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Ring-Opening Reaction of Methylenecyclopropanes Derived from Methylenecyclopropyl Aldehydes through Cope Rearrangement

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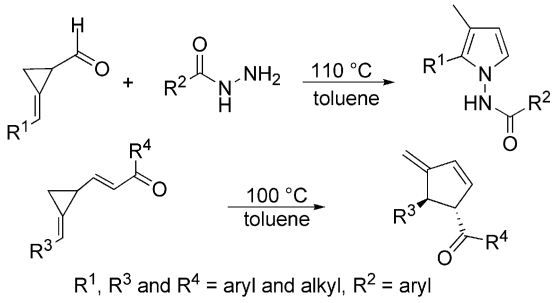
Tandem Wittig reaction/Cope rearrangement of methylenecyclopropyl aldehydes **1** with cinnamyltriphenylphosphonium bromide afforded a convenient method for the synthesis of cyclopentene derivatives **2** in moderate yields in a one-pot manner. Dialkyl 2-[(2-methylenecyclopropyl)methylene]-malonates **3** derived from methylenecyclopropyl aldehydes **1** could produce two kinds of cyclopentene derivatives, **4** and **5**, in good total yields through a thermally induced Cope rearrangement upon heating at 100 °C. Plausible reaction mechanisms are discussed on the basis of previous reports and on control experiments.

Introduction

Methylenecyclopropanes (MCPs) are widely used as building blocks in organic synthesis because of their ready accessibility as well as their diverse reactivity, which is driven by the relief of ring strain.[1] The ring-opening reactions of MCPs are synthetically useful in the construction of complex product structures and have been extensively studied.[2] Over the past decades, Lewis acids and transition-metal-catalyzed reactions involving ring opening of MCPs to form a variety of carbocycles and heterocycles have been extensively investigated.[3] However, the ring-opening reactions of MCPs by thermally induced rearrangements are relatively limited due to fact that high temperature is usually required because of the very large activation energy.[3] Previously, we reported a synthetic route to 2,3-disubstituted pyrrolamides by ring-opening recyclization of benzylidene and alkylidenecyclopropanecarbaldehydes with hydrazides.[4] In addition, we also reported an efficient method to stereospecifically synthesize *trans*-substituted cyclopentene derivatives in moderate to good yields by using the Cope rearrangement of readily available MCP alkenyl ketone derivatives (Scheme 1).[5] On the basis of the previous work, we hypothesized that MCPs with an activated alkene moiety might also be suitable substrates for the ring-opening process upon heating. Herein, we wish to report our investigations on the ring-opening reactions of methylenecyclopropyl aldehydes **1** with cinnamyltriphenylphosphonium bromide as well as on the thermally induced Cope rearrangement of MCP methylenemalonates **3** to furnish the corresponding cyclopentene derivatives **2**, **4**, and **5** in moderate yields.



Scheme 1. Previous studies on the ring-opening reactions of MCP derivatives.

Results and Discussion

We started our work on the synthesis of MCP compounds with an activated alkene moiety by undertaking a Wittig reaction of MCP aldehyde **1a** with cinnamyltriphenylphosphonium bromide in tetrahydrofuran (THF) using *n*-butyllithium (*n*BuLi) as base without heating. To our surprise, the cyclopentene derivative **2a**, rather than the expected MCP alkene, was obtained in 77% yield after usual workup and purification by column chromatography on silica gel, suggesting that the tandem sequence of Wittig reaction/Cope rearrangement could take place easily at room temperature (Table 1, entry 1). Further investigation revealed that the base played an important role in this reaction. The reaction also took place with strong inorganic bases (NaH, NaOH, and KOH), giving the corresponding cylcopentene derivative **2a** in 15–58% yields (Table 1, entries 2, 4, and 5). However, other bases, such as *t*BuOK and

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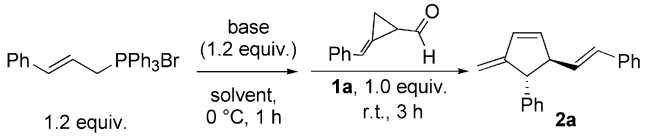
Et_3N, did not promote the reaction (Table 1, entries 3 and 6). When the reaction was conducted in other solvents, such as Et_2O, hexane, or 1,4-dioxane, the corresponding cyclopentene product **2a** was obtained in 7–60% yields using *n*BuLi as base (Table 1, entries 7–9).

