

Acid-promoted C₁-C₂ Bond Fission and Subsequent 1,5-Sulfenyl Shift of 1-Acceptor-1-sulfenyl-substituted 2-Vinylcyclopropanes. Formation of 6-Sulfenyl- $\alpha,\beta,\gamma,\delta$ -unsaturated Carboxylic Esters and Nitriles

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1-Acceptor-1-sulfenyl-substituted 2-vinylcyclopropanes were isomerized to 6-sulfenyl- $\alpha,\beta,\gamma,\delta$ -unsaturated carboxylic esters and nitriles *via* a C₁-C₂ bond fission and *via* a 1,5-sulfenyl shift using an acid catalyst.

The cyclopropane ring is subject to a number of chemical transformations because of its unique bonding and high energy content.¹ Vinylcyclopropanes are the most important compounds among cyclopropane derivatives for the synthesis of complex molecules.² Although various types of vinylcyclopropanes have been utilized as versatile intermediates in synthetic transformations, 1-acceptor-1-sulfenyl-substituted vinylcyclopropanes have received considerably less attention.³ Therefore, we intended to explore the novel transformation of 1-acceptor-1-sulfenyl-substituted 2-vinylcyclopropanes (**I**). There are

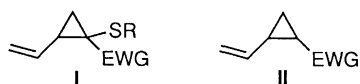
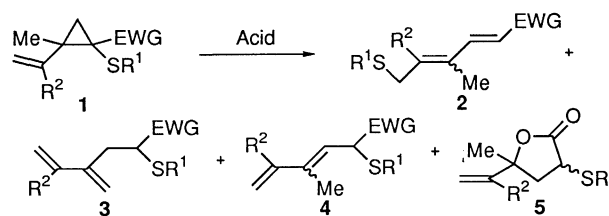


Figure 1.

several reports on the transformations of 1-acceptor-substituted 2-vinylcyclopropanes (**II**), mainly chrysanthemic acid derivatives, under acidic conditions.⁴ We recently discovered the C₁-C₂ bond fission and 1,5-sulfenyl rearrangement of vinylcyclopropyl sulfides (**I**) by treatment with acids (Scheme 1). There has been reported only one example of the 1,5-alkylthio shift catalyzed by a base;⁵ our finding, however, is the first example of the acid promoted 1,5-sulfenyl shift. We now report the C₁-C₂ bond cleavage followed by a 1,5-sulfenyl shift and formation of conjugated dienes.

Vinylcyclopropyl sulfides **1** were prepared according to the literature.³ First, we examined an acid catalyst and solvent effects on the reaction of vinylcyclopropyl sulfide **1a**⁶ (Table 1). The use of 42 % HBF₄, CF₃CO₂H and BF₃·Et₂O as an acid gave γ -lactone **5a** as the major product (entries 1, 2 and 5). The C₁-C₂ bond fission and 1,5-sulfenyl shift efficiently took place using a sulfonic acid such as *p*-toluenesulfonic acid monohydrate (*p*-TsOH) and CF₃SO₃H in benzene, a nonpolar solvent, under reflux (entries 3 and 4). In entry 3, the rearranged diene **2a** formed by the 1,5-phenylthio shift was provided in 49% yield as a mixture of geometrical isomers, whose structures were characterized by the NOE technique, accompanied by an inseparable mixture of the ring-opened dienes **3a** and **4a** (the yields were estimated from the intensities of the signals in the ¹H NMR spectrum). When the reaction was carried out in EtOH, a polar protic solvent, γ -lactone **5a** was provided in 60% yield and no ring-opened diene was obtained (entry 6). Polar aprotic solvents, especially DMF and 1,2-dichloroethane, were ineffective for the C₁-C₂ bond fission and/or the 1,5-sulfenyl shift (entries 7 and 9). A considerable amount of diphenyl disulfide was obtained (36-41%) when EtOH, DMF or 1,2-dichloroethane was used as the solvent.



