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Ring-opening reactions of diarylvinylidenecyclopropanes by iodine and bromine

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Abstract—Diarylvinylidenecyclopropanes undergo a novel ring-opening reaction upon treatment with iodine or bromine at 0–25 °C in 1,2-dichloroethane to give the corresponding iodinated or brominated naphthalene derivatives in good to high yields within 3 h. The further transformation of the corresponding iodinated or brominated naphthalene derivatives has been disclosed.

Thermal and photochemical skeletal conversions of vinylidenecyclopropanes **1** have attracted much attention from mechanistic, theoretical, spectroscopic, and synthetic viewpoints in the past decades.[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]

Previously, we reported that arylvinylidenecyclopropanes **1** 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.[4] In this letter, we wish to report the addition reactions of diarylvinylidenecyclopropanes **1** with iodine or bromine under similar conditions to give the corresponding cyclopropane ring-opened addition products. We first carried out the reaction of diphenylvinylidenecyclopropane **1a** with iodine (I_2) in a variety of organic solvents and found that in the corresponding iodinated naphthalene derivative either **2a** or **3a** was formed in good yield depending on the employed amounts of iodine. The results are summarized in Table 1. With the molar ratio of **1a**:I_2 = 1:1, the corresponding iodinated naphthalene derivative **2a** was obtained in 51% yield along with trace of **3a** in 1,2-dichloroethane (DCE) at 0 °C (Table 1, entry 1). However, with the molar ratio of **1a**:I_2 = 1:2, the iodinated naphthalene derivative **3a** was obtained in 60% yield along with trace of **2a** under identical conditions (Table 1, entry 2). The yield of **3a** can be improved to 95% yield using large excess amounts of iodine (molar ratio of **1a**:I_2 = 1:40) (Table 1, entry 4). In addition, when this reaction was carried out at 0 °C and 25 °C (room temperature) with the molar ratio of **1a**:I_2 = 1:10, the corresponding iodinated naphthalene derivative **3a** can still be obtained in high yields (93% and 95% isolated yields, respectively) (Table 1, entries 5 and 6). This reaction is fairly effective and can complete within 3 h at 0 °C or 25 °C. The solvent effects have been examined under identical conditions (Table 1, entries 7–9). We found that DCE is the best solvent in this reaction. In the bromination of **1a** under similar conditions, with the molar ratio of **1a**:Br_2 = 1:10 or 1:20, the corresponding brominated naphthalene derivative **3a** was obtained similarly in 75% and 78% yields at 25 °C in DCE (Table 1, entries 10 and 11).

A wide range of electronically and structurally diverse diarylvinylidenecyclopropanes **1** can be employed in this reaction under these optimized conditions. The results are summarized in Table 2. As can be seen from Table 2, with respect to the electron-rich, electron-neutral, and electron-poor diarylvinylidenecyclopropanes **1** (R^1

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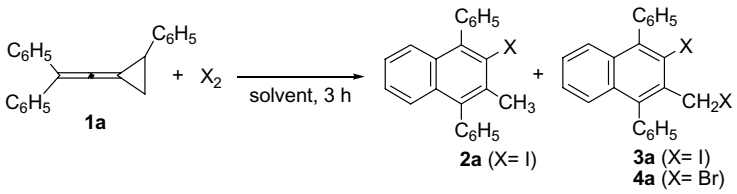
Table 1. The ring-opening reaction of diphenylvinylidenecyclopropane **1a** with iodine or bromine in a variety of solvents

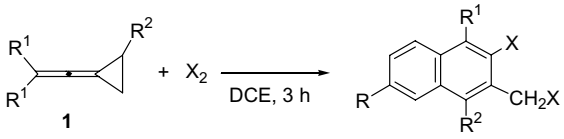


1a **2a** (X= I) **3a** (X= I) **4a** (X= Br)

Entry	Solvent	X_2	Molar ratio **1a**:X_2	Temp./(°C)	Yield/(%)[a] **2a**	Yield/(%)[a] **3a** or **4a**
1	DCE	I_2	1:1	0	51	Trace
2	DCE	I_2	1:2	0	Trace	60
3	DCE	I_2	1:5	0	0	83
4	DCE	I_2	1:40	0	0	95
5	DCE	I_2	1:10	0	0	93
6	DCE	I_2	1:10	25	0	95
7	THF	I_2	1:10	0	0	62
8	Toluene	I_2	1:10	0	0	56
9	MeCN	I_2	1:10	0	0	61
10	DCE	Br_2	1:20	25	0	78
11	DCE	Br_2	1:10	25	0	75

[a] Isolated yields.