Table 1. Tandem Wittig reaction/Cope rearrangement of phosphonium salt with MCP aldehyde **1a**.



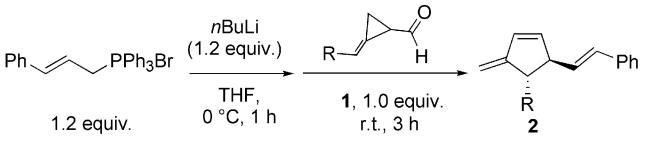
Entry	Base	Solvent	Yield of **2a** [%][a]
1	*n*BuLi	THF	77
2	NaH	THF	58
3	*t*BuOK	THF	traces
4	NaOH	THF	15
5	KOH	THF	21
6	Et_3N	THF	n.r.
7	*n*BuLi	Et_2O	7
8	*n*BuLi	hexane	60
9	*n*BuLi	1,4-dioxane	36

[a] Isolated yield.

With these optimized reaction conditions in hand (Table 1, entry 1), we then examined the generality of the reaction by using a variety of MCP aldehydes **1** and by using *n*BuLi as base in THF. The results are shown in Table 2. The MCP aldehydes **1c**–**d** and **1e**–**g** having electron-withdrawing or electron-donating group on the benzene rings, gave the corresponding cyclopentene derivatives **2c**–**d** and **2e**–**g** in 62–77% yields, respectively (Table 2, entries 2–4 and 6–7). For MCP aldehyde **1b**, bearing an electron-withdrawing bromine atom at the *para*-position of the benzene ring, the corresponding cyclopentene product **2b** was formed in 50% yield. In this case, the slightly lower yield might be due to a Br–Li exchange, giving some unidentified byproducts (Table 2, entry 1). We also examined alkyl group substituted substrate **1h** ($R^1 = C_7H_{15}$) and found its reaction with cinnamyltriphenylphosphonium bromide gave the cyclopentene product **2h** in 69% yield (Table 2, entry 8). Moreover, it should also be noted that, using (*Z*)-2-benzylidenecyclopropanecarbaldehyde (*Z*)-**1a** as the substrate, the same product **2a** as that derived from (*E*)-**1a** could be formed in 62% yield under identical conditions, indicating the broad substrate generality of this reaction (Table 2, entry 5).

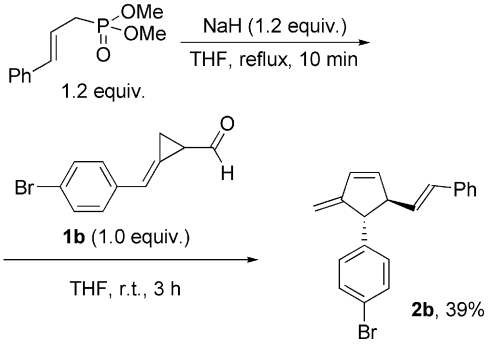
A control experiment was conducted to obtain the reaction intermediate by treating MCP aldehyde **1b** (1.0 equiv.) with dimethyl cinnamylphosphonate (1.2 equiv.)[6] in the presence of NaH (1.2 equiv.) in THF for 3 h at room temperature (Scheme 2). We found that cyclopentene derivative **2b** was obtained in 39% yield, however, the MCP alkenyl intermediate could not be isolated, which further proved that the Cope rearrangement of alkene-activated MCP took place too fast to allow isolation of the intermediate at room temperature (Scheme 2).

Table 2. Scope of the reaction.



