, *14*, 2683. (o) Gompper, R.; Lach, D. *Tetrahedron Lett.* **1973**, *14*, 2687. (p) Pasto, D. J.; Wampfler, D. *Tetrahedron Lett.* **1974**, 1933. (q) Sasaki, T.; Eguchi, S.; Ohno, M. *J. Am. Chem. Soc.* **1975**, *97*, 4413. (r) Pasto, D. J.; Whitmer, J. L. *J. Org. Chem.* **1980**, *45*, 1987. (s) Pasto, D. J.; Brophy, J. E. *J. Org. Chem.* **1991**, *56*, 4556. (t) Cairns, P. M.; Combie, L.; Pattenden, G. *Tetrahedron Lett.* **1982**, *23*, 1405. (u) Combie, L.; Maddocks, P. J.; Pattenden, G. *Tetrahedron Lett.* **1978**, *19*, 3483.

(4) (a) Shi, M.; Xu, B. *Org. Lett.* **2002**, *4*, 2145. (b) Shi, M.; Chen, Y.; Xu, B.; Tang, J. *Tetrahedron Lett.* **2002**, *43*, 8019. On the other hand, Kilburn reported Lewis acid mediated cascade reactions of silyl-substituted methylenecyclopropane with ketones and aldehydes: (c) Peron, G. L. N.; Kitteringham, J.; Kilburn, J. D. *Tetrahedron Lett.* **2000**, *41*, 1615. (d) Peron, G. L. N.; Norton, D.; Kitteringham, J.; Kilburn, J. D. *Tetrahedron Lett.* **2001**, *42*, 347. (e) Patient, L.; Berry, M. B.; Kilburn, J. D. *Tetrahedron Lett.* **2003**, *44*, 1015.

(5) (a) Xu, B.; Shi, M. *Org. Lett.* **2003**, *5*, 1415. (b) Shao, L.-X.; Shi, M. *Eur. J. Org. Chem.* **2004**, 426. (c) Shi, M.; Xu, B.; Huang, J.-W. *Org. Lett.* **2004**, *6*, 1175.

(6) For isomerization of alkenylidenecyclopropanes catalyzed by Lewis acids: Fitjer, L. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 360.

(7) The ^{1}H and ^{13}C NMR spectral data and analytic data of the compounds shown in Tables 1 and 2 and Scheme 2, and detailed experimental procedures for their preparation, are available upon request from the author.

(8) The high-level ab initio calculations predict the heats of formation of these 1-cyclopropylvinyl cations **A-1**, **A-2**, and **A-3** to be 238.6, 242.5, and 256 kcal mol^{-1}, respectively; thus, initial protonation might take place to give the most thermodynamically stable cationic intermediate **A-1** (Figure 1): (a) Siehl, H.-U.; Aue, D. H. *Dicoordinated Carbocations*; Rappoport, Z.; Stang, P. J., Eds.; John Wiley & Sons: New York, **1997**, 137–138. (b) The stabilizing effect of cyclopropyl substituents on carbocations is well documented: Olah, G. A.; Reddy, V. P.; Prakash, G. K. S. *Chem. Rev.* **1992**, *92*, 69.

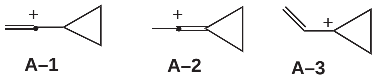


Figure 1

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

(10) Typical reaction procedure for the rearrangement of diarylvinylidenecyclopropanes: To a solution of diarylvinylidenecyclopropane **1d** (64 mg, 0.2 mmol) in DCE (2.0 mL) was added $Sn(OTf)_2$ (8 mg, 0.02 mmol), the reaction mixture was stirred for 10 h at 80 °C (monitored by TLC). After the starting materials (diarylvinylidenecyclopropans **1**) were consumed, the solvent was removed under reduced pressure and the residue was subjected to flash column chromatography to give the desired product **2d** (58 mg, 91%) as a colorless liquid. 2-Methyl-1-phenyl-4-(*para*-methylphenyl)-7-methylnaphthalene (**2d**): colorless oil; IR (CH_2Cl_2): 3053, 3023, 2954, 2923, 2855, 1620, 1600, 1516, 1507, 1440, 1381, 1362, 1029, 883, 824, 760, 703, 526 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.22 (3 H, s, CH_3), 2.34 (3 H, s, CH_3), 2.45 (3 H, s, CH_3), 7.15–7.22 (2 H, m, Ar), 7.28–7.31 (5 H, m, Ar), 7.40–7.53 (5 H, m, Ar), 7.82 (1 H, d, J = 8.7 Hz, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9, 21.3, 21.8, 125.4, 125.8, 126.9, 126.9, 128.4, 128.4, 128.8, 128.9, 130.0, 130.2, 132.7, 133.4, 135.2, 136.8, 137.0, 138.0, 139.2, 140.0; MS (EI): m/z (%) = 322 (100) [M^{+}], 307 (10.3), 292 (7.6), 229 (3.8), 215 (5.1), 91 (1.7); HRMS (MALDI): m/z calcd for $C_{25}H_{23}$ (M^{+} + 1), 323.1794; found, 323.1786.