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LDA-mediated domino carbolithiation reactions of vinylidenecyclopropanes with but-3-yn-2-one and 1-phenylprop-2-yn-1-one

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ABSTRACT

A novel domino carbolithiation reaction of vinylidenecyclopropanes **1** with but-3-yn-2-one and 1-phenylprop-2-yn-1-one by treating with LDA in THF was observed to give the corresponding adducts in moderate to good yields. The scope and limitations as well as the plausible mechanism have been discussed on the basis of control experiments.

Organolithium chemistry is of unquestionable importance in organic synthesis.[1] Owing to the strongly polarized lithium-carbon bond, organolithium compounds are used as highly reactive nucleophiles and strong bases in most of C–C bond forming reactions. Their applications range from simple deprotonation and anionic polymerization reactions to carbolithiations and asymmetric syntheses. Recently, LDA (lithium diisopropylamide)-mediated reaction of vinylidenecyclopropanes[2] with a variety of electrophiles has been extensively disclosed. For example, we previously reported the LDA-mediated selective carbolithiation reactions of vinylidenecyclopropanes **1** with a variety of electrophiles to give the corresponding adducts in good yields under mild conditions along with the further transformation of these products.[3]

During our ongoing investigation, we found that the LDA-mediated domino carbolithiation reactions of vinylidenecyclopropanes **1** with but-3-yn-2-one **2a** and 1-phenylprop-2-yn-1-one **2b** could take place smoothly to afford a variety of interesting products in moderate to good yields and moderate diastereoselectivities. Herein, we wish to report these novel results in this Letter along with a mechanistic discussion.

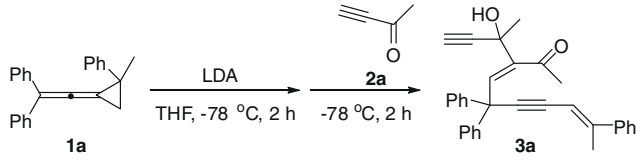
We started our work by examining the LDA-mediated reaction of vinylidenecyclopropane (VDCP) **1a** (1.0 equiv) with but-3-yn-2-one **2a** (2.0 equiv) at −78 °C in tetrahydrofuran (THF). It was found that product **3a** derived from a domino addition reaction was formed in 80% yield (Table 1, entry 1). Further investigation on the reaction conditions revealed that increasing the employed amount of **2a** to 2.5 or 3.0 equiv afforded **3a** in 88% yield under the standard conditions (Table 1, entries 2 and 3).

Having these optimized reaction conditions in hand, we next examined the generality of this interesting domino reaction and the results of these experiments are summarized in Table 2. It was found that the corresponding domino addition products **3b–i** were obtained in 70–85% yields (Table 2, entries 1–8). The substituents on the aromatic rings did not have significant influence on the reaction outcomes. As for VDCPs **1f** and **1i** in which R^4 = Me, the corresponding domino adducts **3f** and **3i** were produced stereospecifically as trans-configuration on the basis of previous results[3] and NMR spectroscopic data in 85% and 81% yield, respectively (Table 2, entries 5 and 8).

Moreover, using 1-phenylprop-2-yn-1-one **2b** instead of **2a**, the corresponding domino adducts **4a–e** were formed in 55–63% yields under the standard conditions as shown in Table 3.

Their structures were determined by ^{1}H and ^{13}C NMR spectroscopy and HRMS. The crystal structure of **3a** was determined by X-ray diffraction (Fig. 1) and its CIF data are presented in the Supplementary data.[4]

Table 1
Optimization of the reaction conditions of LDA-mediated domino reactions of VDCP **1a** with but-3-yn-2-one **2a**



Entry[a]	Molar ratio of **1a** and **2a**	Yield[b] (%)
1	1:2.0	80
2	1:2.5	88
3	1:3.0	88

[a] After vinylidenecyclopropane **1a** (0.2 mmol) was lithiated by LDA (0.4 mmol) at −78 °C for 2 h, but-3-yn-2-one **2a** (0.4–0.6 mmol) was added into the reaction mixture. Then, the reaction was quenched by the addition of saturated aqueous ammonium chloride solution after 2 h.
[b] Yield of isolated products.