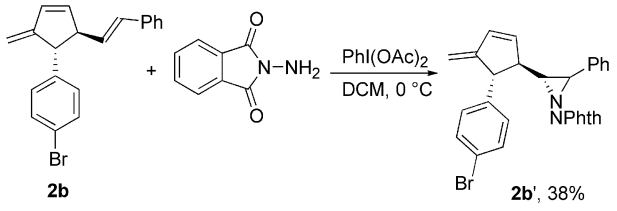
Entry	R	Yield of **2** [%][a]
1	$pBrC_6H_4$	55
2	$pClC_6H_4$	64
3	$pPhC_6H_4$	77
4	$3,4,5\text{-}(MeO)_3C_6H_2$	66
5	(*Z*)-**1a**, C_6H_5	62
6	$pMeOC_6H_4$	63
7	$3,4\text{-}Me_2C_6H_3$	73
8	(*E*) and (*Z*)-nC_7H_{15}	69

[a] Isolated yield.



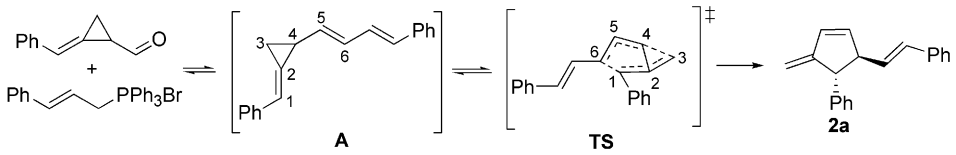
Scheme 2. Tandem Horner–Wadsworth–Emmons olefination/Cope rearrangement of MCP aldehyde **1b** with dimethyl cinnamylphosphonate.

In addition, compound **2b** could be easily transformed into the synthetically more interesting aziridine derivative. In the presence of 2-aminoisoindoline-1,3-dione and $PhI(OAc)_2$, **2b** could react with the nitrene generated in situ, to deliver the corresponding aziridine derivative **2b′** in 38% yield (Scheme 3).[7] The structure of **2b′** was unambiguously confirmed by X-ray single-crystal analysis[8] (CIF data are presented in the Supporting Information). On the basis of this structural analysis, the two substituents on the cyclopentene ring were identified as adopting a *trans* arrangement.



Scheme 3. Azacyclopropanation of **2b**.

On the basis of previous studies,[4,5] a plausible mechanism for the formation of **2** is outlined in Scheme 4. According to this scheme, the Wittig reaction of MCP aldehyde **1** with cinnamyltriphenylphosphonium bromide (or

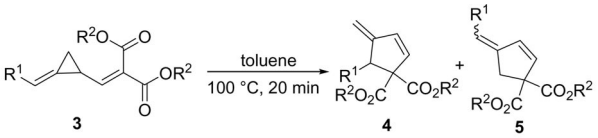


Scheme 4. A plausible reaction mechanism.

dimethyl cinnamylphosphonate) affords MCP alkenyl intermediate **A** in the presence of a base, which undergoes a Cope rearrangement via a chair-like transition state (**TS**) to give the corresponding cyclopentene product **2a**. In the chair-like transition state, the steric interaction between the substituents is minimal.

Having obtained good results in the tandem Wittig reaction/Cope rearrangement of methylenecyclopropyl aldehydes **1** with cinnamyltriphenylphosphonium bromide, we then investigated the ring-opening reactions of other MCP derivatives, such as MCP alkenyl derivatives with two ester groups. The Knoevenagel condensation of MCP aldehyde with methylmalonate afforded MCP methylenemalonate dimethyl ester **3a**, which could be isolated by column chromatography on silica gel and was stable at room temperature (20 °C). Heating **3a** at 100 °C for 20 min led to the formation of two products, which were identified as the normal cyclopentene product **4a** (33% yield), generated through the Cope rearrangement, and a second cyclopentene product **5a** (36% yield), which was formed as a pair of *E* and *Z* isomers (Table 3, entry 1). When R^2 was changed to a benzyl group (Bn) or a *p*-bromobenzyl (*p*BrBn) group, both **4** and **5** were also formed in good total yields with the latter being formed as the major products (Table 3, entries 2 and 3). Similarly, using (*Z*)-dimethyl 2-[(2-benzylidenecyclopropyl)methylene]malonate [(*Z*)-**3a**] as substrate, the same products **4a** and **5a** were obtained in 30 and 35% yields, respectively (Table 3, entry 4). On the basis of ^{1}H NMR spectroscopic data, the ratios of *E* and Z isomers of products **5** were determined to be almost 1:1 (see the Supporting Information for details). In the case of MCPs **3d**–**f**, which were derived from the Knoevenagel condensation of MCP aldehydes with Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione), these reactions proceeded rapidly to give the corresponding cyclopentene products **4d**–**f** in 32–49% yield within 5 min without formation of products **5**, probably due to the instability of the latter cyclopentene products at 100 °C (Table 3, entries 5–7). It should also be noted that the formation of **5c** was greatly affected by the addition of a radical inhibitor such as TEMPO (see the Supporting Information). Furthermore, the structure of **5c** was unambiguously determined by X-ray single-crystal analysis,[9] and its CIF data are presented in the Supporting Information.

