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# An $X^-$ (X = I, Br)-Triggered Ring-Opening Cyclization of Cyclopropenyl-Substituted Alkyl Halides or Mesylates: An Efficient and Highly Regio- and Stereoselective Approach to (*E*)-Haloalkylidene 4−7-Membered Cyclic Compounds

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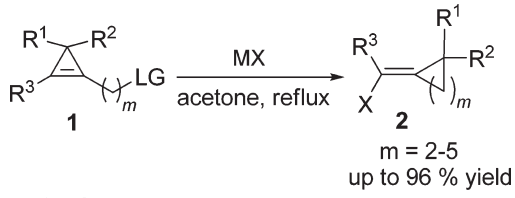


$R^1$, $R^2$ = $CO_2Me$, COMe, $SO_2Ph$
LG = Br, OMs
$R^3$ = Ph, *p*-$CH_3C_6H_{14}$, *n*-$C_4H_9$, Et, H

Polyfunctionalized (*E*)-haloalkylidene cyclic products were efficiently synthesized in moderate to excellent yields via a regio- and stereoselective $X^-$ (X = I or Br)-triggered ring-opening intramolecular trapping of cyclopropenes **1**. The reaction can be used for construction of 4−7-membered products. The *E*-stereoselectivity of the *exo*-C=C bond is very high. The carbon−halogen bond in the *exo*-C=C bond may further be elaborated to prepare differently substituted cyclic products with a stereodefined C=C bond.

Efficient synthesis of carbocycles and heterocycles is one of the main themes in organic synthesis due to the importance of cyclic compounds.[1−3] Recently functionalized allenes have been developed as a class of powerful starting materials for the construction of cyclic compounds.[4] As two classes of very similar analogues to allenes, alkylidenecyclopropanes[5,6] and even cyclopropenes[5t,5u,7,8] have also caught the attention of organic chemists.

In 2003, we described a regioselective cycloisomerization of cyclopropenyl ketones leading to 2,3,4-trisubstituted furans or 2,3,5-trisubstituted furans by using CuI or $PdCl_2(CH_3CN)_2$ as the catalysts, respectively.[9] In the same year, we noticed an $X^-$ (X = I, Br)-triggered ring-opening

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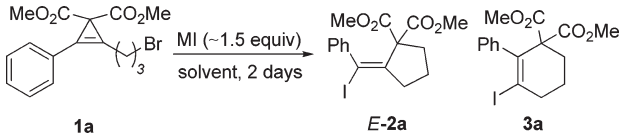
**TABLE 1. Reaction of 1a with MI under Different Reaction Conditions**




| entry | MI | solvent | temp (°C) | yield of *E*-**2a**[a] (%) |
|---|---|---|---|---|
| 1[b] | NaI | acetone | reflux | 78 |
| 2[b,c] | NaI | acetone | reflux | 70 |
| 3 | NaI | acetone | reflux | 80 |
| 4 | AgI | acetone | reflux | 0[d] |
| 5 | CuI | acetone | reflux | 0[e] |
| 6 | LiI | acetone | reflux | 58 |
| 7 | NaI | $CH_3CN$ | reflux | 74 |
| 8 | NaI | THF | reflux | 74 |
| 9 | NaI | $CH_3NO_2$ | 80 | 71 |
| 10 | NaI | dioxane | 80 | 73 |
| 11 | NaI | DCE | 80 | 67 |

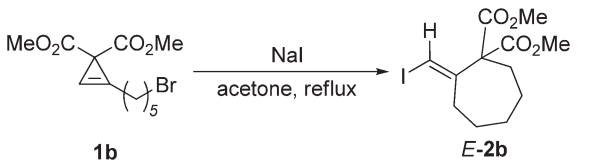
[a] Isolated yield. [b] 0.5 equiv of $Na_2CO_3$ was used. [c] 1.2 equiv of NaI was used. [d] 89% of **1a** was recovered. [e] 83% of **1a** was recovered.