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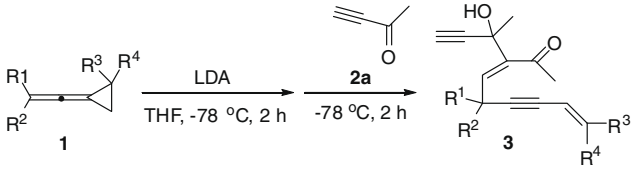
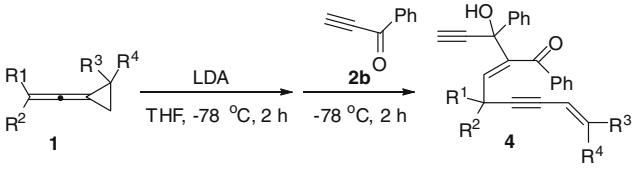
Table 2
LDA-mediated domino reactions of VDCPs **1** with but-3-yn-2-one **2a**



Entry[a]	1 ($R^1/R^2/R^3/R^4$)	Yield[b] (%)
1	**1b** ($C_6H_5/C_6H_5/C_6H_5/C_6H_5$)	**3b**, 70
2	**1c** ($C_6H_5/C_6H_5/p$-FC_6H_4/p-FC_6H_4)	**3c**, 75
3	**1d** ($C_6H_5/C_6H_5/p$-ClC_6H_4/p-ClC_6H_4)	**3d**, 76
4	**1e** (p-MeC_6H_4/p-$MeC_6H_4/C_6H_5/C_6H_5$)	**3e**, 79
5	**1f** (p-FC_6H_4/p-FC_6H_4/C_6H_5/Me)	**3f**, 85
6	**1g** ($C_6H_5/C_6H_5/p$-MeC_6H_4/p-MeC_6H_4)	**3g**, 81
7	**1h** (p-FC_6H_4/p-FC_6H_4/p-MeC_6H_4/p-MeC_6H_4)	**3h**, 81
8	**1i** (p-MeC_6H_4/p-MeC_6H_4/C_6H_5/Me)	**3i**, 81

[a] After vinylidenecyclopropanes **1** (0.2 mmol) were lithiated by LDA (0.4 mmol) at −78 °C for 2 h, but-3-yn-2-one **2a** (0.5 mmol) was added into the reaction mixture. Then, the reactions were quenched by the addition of saturated aqueous ammonium chloride solution after 2 h.
[b] Yield of isolated products.

Table 3
LDA-mediated domino reactions of VDCPs **1** with 1-phenylprop-2-yn-1-one **2b**



Entry[a]	1 ($R^1/R^2/R^3/R^4$)	Yield[b] (%)
1	**1a** ($C_6H_5/C_6H_5/C_6H_5$/Me)	**4a**, 55
2	**1b** ($C_6H_5/C_6H_5/C_6H_5/C_6H_5$)	**4b**, 63
3	**1d** ($C_6H_5/C_6H_5/p$-ClC_6H_4/p-ClC_6H_4)	**4c**, 59
4	**1g** ($C_6H_5/C_6H_5/p$-MeC_6H_4/p-MeC_6H_4)	**4d**, 57
5	**1j** (p-ClC_6H_4/p-C!$C_6H_4/C_6H_5/C_6H_5$)	**4e**, 58

[a] After vinylidenecyclopropanes **1** (0.2 mmol) were lithiated by LDA (0.4 mmol) at −78 °C for 2 h, 1-phenylprop-2-yn-1-one **2b** (0.5 mmol) was added into the reaction mixture. Then, the reactions were quenched by the addition of saturated aqueous ammonium chloride solution after 2 h.
[b] Yield of isolated products.