Table 3. Rearrangement of MCP methylenemalonate diesters **3**.

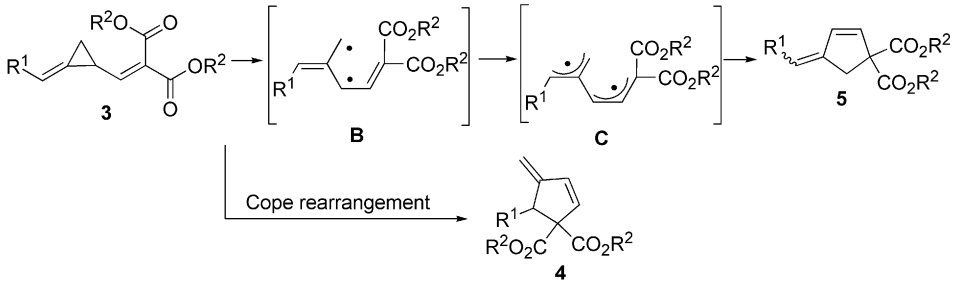


3 4 5

Entry	R^1	R^2	Yield (%)[a] 2	Yield (%)[a] 2
1	C_6H_5, **3a**	Me	**4a**, 33	**5a**, 36
2	*p*BrC_6H_4, **3b**	Bn	**4b**, 27	**5b**, 40
3	*p*BrC_6H_4, **3c**	*p*BrBn	**4c**, 21	**5c**, 30
4	C_6H_5, ***Z*-3a**	Me	**4a**, 30	**5a**, 35
5[b]	C_6H_5, **3d**		**4d**, 49	**5d**, –[c]
6[b]	*p*MeC_6H_4, **3e**		**4e**, 49	**5e**, –[c]
7[b]	*p*ClC_6H_4, **3f**		**4f**, 32	**5f**, –[c]

[a] Isolated yield. [b] The reaction time was reduced to 5 min. [c] No product was obtained, probably due to its instability.

A plausible mechanism for the formation of **4** and **5** is outlined in Scheme 5. Cyclopentenes **4** are formed through the Cope rearrangement of **3** in a manner similar to that of intermediate **A** shown in Scheme 4. Alternatively, substrate **3** can also generate a biradical species **C** through intermediate **B** upon heating,[10] followed by a recombination of the two radicals to give cyclopentene **5** as a mixture of *E* and *Z* isomers. In this case, the biradical species **C** is stabilized by the diester and allyl groups, leading to the product **5** as a major product. Other MCP alkenyl substrates cannot provide such strong stabilization of the biradical species as occurs in **3**, resulting in Cope rearrangement exclusively to give cyclopentene **4** as the product.



Scheme 5. A plausible reaction mechanism.

In conclusion, we have explored a tandem Wittig reaction/Cope rearrangement of methylenecyclopropyl aldehydes **1** with cinnamyltriphenylphosphonium bromide at room temperature in the presence of base, affording an efficient synthetic protocol for the preparation of functionalized cyclopentene derivatives in moderate yields. Moreover, two kinds of cyclopentene products were obtained simultaneously using MCP methylenemalonate diesters **3** as substrates. In addition, the rearrangement of substrates **3d**–**f**, which were derived from the Knoevenagel condensation of MCP aldehydes with Meldrum's acid, gave **4** in moderate yields. Potential uses and an extension of the scope of the methodology are under investigation.

