JOC*Note*

Substrate-Controlled Selective Proximal and Distal C−C Bond Cleavage via Lewis Acid Mediated O-Acylation of 2-(Arylmethylene)cyclopropylaldehyde: A Stereoselective Synthesis of Bifunctional Methylenecyclobutanes and 1,3-Conjugated Dienes

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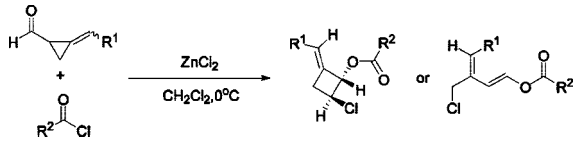
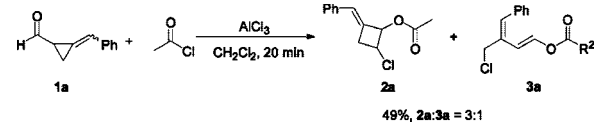


$ZnCl_2$-mediated reactions of (*E*)-2-(arylmethylene)cyclopropylaldehyde **1** with various acyl chlorides provide a novel method for stereoselective synthesis of bifunctional methylenecyclobutanes via a proximal-bond cleavage process. Nevertheless, when (*Z*)-**1** was employed, the reactions give 1,3-conjugated dienes through distal-bond cleavage.

Methylenecyclopropanes (MCPs) are highly strained but readily accessible carbocyclic molecules that have served as useful building blocks in organic synthesis.[1] In the past decades, mounting attention has been paid to the transition metal[2] (Pd, Ni, Pt, and Rh) and Lewis acid[3] catalyzed reactions of MCPs, which have been employed for the construction of highly complex and interesting organic molecules. However, an attractive but often troublesome feature of MCPs is their multiform reactivities that may lead to formation of a variety of products. Thus controlling the regio- and stereoselective reactions of MCPs is a formidable challenge in organic synthesis.

SCHEME 1. Reaction of 1a (*E*:*Z* = 2.5:1) with Acetyl Chlorides[a]



[a] Reaction conditions: mixture of **1a** (0.5 mmol) reacted with acetyl chloride (0.75 mmol) in the presence of $AlCl_3$ (0.5 mmol). The ratio of the crude products was determined by ^1H NMR.

Recently, MCPs with functional groups attached to a cyclopropyl ring have received considerable attention.[4] In principle, the presence of functional groups may facilitate the selective cleavage of C−C bonds of MCPs, thus delicately tuning the regio- and stereoselectivity of the reactions. Ma[4a] previously reported a highly selective ring-opening cycloisomerization of methylene- or alkylidenecyclopropyl ketones catalyzed by Pd(II) catalyst, and Lautens[4c] has shown a novel ring expansion of secondary methylenecyclopropyl amides in the presence of MgI_2, leading to useful compounds with synthetic and biological importance. Herein, we wish to disclose a novel Lewis acid mediated reaction of formyl-substituted MCPs with acyl chloride to afford a selective synthesis of bifunctional methylenecyclobutanes (MCBs) and 1,3-conjugated dienes.

Initially, we examined the reaction of **1a** (*E*:*Z* = 2.5:1) with acetyl chloride in CH_2Cl_2 at room temperature in the presence of 1.0 equiv of $AlCl_3$, affording a mixture of MCB **2a** and 1,3-conjugated diene **3a** (**2a**:**3a** = 3:1) in 49% yield (Scheme 1). With these results, we presumed that the O-acylation−ring-expansion reaction or O-acylation−ring-opening reaction of **1a** might afford **2a** or **3a**. In order to confirm the pathway of this reaction, we then conducted the reaction using (*E*)-**1a** and (*Z*)-**1a**, respectively. Gratifyingly, we found that the reaction gave **2a** as the only product in 52% yield when (*E*)-**1a** was employed (Table 1, entry 2).