coupling reaction of cyclopropenyl carboxylates with organic halides providing an efficient and highly regio- and stereoselective route to a series of polyfunctionalized (1*E*)-alkenyl halides.[10] However, in the presence of imines, the NaI-catalyzed reaction of cyclopropenyl carboxylates provided a highly regio- and stereoselective route to a series of polyfunctionalized vinyl aziridines.[11] Herein, we wish to report an $X^-$ (X = I, Br)-triggered ring-opening cyclization of cyclopropenyl-substituted alkyl halides or mesylates, providing a highly regio- and stereoselective approach to the synthesis of (*E*)-haloalkylidene 4−7-membered cyclic compounds.

The reaction of dimethyl 2-(3-bromopropyl)-3-phenylcycloprop-2-ene-1,1-dicarboxylate **1a** with 1.5 equiv of NaI in the presence of 0.5 equiv of $Na_2CO_3$ in acetone under reflux was studied. To our delight, the reaction smoothly led to the formation of (*E*)-iodobenzylidenecyclopentane derivative *E*-**2a** in 78% yield with excellent regio- and stereoselectivity, which was established by the X-ray diffraction study of *E*-**2a** (Figure S1, Supporting Information).[12] It should be noted that in all the cases the formation of six-membered ring **3a** was not observed, which indicated that the iodide anion attacked regioselectively at the $sp^2$-carbon atom connected to the phenyl group in **1a**.

With 1.2 equiv of NaI, the yield of *E*-**2a** is lower (entry 2, Table 1); control experiment indicated that the addition of $Na_2CO_3$ is not necessary in this case (entry 3, Table 1); no reaction was observed with AgI or CuI (entries 4 and 5, Table 1); the reaction with LiI afforded *E*-**2a** in much lower yield (entry 6, Table 1); study on the solvent effect implied that acetone is the best solvent for this transformation (compare entries 7−11 with entry 3, Table 1).

**TABLE 2. Reaction of 1b with NaI under Different Reaction Conditions**




| entry | NaI (equiv) | additive[a] | M[b] (mol/L) | time (h) | yield of *E*-**2b**[c] (%) |
|---|---|---|---|---|---|
| 1 | 1.5 | none | 0.067 | 18 | 9 |
| 2 | 1.5 | $Na_2CO_3$ (0.6) | 0.067 | 16.5 | 23 |
| 3 | 1.7 | $Na_2CO_3$ (0.7) | 0.05 | 20 | 57 |
| 4 | 1.6 | $Na_2CO_3$ (0.6) | 0.025 | 20 | 47 |

[a] Equiv of $Na_2CO_3$ used. [b] M = the concentration of **1b**. [c] Isolated yield.

However, when we applied the optimized reaction conditions to the reaction of 5-(3′,3′-bis(methoxycarbonyl)-cyclopropenyl)pentyl bromide **1b**, the yield of the 7-membered product *E*-**2b** was only 9% (entry 1, Table 2). It was observed that the reaction with the addition of 0.6 equiv of $Na_2CO_3$ afforded *E*-**2b** in a slightly higher yield (entry 2, Table 2). Thus, further study for the effect of concentration of **1b** was conducted (Table 2). When the concentration of **1b** was adjusted to 0.05 M, we were pleased to find that the reaction of **1b** in the presence of 0.7 equiv of $Na_2CO_3$ occurred smoothly to give the product *E*-**2b** in 57% yield (entry 3, Table 2). The stereochemistry was also established by its X-ray diffraction study (Figure S2, Supporting Information).[13] Here again, the regioselectivity is very high with $I^-$ attacking the less substituted $sp^2$ carbon atom, which is the same as reported in our previous studies.[10]

With the optimized reaction conditions in hand, the scope of the reaction of the mesylates was studied with some of the typical results being summarized in Table 3. $R^1$ or $R^2$ may be $COCH_3$, $CO_2Me$, $CO_2Et$, and $SO_2Ph$. Besides NaI, $LiBr \cdot H_2O$ may also be used as the metallic halide to give the corresponding (*E*)-bromomethylene 5-membered products in moderate to excellent yields (entries 2, 4, 6, and 8, Table 3). Even the 4-membered product *E*-**2l** was prepared in 27% yield from the ring-opening reaction of **1h** (entry 10, Table 3).