Experimental Section

General Procedure for the Tandem Wittig Reaction/Cope Rearrangement of Methylenecyclopropyl Aldehydes 1 with Cinnamyltriphenylphosphonium Bromide: Cinnamyltriphenylphosphonium bromide (0.6 mmol) and freshly distilled THF (5.0 mL) were added into a Schlenk tube. After cooling to 0 °C, *n*BuLi (1.6 M in hexane, 0.6 mmol) was added dropwise and the reaction was stirred for an additional 1 h at 0 °C. After the addition was complete, MCP aldehyde **1** (0.5 mmol) in THF (1.0 mL) was added dropwise. The reaction mixture was stirred for 3 h and then the solution was slowly warmed to room temp. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography to give cyclopentene products **2**.

General Procedure for the Tandem Horner–Wadsworth–Emmons Olefination/Cope Rearrangement of MCP Aldehydes 1 with Dimethyl Cinnamylphosphonate: NaH (0.48 mmol) and freshly distilled THF (2.0 mL) were added into a Schlenk tube and then dimethyl cinnamylphosphonate (0.4 mmol) in THF (1.0 mL) was added dropwise at room temp. The reaction mixture was heated to reflux for approximately 10 min, then cooled to room temp. MCP aldehyde **1** in THF (1.0 mL) was added and the reaction mixture was stirred at room temp. for 3 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography.

General Procedure for the Preparation of 2b′: To a Schlenk tube was added **2b** (0.2 mmol), CH_2Cl_2 (4.0 mL), phthalhydrazide (0.3 mmol), and iodosobenzene diacetate (0.3 mmol). The reaction mixture was stirred at 0 °C for 2 h, then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography.

General Procedure for the Rearrangement of MCP Methylenemalonate Diesters 3: To a Schlenk tube was added **3** (0.2 mmol) and toluene (2.0 mL), then the reaction mixture was stirred at 100 °C for 20 min. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography.

Compound 2a: Yellow oil (99 mg, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.60–3.62 (m, 1 H), 3.63–3.65 (m, 1 H), 4.57 (s, 1 H), 5.02 (d, J = 2.4 Hz, 1 H), 6.07–6.09 (m, 1 H), 6.21 (dd, J = 16.0, 7.6 Hz, 1 H, CH), 6.31–6.38 (m, 2 H), 7.20–7.25 (m, 4 H, ArH), 7.28–7.35 (m, 6 H, ArH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 55.8, 59.2, 105.9, 126.2, 126.3, 127.2, 128.1, 128.4, 128.5, 129.8, 131.8, 134.3, 137.3, 139.1, 144.3, 157.5 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3059, 3027, 3000, 2923, 1712, 1600, 1494, 1452, 1361, 1221, 1178 cm^{-1}. MS (EI): *m*/*z* (%) = 258 (100.0) $[M]^+$, 167 (93.8), 165 (51.3), 154 (46.3), 153 (43.5), 152 (34.9), 115 (36.7), 91 (46.2). HRMS (EI): calcd. for $C_{20}H_{18}$ $[M]^+$ 258.1409; found 258.1398.

Compound 2b′: Yellow solid (38 mg, 38%); m.p. 165–167 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.12–3.13 (m, 1 H), 3.63 (d, J = 6.0 Hz, 1 H), 3.96–3.99 (m, 1 H), 5.10–5.11 (m, 1 H), 6.09–6.12 (m, 1 H), 6.33–6.44 (m, 1 H), 6.29–6.38 (m, 2 H), 7.15 (d, J = 8.0 Hz, 2 H, ArH), 7.18–7.26 (m, 4 H, ArH), 7.39–7.42 (m, 2 H, ArH), 7.56–7.63 (m, 5 H, ArH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 48.2, 50.2, 51.0, 57.8, 122.8, 128.1, 128.5, 128.6, 128.9, 129.4, 129.9, 131.2, 131.5, 133.9, 135.6, 136.2, 144.0, 157.0 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3059, 3025, 3000, 2954, 2920, 2876, 1712, 1631, 1600, 1577, 1502, 1449, 1361, 1220 cm^{-1}. MS (EI): *m*/*z* (%) = 496 (1.4) $[M]^+$, 264 (74.5), 263 (100.0), 165 (26.3), 154 (33.9), 153 (27.1), 116 (35.7), 104 (27.2). HRMS (EI): calcd. for $C_{28}H_{21}N_2O_2Br$ $[M]^+$ 496.0786; found 496.0789.