With this encouraging result, a systematic study on optimizing the reaction conditions was immediately undertaken. We first investigated the reaction of (*E*)-**1a** (0.5 mmol) with acetyl chloride (0.75 mmol) in CH_2Cl_2 at room temperature by employing various Lewis acids (0.5 mmol). As indicated in Table 1, except for $AlCl_3$, other Lewis acids, e.g., $TiCl_4$, $BF_3 \cdot Et_2O$, and $ZrCl_4$, could also promote the reaction (Table 1, entries 1−5). The best result was obtained when $ZnCl_2$ was used as Lewis acid, and **2a** could be obtained in 89% yield (Table 1, entry 6). The following examination of the solvent

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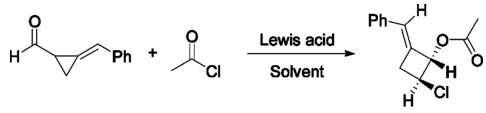
TABLE 1. Effects of Reaction Conditions on the Reaction of (*E*)-1a with Acetyl Chloride in the Presence of Lewis Acid[a]



(*E*)-1a 2a

entry	Lewis acid (equiv)	temp (°C)	solvent	time (min)[b]	yield of **2a** (%)[c]
1	$FeCl_3$ (1.0)	25	CH_2Cl_2	5	22
2	$AlCl_3$ (1.0)	25	CH_2Cl_2	5	52
3	$TiCl_4$ (1.0)	25	CH_2Cl_2	3	72
4	$BF_3 \cdot Et_2O$ (1.0)	25	CH_2Cl_2	20	78
5	$ZrCl_4$ (1.0)	25	CH_2Cl_2	12	87
6	$ZnCl_2$ (1.0)	25	CH_2Cl_2	15	89
7	$ZnCl_2$ (1.0)	25	toluene	20	81
8	$ZnCl_2$ (1.0)	25	THF	120	tr[d]
9	$ZnCl_2$ (1.0)	25	DCE	20	87
10	$ZnCl_2$ (1.0)	−20	CH_2Cl_2	80	78
11	**$ZnCl_2$ (1.0)**	**0**	**CH_2Cl_2**	**20**	**91**
12	$ZnCl_2$ (1.0)	40	CH_2Cl_2	20	39
13	$ZnCl_2$ (0.1)	0	CH_2Cl_2	120	46
14	$ZnCl_2$ (2.0)	0	CH_2Cl_2	20	88

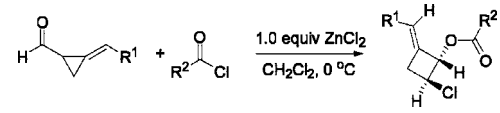
[a] Unless otherwise specified, the reaction was carried out using (*E*)-**1a** (0.5 mmol) and acetyl chloride (0.75 mmol) in 5 mL of CH_2Cl_2 in a N_2 atmosphere. [b] The reaction was monitored by TLC. [c] Isolated yields. [d] 58% of (*E*)-**1a** was recovered.

effects indicated that CH_2Cl_2 was the most suitable solvent. Slightly lower yields were observed when the reaction was carried out in solvents such as toluene and DCE (Table 1, entries 6, 7, and 9). Nevertheless, the solvent THF turned out to be totally disfavored (Table 1, entry 8). Our further experiments to examine the temperature effects (Table 1, entries 10−12) showed that the yield could be enhanced to 91% when the reaction was conducted at 0 °C (Table 1, entry 11). Moreover, the ratios of catalyst also affected the yields of **2a** (Table 1, entries 13 and 14), and using stoichiometric amount of $ZnCl_2$ is a necessity. Thus, the best conditions are to carry out the reaction in CH_2Cl_2 at 0 °C using 1.0 equiv of $ZnCl_2$ (Table 1, entry 11).