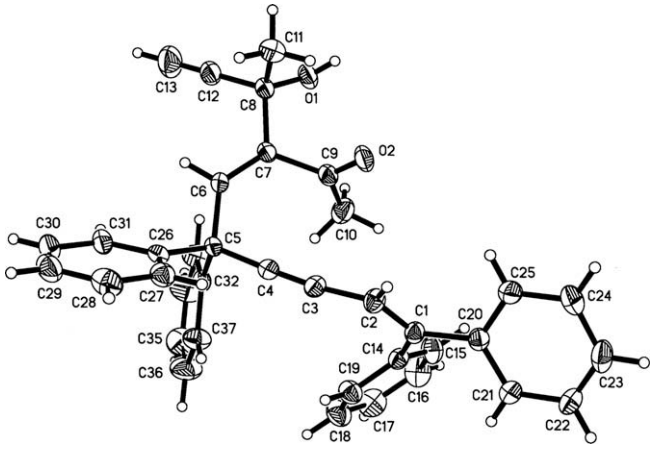


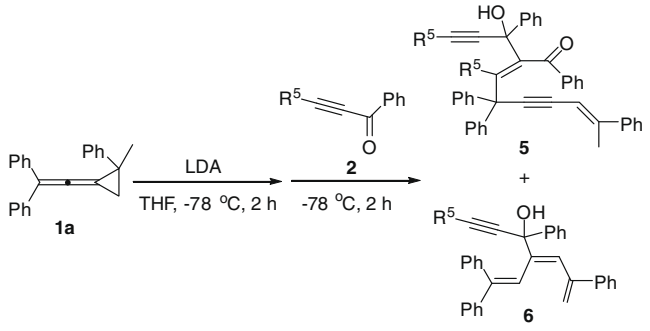
Figure 1. ORTEP drawing of **3a**.

It should be also noted that using 1,3-diphenylprop-2-yn-1-one **2c** and 1-phenyl-3-(trimethylsilyl)prop-2-yn-1-one **2d** as the substrates led to the domino addition products **5a** and **5b** along with another addition products **6a** and **6b** in 61% and 72% total yield, respectively as depicted in Table 4, suggesting that the substituent on the terminal of alkyne can significantly affect the reaction outcome.

Using hex-3-yn-2-one **2e** as the electrophile in the LDA-mediated reactions with VDCPs **1a**, **1k,** and **1l** under the standard conditions, the addition products **7a–c** derived from LDA-mediated 1,2-addition and the products **8a–c** derived from LDA-mediated 1,4-addition (Michael addition) were obtained as product mixtures in good yields and 1.22:1–2.67:1 ratios (Table 5, entries 1–3).

However, using VDCPs **1b**, **1g**, and **1m** as the substrates to react with **2e** under the standard conditions, the corresponding 1,4-addition products **9a–9c** were formed exclusively in good yields (Table 6, entries 1–3).

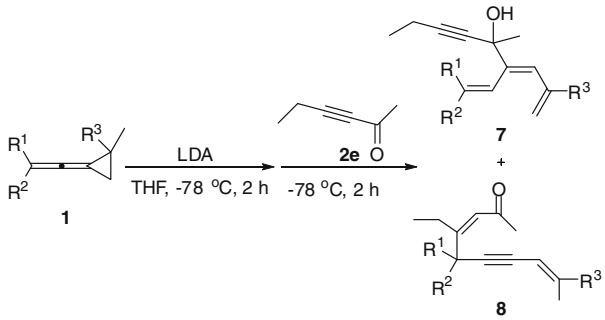
Table 4
LDA-mediated domino reactions of VDCPs **1a** with Yn-2-ones **2c** and **2d**



Entry[a]	2 (R^5)	Yield[b] (%) (**5**:**6**)
1	**2c** (Ph)	**5a** and **6a**, 61 (1.30:1)[c]
2	**2d** (TMS)	**5b** and **6b**, 72 (1.76:1)[c]

[a] After vinylidenecyclopropane **1a** (0.2 mmol) was lithiated by LDA (0.4 mmol) at −78 °C for 2 h, yn-2-one **2c** or **2d** (0.5 mmol) was added into the reaction mixture. Then, the reaction was quenched by the addition of saturated aqueous ammonium chloride solution after 2 h.
[b] Yield of isolated products.
[c] These products were isolated as product mixtures and their ratios were determined by ^{1}H NMR spectroscopic data.