Compound 4a: Yellow oil (23 mg, 33%). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.10 (s, 3 H, CH_3), 3.78 (s, 3 H, CH_3), 4.78 (s, 1 H, CH), 4.92 (t, J = 2.0 Hz, 1 H, CH), 5.20 (d, J = 2.0 Hz, 1 H, CH), 6.16 (dd, J = 5.6, 2.0 Hz, 1 H, CH), 6.56 (d, J = 5.6 Hz, 1 H, CH), 7.18–7.27 (m, 5 H, ArH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 51.9, 53.1, 53.4, 72.6, 109.3, 127.1, 127.9, 129.6, 133.5, 137.9, 140.0, 154.3, 169.1, 170.2 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3085, 3062, 3031, 3002, 2952, 1737, 1637, 1494, 1454, 1434, 1249, 1208 cm^{-1}. MS (EI): *m*/*z* (%) = 272 (20.3) $[M]^+$, 213 (22.5), 212 (68.5), 181 (26.2), 180 (19.5), 154 (30.6), 153 (100.0), 152 (50.4). HRMS (EI): calcd. for $C_{16}H_{16}O_4$ $[M]^+$ 272.1049; found 272.1048.

Compound 5a: Pair of diastereoisomers, *syn*:*anti* = 1:1. Yellow oil (26 mg, 36%). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.32 (d, J = 2.4 Hz, 1 H), 3.48 (d, J = 2.4 Hz, 1 H), 3.76 (s, 3 H, CH_3), 3.77 (s, 3 H, CH_3), 6.17 (dd, J = 5.6, 0.8 Hz, 0.5 H), 6.30 (dd, J = 5.6, 0.8 Hz, 0.5 H), 6.37 (br. s, 0.5 H), 6.44–6.47 (m, 1 H, CH), 6.89 (dd, J = 5.6, 0.8 Hz, 0.5 H), 7.20–7.39 (m, 5 H, ArH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 36.8, 38.6, 52.9, 53.0, 64.5, 66.7, 121.5, 123.2, 126.6, 126.8, 128.1, 128.2, 128.3, 128.5, 132.6, 133.6, 136.6, 137.3, 137.8, 139.5, 142.8, 143.7, 170.7, 170.8 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3088, 3062, 3024, 2954, 2843, 1738, 1638, 1597, 1494, 1434, 1257, 1197, 1167 cm^{-1}. MS (EI): *m*/*z* (%) = 272 (21.5) $[M]^+$, 213 (30.8), 212 (34.7), 181 (15.1), 154 (24.9), 153 (100.0), 152 (14.6), 121 (33.6). HRMS (EI): calcd. for $C_{16}H_{16}O_4$ $[M]^+$ 272.1049; found 272.1050.

Supporting Information (see also the footnote on the first page of this article): Spectroscopic data of all the new compounds and detailed descriptions of experimental procedures as well as X-ray crystal data of **2b′** and **5c**.

Acknowledgments

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[1] For selected reviews on MCPs, see: a) M. Lautens, W. Klute, W. Tam, *Chem. Rev.* **1996**, *96*, 49–92; b) A. de Meijere, S. I. Kozhushkov, A. F. Khlebnikov, *Top. Curr. Chem.* **2000**, *207*, 89–147; c) P. Binger, P. Wedemann, S. I. Kozhushkov, A. de Meijere, *Eur. J. Org. Chem.* **1998**, 113–119; d) A. de Meijere, S. I. A. Kozhushkov, *Eur. J. Org. Chem.* **2000**, 3809–3822; e) I. Nakamura, Y. Yamamoto, *Adv. Synth. Catal.* **2002**, *344*, 111–129; f) A. Brandi, S. Cicchi, F. M. Cordero, A. Goti, *Chem. Rev.* **2003**, *103*, 1213–1270; g) E. Nakamura, S. Yamago, *Acc.*