It should also be noted that 3,3-bis(methoxycarbonyl)-2-alkyl or aryl-substituted cyclopropenylalkyl bromides **1i**, **1j**, and **1k** also smoothly afforded the corresponding products *E*-**2m**, *E*-**2n**, and *E*-**2o** with the excellent regioselectivity directing the X to the $sp^2$ carbon atom at the 1-position (Scheme 1).

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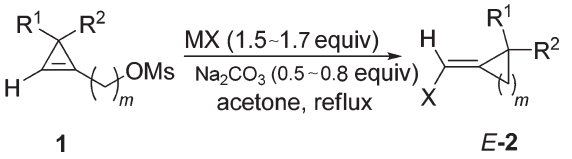
(12) Crystal data for compound *E*-**2a**: $C_{16}H_{17}O_4I$, MW = 400.20, monoclinic, space group *P*2(1)/*c*, final *R* indices [$I > 2\sigma(I)$], R1 = 0.0332, *w*R2 = 0.0847, *R* indices (all data), R1 = 0.0394, *w*R2 = 0.0878, *a* = 9.1568 (7) Å, *b* = 19.9575 (16) Å, *c* = 9.6108 (7) Å, α = 90°, *β* = 114.2340(1)°, *γ* = 90°, *V* = 1601.6 (2) Å$^3$, *T* = 293(2) K, *Z* = 4, reflections collected/unique: 9277/3483 (*R*(int) = 0.0446), number of observations [$> 2\sigma(I)$] 2984, parameters 193. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 694977. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223/336- 033; E-mail: deposit@ccdc.cam.ac.uk).
(13) Crystal data for compound *E*-**2b**: $C_{12}H_{17}O_4I$, MW = 352.16, monoclinic, space group *P*2(1)/*c*, final *R* indices [$I > 2\sigma(I)$], R1 = 0.0416, *w*R2 = 0.1048, *R* indices (all data), R1 = 0.0460, *w*R2 = 0.1075, *a* = 8.2163(9) Å, *b* = 13.1526(15) Å, *c* = 12.5835(14) Å, α = 90°, *β* = 95.994(2)°, *γ* = 90°, *V* = 1352.4 (3) Å$^3$, *T* = 293(2) K, *Z* = 4, reflections collected/unique: 7777/2944 (*R*(int) = 0.0900), number of observations [$> 2\sigma(I)$] 2565, parameters 157. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 694978. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223/336- 033; E-mail: deposit@ccdc.cam.ac.uk).

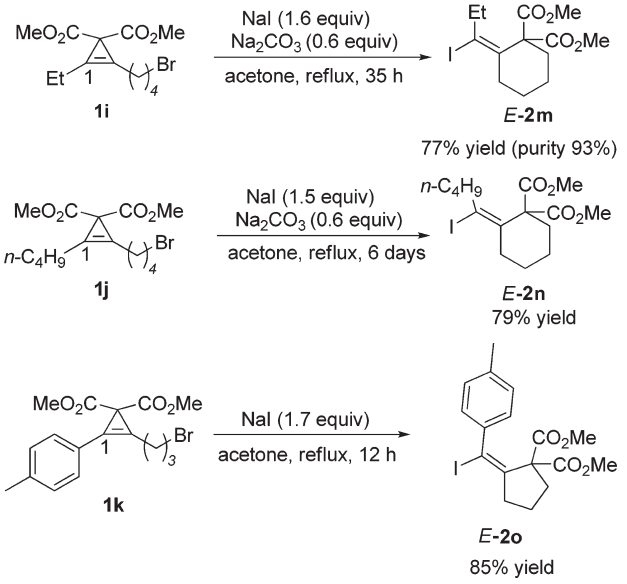
**TABLE 3. Scope of the Ring-Opening Cyclization Reaction**