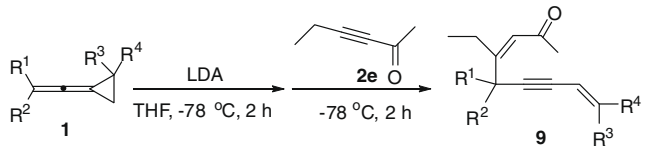
Table 5
LDA-mediated reactions of VDCPs **1a**, **1k**, and **11** with hex-3-yn-2-one **2e**



Entry[a]	1 ($R^1/R^2/R^3$)	Yield[b] (%) (**7**:**8**)
1	**1a** ($C_6H_5/C_6H_5/C_6H_5$)	**7a** and **8a**, 85 (1.22:1)[c]
2	**1k** ($C_6H_5/C_6H_5/p$-MeC_6H_4)	**7b** and **8b**, 83 (2.67:1)[c]
3	**1l** ($C_6H_5/C_6H_5/p$-ClC_6H_4)	**7c** and **8c**, 81 (1.24:1)[c]

[a] After vinylidenecyclopropane **1a, 1k,** or **1l** (0.2 mmol) was lithiated by LDA (0.4 mmol) at −78 °C for 2 h, hex-3-yn-2-one **2e** (0.5 mmol) was added into the reaction mixture. Then, the reactions were quenched by the addition of saturated aqueous ammonium chloride solution after 2 h.
[b] Yield of isolated products.
[c] These products were isolated as product mixtures and their ratios were determined by ^{1}H NMR spectroscopic data.

Table 6
LDA-mediated reactions of VDCPs **lb**, **lg**, and **lm** with hex-3-yn-2-one**2e**

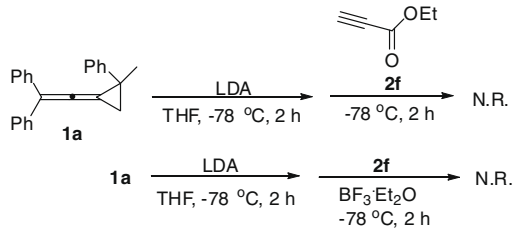


Entry[a]	**1** ($R^1/R^2/R^3/R^4$)	Yield[b] (%)
1	**1b** ($C_6H5/C_6H_5/C_6H5/C_6H5$)	**9a**, 74
2	**1g** ($C_6H5/C6H5/p$-MeC6H4/p-MeC6H$_4$)	**9b**, 75
3	**1m** (p-FC_6H_4/p-$FC_6H_4/C_6H5/C_6H_5$)	**9c**, 78

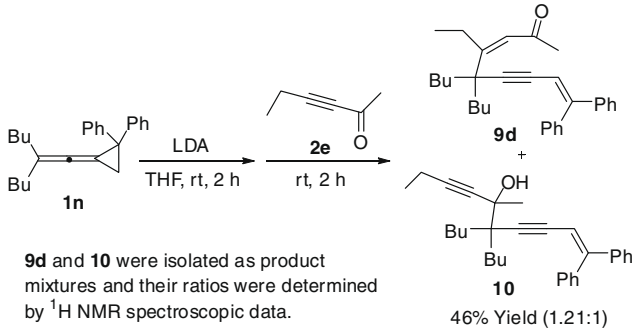
[a] After vinylidenecyclopropanes **1b, 1g,** or **1m** (0.2 mmol) were lithiated by LDA (0.4 mmol) at −78 °C for 2 h, hex-3-yn-2-one **2e** (0.5 mmol) was added into the reaction mature. Then, the reactions were quenched by the addition of saturated aqueous ammonium chloride solution after 2 h.
[b] Yield of isolated products.