Table 2. The ring-opening reaction of arylvinylidenecyclopropane **1** with excess iodine or bromine in DCE at 0 or 25 °C



1 **3** or **4**

R = Me, MeO, F substituents in R^1 group

Entry[a]	**1** (R^1/R^2)	X_2	Temp./°C	Yield/(%)[b] **3** or **4**
1	**1b** (C_6H_5/*p*-MeC_6H_4)	I_2	0	**3b**, 68
2	**1c** (C_6H_5/*p*-$MeOC_6H_4$)	I_2	0	**3c**, 64
3	**1d** (*p*-MeC_6H_4/C_6H_5)	I_2	0	**3d**, 85
4	**1e** (*p*-$MeOC_6H_4$/C_6H_5)	I_2	0	**3e**, 84
5	**1f** (*p*-FC_6H_4/C_6H_5)	I_2	0	**3f**, 20
6	**1f** (*p*-FC_6H_4/C_6H_5)	I_2	25	**3f**, 73
7	**1b** (C_6H_5/*p*-MeC_6H_4)	Br_2	25	**4b**, 44
8	**1c** (C_6H_5/*p*-$MeOC_6H_4$)	Br_2	25	**4c**, 61
9	**1e** (*p*-$MeOC_6H_4$/C_6H_5)	Br_2	25	**4d**, 46

[a] All the reactions were carried out in a ratio of **1**:I_2 = 1:10.
[b] Isolated yields.

and R^2 = aromatic group), these reactions with iodine or bromine proceeded smoothly to give the corresponding naphthalene derivatives **3** or **4** in moderate to good yields within 3 h in most cases (Table 2, entries 1 to 9). For di(*p*-fluorophenyl)vinylidenecyclopropane **1f**, the corresponding rearranged product **3f** was obtained in 73% yield at 25 °C (Table 2, entry 6). The structures of **2a** and **3** were determined by ^1H and ^{13}C NMR spectroscopic data, and HRMS or microanalyses. Their spectroscopic and analytic data are shown in Supporting Information. The crystal structure of **3b** was further determined by X-ray diffraction (Fig. 1).[5]

On the basis of our previous investigation on the Lewis acids or Brønsted acids catalyzed rearrangement of diarylvinylidenecyclopropanes **1**,[4] a plausible mechanism for the reaction of diarylvinylidenecyclopropanes **1** with iodine is outlined in Scheme 1. The addition of iodine to diphenylvinylidenecyclopropane **1a** produces the intermediate **A**, which undergoes the cyclopropane ring-opening reaction to form the cationic intermediate **B**.[6] The intramolecular Friedel–Crafts reaction affords the intermediate **C**. The reprotonation and aromatization of the intermediate **D** furnish the iodinated naphthalene derivative **2a** (Scheme 1). On the other hand, in the pres-

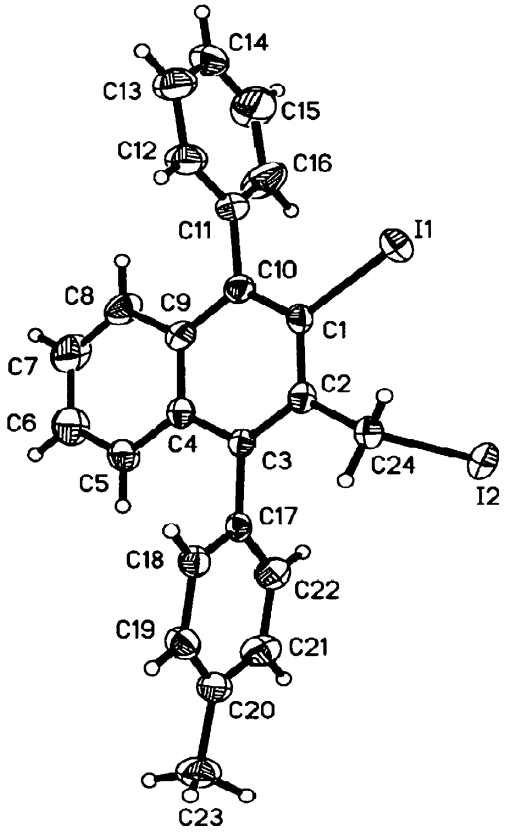
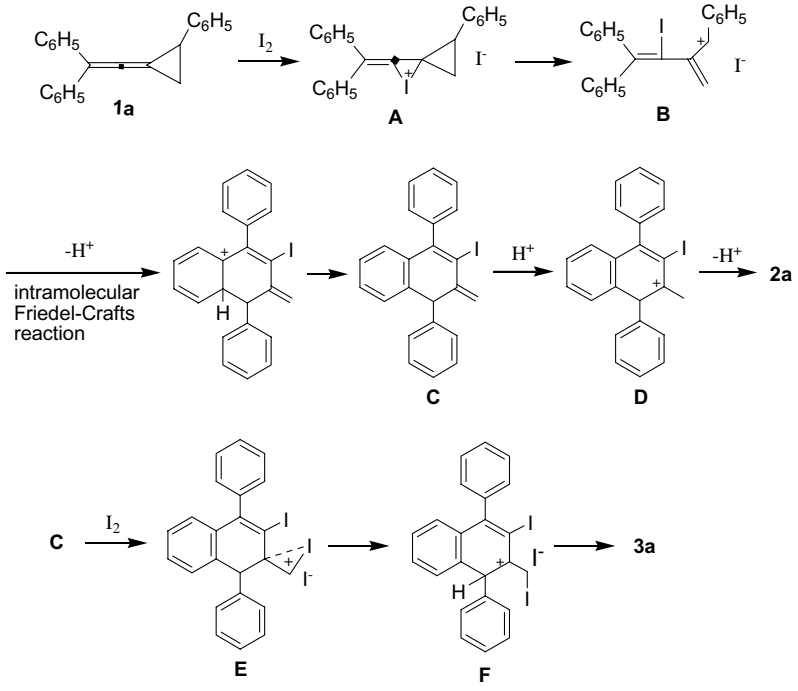