| | 1 | | | | | |
|---|---|---|---|---|---|---|
| entry | $R^1$ | $R^2$ | $m$ | MX[a] | time (h) | yield of **2**[b,c] (%) |
| 1 | $CO_2Me$ | $CO_2Me$ | 3 (**1c**) | A | 0.8 | 81 (61) (*E*-**2c**)[d] |
| 2 | $CO_2Me$ | $CO_2Me$ | 3 (**1c**) | B | 2.7 | 96 (86) (*E*-**2d**) |
| 3 | $CH_3CO$ | $CO_2Et$ | 3 (**1d**) | A | 0.5 | 82 (65) (*E*-**2e**) |
| 4 | $CH_3CO$ | $CO_2Et$ | 3 (**1d**) | B | 1 | 84 (87) (*E*-**2f**) |
| 5 | $CH_3CO$ | $SO_2Ph$ | 3 (**1e**) | A | 3 | 76 (92) (*E*-**2g**) |
| 6 | $CH_3CO$ | $SO_2Ph$ | 3 (**1e**) | B | 3 | 77 (85) (*E*-**2h**) |
| 7 | $CO_2Me$ | $SO_2Ph$ | 3 (**1f**) | A | 4 | 79 (75) (*E*-**2i**) |
| 8 | $CO_2Me$ | $SO_2Ph$ | 3 (**1f**) | B | 16 | 71 (81) (*E*-**2j**)[e] |
| 9 | $CO_2Me$ | $CO_2Me$ | 4 (**1g**) | A | 1 | 69 (76) (*E*-**2k**)[f] |
| 10 | $CO_2Me$ | $CO_2Me$ | 2 (**1h**) | A | 10 | 22 (27) (*E*-**2l**) |

[a] A = NaI, B = $LiBr\cdot H_2O$. [b] Isolated yield. [c] The numbers in parentheses are isolated yields for the reactions carried out in the absence of $Na_2CO_3$. [d] 2.4 equiv of NaI were used. [e] 2.4 equiv of $LiBr\cdot H_2O$ were used. [f] When **1l** was applied to the reaction with 0.6 equiv of $Na_2CO_3$ as the additive, the yield of *E*-**2k** was 78%.

**SCHEME 1. The Reactions of Cyclopropenes 1i, 1j, and 1k with NaI**



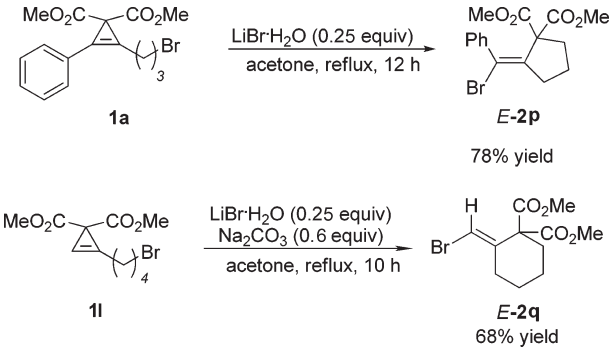

As expected, the reactions of **1a** and **1l** with $LiBr\cdot H_2O$ occurred smoothly with only a catalytic amount of $LiBr\cdot H_2O$ (Scheme 2).

The synthetic utilities of the product *E*-**2** were demonstrated by the transformation of the representative product *E*-**2c** (Scheme 3). Treatment of *E*-**2c** with phenyl boronic acid or diethyl zinc gave the coupling products *E*-**4a** and *E*-**5a** in 76% and 73% yields, respectively. Phenylacetylene and 1-hexyne underwent the Sonogashira coupling reaction with *E*-**2c** to afford stereodefined conjugated enynes *E*-**6a** and *E*-**6b** in excellent yields.