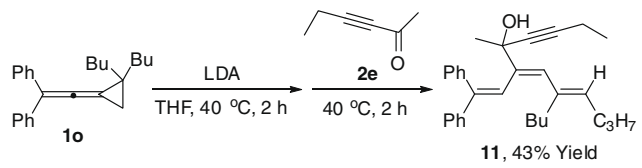
The results shown in Tables 5 and 6 suggested that when R^4 = Me, [1,5]-H shift or [1,5]-Li shift could provide a driving force for the formation of addition product **7**.[3b] More interestingly, we found that compound **8** could be transformed into compound **7** in a NMR tube with $CDCl_3$ after 24 h presumably via a 3,3-sigmatropic rearrangement (see Supplementary data), suggesting that compound **7** is thermodynamically more stable than **8**.

On the other hand, using ethyl propiolate **2f** as the electrophile instead of **2a**, no reaction occurred under the standard conditions or even in the presence of Lewis acid $BF_3{\cdot}OEt_2$, presumably due to that **2f** is less electrophilic than **2a** (Scheme 1).



Scheme 1. LDA-mediated reactions of VDCP **1a** with Ethyl Propiolate **2f**.





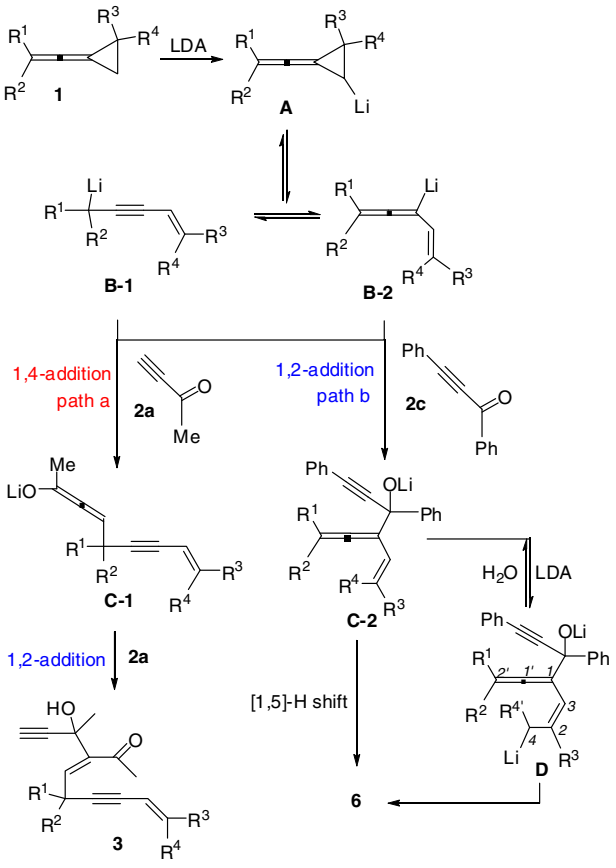
Scheme 2. LDA-mediated reactions of VDCPs **1n** and **1o** having aliphatic group with Hex-3-yn-2-one **2e**.

Moreover, as for VDCPs **1n** and **1o** having aliphatic groups, the corresponding 1,2- and 1,4-addition compounds **10**, **11**, and **9d** were obtained in the reaction with **2e** either as the product mixtures or as the sole product at room temperature (20 °C) or at 40 °C in moderate yields without the formation of the domino addition product (Scheme 2). The configuration of **11** was determined by NOESY spectrum (see Supplementary data).

On the basis of these results, a plausible mechanism for the formation of the domino addition product is outlined in Scheme 3 using the reaction of **1** with **2a** and **2c** as a model. First, the lithiation of cyclopropyl ring of vinylidenecyclopropane **1** gives the corresponding cyclopropyl carbanion intermediate **A** by treatment with LDA.[5] Intermediate **A** can be transformed into anionic intermediates **B-1** and **B-2** and there is an equilibrium between all these anionic species as intermediates **A**, **B-1,** and **B-2**.[6] When **2a** is used as an electrophile, intermediate **C-1** is formed by the Michael addition (1,4-addition) of intermediate **B-1** with **2a**, which subsequently undergoes 1,2-addition with another molecule of **2a** to give the corresponding domino addition product **3** (Scheme 3, path a). Using **2c** as an electrophile, the 1,2-addition of intermediate **B-2** with **2c** can take place to give the corresponding product **6** via intermediate **C-2** (Scheme 3, path b) along with product **3** via the domino addition process (path a). On the other hand, intermediate **D** can also be formed by lithiation of intermediate **C-2** (R^4 is an alkyl group), which undergoes a [1,5]-lithium shift to give product **6** as well (Scheme 3, path b).[3b]