- a: EWG=CO₂Me, R¹=Ph, R²=Me;
b: EWG=CO₂Me, R¹=*m*-MeC₆H₄, R²=Me;
c: EWG=CO₂Me, R¹=*p*-ClC₆H₄, R²=Me;
d: EWG=CO₂Me, R¹=Ph, R²=H;
e: EWG=CO₂Me, R¹=R²=Me;
f: EWG=CN, R¹=Ph, R²=Me;
g: EWG=CN, R¹=*p*-ClC₆H₄, R²=Me;
h: EWG=CN, R¹=Ph, R²=H;

Scheme 1.

Table 1. Acid-promoted isomerization of vinylcyclopropyl sulfide **1a**

Entry	Conditions	Products (%yield)			
		2a(Z:E) ^a	3a ^b	4a(E) ^b	5a ^c
1	42% HBF ₄ (1.0), THF, r.t., 24h	-	-	-	50
2	CF ₃ CO ₂ H(1.0), benzene, r.t., 24h	-	-	-	31
3	<i>p</i> -TsOH(0.1), benzene, reflux, 18h	49(1:3)	24	10	8
4	CF ₃ SO ₃ H(0.1), benzene, reflux, 20h	41(2:3)	^d	11	14
5	BF ₃ ·Et ₂ O(1.0), benzene, reflux, 14h	4(2:3)	-	-	31
6	<i>p</i> -TsOH(0.1), EtOH, reflux, 9h	-	-	-	60 ^e
7	<i>p</i> -TsOH(0.1), DMF, 80°C, 9h	-	-	-	15 ^e
8	<i>p</i> -TsOH(0.1), THF, reflux, 9h	25(1:1)	25	-	43
9	<i>p</i> -TsOH(0.1), (ClCH ₂) ₂ , reflux, 9h	-	-	-	26 ^e

^aZ:E ratio was determined by ¹H NMR. ^b**3** and **4** were isolated as an inseparable mixture. Yields were estimated by ¹H NMR.

^cDiastereomeric mixture (ca. 1:1, estimated by ¹H NMR). ^dt: trace.

^eA considerable amount of (PhS)₂ was obtained in 36-41% yield.

Next, several vinylcyclopropyl sulfides **1a-h** were treated with 0.1 or 1.0 equiv. of *p*-TsOH in toluene under reflux (Table 2). Vinylcyclopropyl sulfides, **1a-d**, **f-h**, carrying an arylthio group provided 6-sulfenyl- $\alpha,\beta,\gamma,\delta$ -unsaturated carboxylic esters and nitriles **2a-d**, **f-h** in moderate to good yields, respectively. The rearranged dienes **2d** and **2h** were obtained as single isomers. The rearranged products **2f-h** having a cyano group were less stable than those bearing an ester group. The substituent effect of an arylthio group was slightly observed (entries 1-3). The yield of **2c** with an electron-withdrawing chloro substituent was lower than that of **2a**. In the reaction of **1b** bearing an electron-releasing methyl group, **4b** was not obtained because the rate of the arylthio shift of **4b** was faster than that of **4c**. The methylthio group was ineffective for the C₁-C₂ bond cleavage and for the 1,5-methylthio shift (entry 5), and no rearranged diene was isolated.

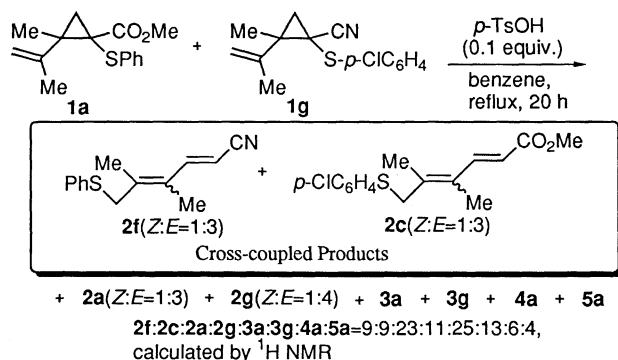
Table 2. Reactions of several vinylcyclopropyl sulfides **1** with *p*-toluenesulfonic acid•H₂O

Entry	Compd No.	Equiv. of <i>p</i> -TsOH	Time(h)	Products (%yield)			
				2(Z:E) ^a	3 ^b	4(Z:E) ^b	5 ^c
1	1a	0.1	12	67(1:3)	8	t(E) ^d	5
2	1b	0.1	12	68(1:3)	6	-	4
3	1c	0.1	12	63(1:3)	8	3(E)	2
4	1d	0.1	10	60(E)	7	3(1:2)	6
5	1e	1.0	20	complex mixture			
6	1f	1.0	3	60(1:2)	4	-	-
7	1g	1.0	3	55(1:3)	3	-	-
8	1h	1.0	3	42(E)	-	-	-