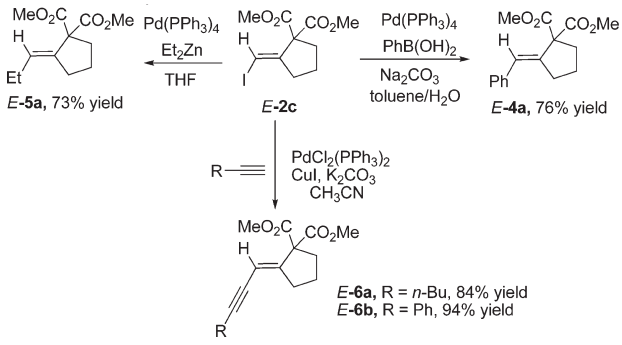
The plausible mechanism for this transformation is depicted in Scheme 4. The nucleophile $X^-$ ($I^-$ and $Br^-$) attacked regioselectively the $sp^2$ carbon atom at the 1-position of cyclopropenes **1** to give a stereodefined carbanion **7**, which would undergo intramolecular nucleophilic substitutions to afford *E*-**2**.

In conclusion, we have developed an $X^-$ (X = I, Br)-triggered ring-opening intramolecular trapping of cyclopropenyl-substituted alkyl bromides or mesylates providing an efficient highly regio- and stereoselective approach to the synthesis of (*E*)-haloalkylidene cyclic compounds. Further studies on the scope of the reaction and the synthetic application are now being carried out in our laboratory.

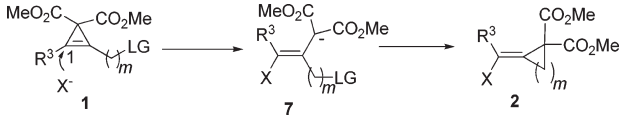
**SCHEME 2. The Reactions of Cyclopropenes 1a and 1l with a Catalytic Amount of $LiBr\cdot H_2O$**




**SCHEME 3. The Synthetic Utilities of the Product *E*-2c**




**SCHEME 4. The Plausible Mechanism for the Ring-Opening Cyclization Reaction**




## Experimental Section

**General Procedure for the Ring-Opening Cyclization Reaction.** To a reaction tube were added sequentially NaI (35 mg, 0.23 mmol), 1.5 mL of acetone, **1a** (54 mg, 0.15 mmol), and 1.5 mL of acetone. The resulting mixture was refluxed for 2 days as monitored by TLC. Evaporation and column chromatography on silica gel (eluent: petroleum ether/$Et_2O$ = 10/1) afforded *E*-**2a**[14] (49 mg, 80%): solid,

(14) Kitagawa, O.; Inoue, T.; Hirano, K.; Taguchi, T. *J. Org. Chem.* **1993**, *58*, 3106.

m.p. 90−91 °C (petroleum ether/ethyl acetate); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.35−7.30 (m, 2H), 7.27−7.13 (m, 3H), 3.38 (s, 6H), 2.67 (t, $J$ = 7.5 Hz, 2H), 2.55 (t, $J$ = 6.9 Hz, 2H), 1.78−1.65 (m, 2H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 170.0, 146.2, 142.9, 128.8, 127.9, 127.6, 98.2, 64.9, 52.5, 42.7, 40.9, 22.8; MS (ESI) $m/z$ 455 ($M + CH_3OH + Na^+$), 423 ($M + Na^+$), 401 ($M + H^+$); IR (KBr) 2951, 1731, 1433, 1267 cm$^{-1}$. Anal. Calcd for $C_{16}H_{17}O_4I$: C 48.02; H 4.28. Found: C 48.22; H 4.51.

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**Supporting Information Available:** Experimental procedures, characterization of the products, and the CIF files of *E*-**2a** and *E*-**2b**. This material is available free of charge via the Internet at http://pubs.acs.org.