Figure 1. The ORTEP drawing of **3b**.

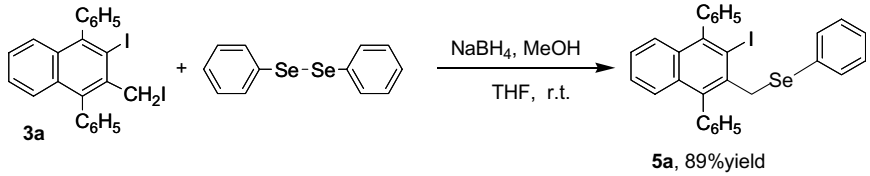
ence of large excess amount of I_2, the addition of iodine to the double bond of the intermediate **C** affords the intermediate **E** which undergoes the ring-opening process to form the cationic intermediate **F**,[7] an allylic cationic intermediate. The aromatization of the cationic intermediate **F** by elimination of HI furnishes the iodinated naphthalene derivative **3a** (Scheme 1).

The further transformation of **3a** is shown in Scheme 2. The coupling reaction of **3a** with diphenyl diselenide (PhSeSePh) in the presence of sodium borohydride ($NaBH_4$) and methanol (MeOH) with a molar ratio of **3a**:PhSeSePh:$NaBH_4$:CH_3OH = 1:0.5:2:5 produced the coupled product **5a** in 89% yield in THF at room temperature (Scheme 2).[8] The further transformation of **5a** by Heck-type coupling reaction with excess amounts of methyl acrylate (CH_2=$CHCO_2CH_3$)[9] in the presence of Pd(II) catalyst and triethylamine (Et_3N) is shown in Scheme 3. The coupled product **6a** was obtained in good yield in DMF at 100 °C (Scheme 3).

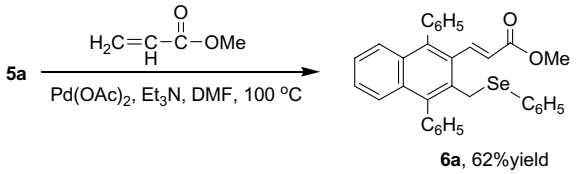
In this letter, we disclosed a novel ring-opening reaction of diarylvinylidenecyclopropanes **1** upon treatment with iodine or bromine to give the corresponding iodinated or brominated naphthalene derivatives in good to high yields within 3 h under mild conditions. In addition, the further possible transformation of **3** has been disclosed. Efforts are underway to elucidate the mechanistic details and to extend the scope of this novel reaction.



Scheme 1. A plausible reaction mechanism of arylvinylidenecyclopropanes **1** with iodine.



Scheme 2. The reaction of **3a** with diphenyldiselenide in the presence of $NaBH_4$ and MeOH.



Scheme 3. Heck-type coupling reaction of **5a** with methyl acrylate.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.08.130.

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5. The crystal data of **3b** have been deposited in CCDC with deposition number 273884. Empirical Formula: $C_{24}H_{18}I_2$; Formula weight: 560.21; Crystal color, habit: colorless, prismatic; Crystal dimensions: $0.516 \times 0.475 \times 0.438$ mm; Crystal system: monoclinic; Lattice type: primitive; Lattice parameters: $a = 11.6109(10)$ Å, $b = 9.9771(9)$ Å, $c = 18.1552(16)$ Å, $\alpha = 90°$, $\beta = 103.249(2)°$, $\gamma = 90°$, $V = 2047.2(3)$ Å^3; Space group: $P2(1)/n$; $Z = 4$; $D_{calc} =$

1.818 g/cm^3; $F_{000} = 1072$; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0466, 0.1068.

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