Chem. Res. **2002**, *35*, 867–877; h) L.-X. Shao, M. Shi, *Curr. Org. Chem.* **2007**, *11*, 1135–1137; i) M. Rubin, M. Rubina, V. Gevorgyan, *Chem. Rev.* **2007**, *107*, 3117–3179; j) S. Yamago, E. Nakamura, *Org. React.* **2002**, *61*, 1–217; k) A. de Meijere, S. I. Kozhushkov, T. Spath, M. von Seebach, S. Lohr, H. Nuske, T. Pohomann, M. Es-Sayed, S. Brase, *Pure Appl. Chem.* **2000**, *72*, 1745–1756; l) X. Greary, *Acc. Chem. Res.* **2006**, *39*, 761–771; m) A. de Meijere, P. von Zezschwitz, S. Brse, *Acc. Chem. Res.* **2005**, *38*, 413–422; n) A. de Meijere, S. I. Kozhushkov, D. Faber, V. Bagutskii, R. Boese, T. Haumann, R. Walsh, *Eur. J. Org. Chem.* **2001**, 3607–3614.

[2] For selected examples on the reactions of MCPs, see: a) B. Hu, S. Y. Xing, Z. W. Wang, *Org. Lett.* **2008**, *10*, 5481–5484; b) M. Shi, L.-P. Liu, J. Tang, *Org. Lett.* **2006**, *8*, 4043–4046; c) M. Shi, B. Xu, J.-W. Huang, *Org. Lett.* **2004**, *6*, 1175–1178; d) X. Huang, Y. Yang, *Org. Lett.* **2007**, *9*, 1667–1670; e) M. Lautens, W. Han, J. H. Liu, *J. Am. Chem. Soc.* **2003**, *125*, 4028–4029; f) M. Lautens, Y. Ren, *J. Am. Chem. Soc.* **1996**, *118*, 10668–10669; g) L. Yu, J. D. Meng, L. Xia, R. Guo, *J. Org. Chem.* **2009**, *74*, 5087–5089; h) S. Ma, J. Zhang, *Angew. Chem.* **2003**, *115*, 193–197; *Angew. Chem. Int. Ed.* **2003**, *42*, 183–187; i) S. Ma, L. Lu, J. Zhang, *J. Am. Chem. Soc.* **2004**, *126*, 9645–9660; j) L. Lu, G. Chen, S. Ma, *Org. Lett.* **2006**, *8*, 835–838; k) M. E. Scott, M. Lautens, *J. Org. Chem.* **2008**, *73*, 8154–8162; l) C. Taillier, M. Lautens, *Org. Lett.* **2007**, *9*, 591–593; m) E. Smolensky, M. Kapon, M. S. Eisen, *Organometallics* **2007**, *26*, 4510–4527; n) V. V. Diev, T. Q. Tung, A. P. Molchanov, *Eur. J. Org. Chem.* **2009**, 525–530; o) B. Hu, J. L. Zhu, S. Y. Xing, J. Fang, D. Du, Z. W. Wang, *Chem. Eur. J.* **2009**, *15*, 324–327; p) V. Bagutski, A. de Meijere, *Adv. Synth. Catal.* **2007**, *349*, 1247–1255; q) X.-C. Hang, Q.-Y. Chen, J.-C. Xiao, *Eur. J. Org. Chem.* **2008**, 1101–1106; r) I. Nakamura, B. H. Oh, S. Saito, Y. Yamamoto, *Angew. Chem.* **2001**, *113*, 1338–1340; *Angew. Chem. Int. Ed.* **2001**, *40*, 1298–1300; s) T. Kurahashi, A. de Meijere, *Angew. Chem. Int. Ed.* **2005**, *44*, 7881–7884; t) X. Huang, H. Zhou, *Org. Lett.* **2002**, *4*, 4419–4422; u) M. Gulias, J. Durán, F. López, L. Castedo, J. L. Mascareñas, *J. Am. Chem. Soc.* **2007**, *129*, 11026–11027; v) T. Matsuda, T. Tsuboi, M. Murakami, *J. Am. Chem. Soc.* **2007**, *129*, 11596–11597; w) M. Shirakura, M. Suginome, *J. Am. Chem. Soc.* **2009**, *131*, 5060–5061; x) N. Hayashi, Y. Hirokawa, I. Shibata, M. Yasuda, A. Baba, *J. Am. Chem. Soc.* **2008**, *130*, 2912–2913; y) S. Xing, W. Pan, C. Liu, J. Ren, Z. Wang, *Angew. Chem.* **2010**, *122*, 3283–3286; *Angew. Chem. Int. Ed.* **2010**, *49*, 3215–3218; z) M. Jiang, L.-P. Liu, M. Shi, Y. Li, *Org. Lett.* **2010**, *12*, 116–119.