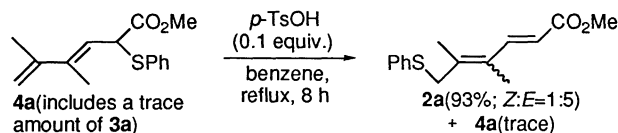
^aZ:E ratio was determined by ¹H NMR. ^b3 and 4 were isolated as an inseparable mixture. Yields and Z:E ratios were estimated by ¹H NMR.

^cDiastereomeric mixture (ca. 1:1, estimated by ¹H NMR). ^dt: trace.

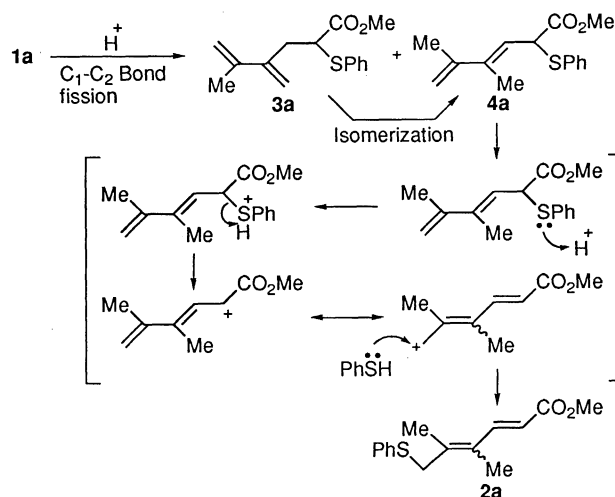
To determine whether the rearranged dienes **2** were formed by an intermolecular or intramolecular 1,5-sulfenyl shift, we carried out the cross-over reaction of vinylcyclopropanes **1a** (131 mg, 0.5 mmol) and **1g** (132 mg, 0.5 mmol) with a catalytic amount of *p*-TsOH (0.01 mmol) in 5 ml of benzene under reflux (Scheme 2). An inseparable mixture of cross-coupled product

**Scheme 2.**

2c and normally rearranged diene **2a**, and that of another cross-coupled diene **2f** and noncross-coupled diene **2g** were isolated in 69 mg and 40 mg yields, respectively. Ring-opened dienes **3a**, **g** and **4a** were obtained as an inseparable mixture (92 mg) with a small amount of γ -lactone **5a**. This experiment revealed that the 1,5-sulfenyl shift proceeded intermolecularly. We also carried out the reaction of diene **4a** including a trace amount of **3a** (obtained from the reaction of **1a** with CF₃SO₃H, Table 1, entry 4) with 0.1 equiv. of *p*-TsOH (Scheme 3). The conjugated diene

**Scheme 3.**

2a was furnished in 93% yield. From these results, the plausible reaction mechanism for the 1,5-sulfenyl shift is assumed as shown in Scheme 4. The ring-opened dienes **3a** and **4a** are first formed by C₁-C₂ bond cleavage followed by deprotonation. The diene **3a** is isomerized to another diene **4a** under acidic conditions. Protonation on a sulfur atom of 2,4-pentadienyl sulfide **4a** followed by elimination of thiophenol gives cationic intermediates, which react with thiophenol at C₆ to provide **2a**.

**Scheme 4.**

In conclusion, the treatment of 1-acceptor-1-sulfenyl-substituted 2-vinylcyclopropanes with a sulfonic acid such as *p*-TsOH and CF₃SO₃H in a nonpolar solvent efficiently caused the C₁-C₂ bond fission and the intramolecular 1,5-sulfenyl shift to give 6-sulfenyl- $\alpha,\beta,\gamma,\delta$ -unsaturated carboxylic esters and nitriles.

References and Note

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- 6 The relative configuration of **1a**, which agreed with the proposed structure from the mechanism for the vinylcyclopropanation,³ was determined by the NOE technique.