The substituent on the terminal of alkyne can retard the reaction rate of Michael addition process and impair such domino addition reaction. Therefore, only using **2a** and **2b** as the electrophiles, the domino addition product was formed exclusively.

In summary, we have disclosed a novel domino carbolithiation reaction of vinylidenecyclopropanes **1** with but-3-yn-2-one and 1-



Scheme 3. A plausible reaction mechanism.

phenylprop-2-yn-1-one by treating with LDA in THF. The scope and limitations of this reaction have been carefully examined. The domino addition products **3** and **4** are important compounds in organic and medicinal chemistry.[7,8] The potential utilization and extension of the scope of this synthetic methodology are currently under investigation.

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.2009.11.012.

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4. The crystal data of **3a** have been deposited in CCDC with number 675542. Empirical formula: $C_{38}H_{32}Cl_2O_2$; formula weight: 591.54; crystal size: $0.479 \times 0.433 \times 0.251$; crystal color, habit: colorless, prismatic; crystal system: triclinic; lattice type: primitive; lattice parameters: $a = 8.7749(11)$ Å, $b = 13.4723(16)$ Å, $c = 14.3018(17)$ Å, $\alpha = 91.855(2)^o$, $\beta = 105.300(2)^o$, $\gamma = 100.532(2)^o$, $V = 1597.5(3)$ Å^3; space group: $P\bar{1}$; $Z = 2$; $D_{calc} = 1.230$ g/cm^3; $F_{000} = 620$; $R_1 = 0.0719$, $wR_2 = 0.1926$. Diffractometer: Rigaku AFC7R.
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8. *Typical reaction procedure*: Under an argon atmosphere, to a solution of vinylidenecyclopropanes **1** (0.2 mmol) in THF (2.0 mL) was added LDA (0.4 mmol) at −78 °C, and the resulting reaction mixture was stirred at −78 °C for about 2 h. Then ynone **2** (0.5 mmol) was added and the reaction solution was further stirred for 2 h at the same reaction temperature. Then the reaction was quenched by the addition of the aqueous solution of ammonium chloride and warmed to room temperature. The reaction solution was diluted with ether (10.0 mL × 3). The organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography.*Compound* **3a**: Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.73 (3H, s, CH_3), 2.27 (3H, s, CH_3), 2.31 (3H, s, CH_3), 2.61 (1H, s, CH), 3.28 (1H, s, CH), 5.96 (1H, s, CH), 6.57 (1H, s, CH), 7.23–7.38 (9H, m, Ar), 7.41–7.48 (6H, m, Ar). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 18.8, 29.7, 34.7, 50.6, 69.4, 73.8, 85.5, 88.2, 97.4, 106.0, 125.4, 127.1, 127.2, 127.6, 127.7, 128.1, 128.3, 128.49, 128.52, 132.1, 140.6, 143.6, 144.8, 145.1, 148.9, 206.4. IR (CH_2Cl_2) ν 3456, 3285, 3082, 3058, 3026, 2987, 2931, 2855, 2318, 2211, 2113, 1953, 1699, 1597, 1490, 1446, 1362, 1228, 1184, 1127, 1030, 930, 847, 758, 698 cm^{-1}. MS (%) (EI) *m/z*: 444 (M^+, 9), 43 (100), 226 (60), 211 (41), 367 (32), 368 (27), 105 (25), 383 (23), 91 (18); HRMS (EI) calcd for $C_{32}H_{28}O_2$: 444.2089. Found: 444.2086.