[3] To the best of our knowledge, thermally induced rearrangement of MCPs are rare, and high temperature is usually required. However, vinylcyclopropane has been investigated extensively and there are a few examples, see: a) K. N. Houk, M. Nendel, O. Wiest, J. W. Storer, *J. Am. Chem. Soc.* **1997**, *119*, 10545–10546; b) J. E. Baldwin, S. Bonacorsi, *J. Am. Chem. Soc.* **1996**, *118*, 8258–8265; c) J. J. Gajewski, *Hydrocarbons Thermal Isomerizations*; Academic: New York, **1980**, pp. 81–87.

[4] X.-Y. Tang, M. Shi, *J. Org. Chem.* **2009**, *74*, 5983–5986.

[5] X.-Y. Tang, M. Shi, *J. Org. Chem.* **2010**, *75*, 902–905.

[6] For the preparation of dimethyl cinnamylphosphonate, see: A. Virginie, L. Hind, R. Sylvie, R. Gerard, *Tetrahedron* **2007**, *63*, 10059–10066.

[7] Following the same procedure reported previously, see: Yu. Y. Liang, L. Jiao, Y. Wang, Y. Chen, L. Ma, J. Xu, S. Zhang, Z.-X. Yu, *Org. Lett.* **2006**, *8*, 5877–5879.

[8] The X-ray crystal data of **2b′**: CCDC-753354 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Empirical formula: $C_{28}H_{21}BrN_2O_2$; formula weight: 497.38, crystal size: $0.395 \times 0.366 \times 0.237$ mm, crystal color: colorless, habit: prismatic, crystal system: triclinic, lattice type: primitive, lattice parameters: a = 10.460(2) Å, b = 11.346(2) Å, c = 12.007(2) Å, α = 107.158(4)°, β = 97.017(4)°, γ = 115.095(3)°; V = 1181.6(4) Å^3, space group: $P\bar{1}$; Z = 2; D_{calc} = 1.398 g/cm^3, $F(000)$ = 508, $R1$ = 0.0525, $wR2$ = 0.1222, diffractometer: Rigaku AFC7R.

[9] The X-ray crystal data of **5c**: CCDC-738021 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Empirical formula: $C_{28}H_{21}Br_3O_4$, formula weight: 661.18, crystal size: $0.388 \times 0.321 \times 0.169$ mm, crystal color: colorless, habit: prismatic, crystal system: monoclinic, lattice type: primitive, lattice parameters: a = 11.9629(14) Å, b = 6.0979(7) Å, c = 35.689(4) Å, α = 90°, β = 92.149(2)°, γ = 90°; V = 2601.6(5) Å^3, space group: $P2_1/n$, Z = 4, D_{calc} = 1.688 g/cm^3, $F(000)$ = 1304, $R1$ = 0.0520, $wR2$ = 0.1156, diffractometer: Rigaku AFC7R.

[10] a) H. M. Frey, *Adv. Phys. Org. Chem.* **1966**, *4*, 147; b) H. M. Frey, R. Walsh, *Chem. Rev.* **1969**, *69*, 103–124.

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