With the optimal conditions in hand, we examined the ring-expansion reaction of a series of (*E*)-**1** with different acyl chlorides. The results are summarized in Table 2. As for (*E*)-**1a**−**g**, the reactions proceeded smoothly with acetyl chloride to give the corresponding products in 85−96% yields (Table 2, entries 1, 6, 9, 11, 14, 16, and 17). The nature and position of substituents on the aromatic ring of (*E*)-**1** have little effect on this reaction. Moreover, heteroaromatic group such as a furan ring in (*E*)-**1** could also been tolerated (Table 2, entry 18). Other acyl chlorides such as isobutyryl chloride, pivaloyl chloride, acryloyl chloride, and benzoyl chloride could also been applied to the current reaction. For example, with acryloyl chloride, the expected MCBs **2g** and **2l** were obtained in 82% and 89% yield, respectively (Table 2, entries 8 and 13). When benzoyl chloride was employed, moderate yields were observed as well (Table 2, entries 2, 7, 10, and 12). However, when using methyl chloroformate as O-acylation reagent under the established conditions, no reaction occurred (Table 2, entry 5).

In all cases only the *trans*-1,4-diastereomers were observed. The structures of these compounds were determined by ^1H NMR, ^{13}C NMR, IR, and HRMS. The structure of **2i** was further confirmed by single-crystal X-ray diffraction analysis (see Supporting Information).

TABLE 2. Reactions of (*E*)-1 with Various Acyl Chlorides in the Presence of $ZnCl_2$[a]



entry	R^1	R^2	yield (%)[b]
1	C_6H_5 [(*E*)-**1a**]	CH_3	**2a**, 91
2	(*E*)-**1a**	C_6H_5	**2b**, 83
3	(*E*)-**1a**	$CH(CH_3)_2$	**2c**, 90
4	(*E*)-**1a**	$(CH_2)_2CH_3$	**2d**, 86
5	(*E*)-**1a**	OMe	*c*
6	*p*-ClC_6H_4 [(*E*)-**1b**]	CH_3	**2e**, 93
7	(*E*)-**1b**	C_6H_5	**2f**, 77
8	(*E*)-**1b**	CH=CH_2	**2g**, 82
9	*p*-BrC_6H_4 [(*E*)-**1c**]	CH_3	**2h**, 96
10	(*E*)-**1c**	C_6H_5	**2i**, 72
11	*p*-$MeOC_6H_4$ [(*E*)-**1d**]	CH_3	**2j**, 85
12	(*E*)-**1d**	C_6H_5	**2k**, 79
13	(*E*)-**1d**	CH=CH_2	**2l**, 89
14	*p*-MeC_6H_4 [(*E*)-**1e**]	CH_3	**2m**, 92
15	(*E*)-**1e**	$C(CH_3)_3$	**2n**, 88
16	*m*-ClC_6H_4 [(*E*)-**1f**]	CH_3	**2o**, 90
17	*o*-BrC_6H_4 [(*E*)-**1g**]	CH_3	**2p**, 89
18	2-furan [(*E*)-**1h**]	$PhCH_2$	**2q**, 74

[a] Unless otherwise specified, the reaction was carried out using *E*-**1** (0.5 mmol) and acyl chloride (0.75 mmol) in 5 mL of CH_2Cl_2 in a N_2 atmosphere. [b] Isolated yields. [c] No reaction occurred.

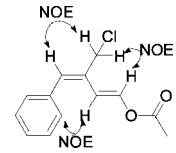
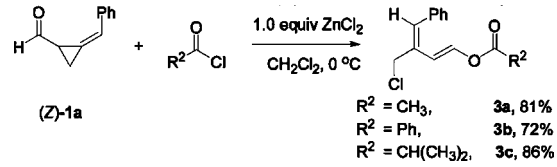


FIGURE 1. Structure of compound **3a**.

SCHEME 2. Reaction of (*Z*)-1a with Various Acyl Chlorides



(*Z*)-1a

Interestingly, when (*Z*)-**1a** was employed as substrate, the reaction gave a different product **3a** in 81% yield (Scheme 2). Benzoyl chloride and isobutyryl chloride were also successfully applied to the reactions, furnishing the corresponding 1,3-conjugated dienes **3b** and **3c** in 72% and 86% yield, respectively (Scheme 2). The structures of these compounds were determined by spectroscopic analysis, and the stereochemistry of **3a** was further established by the NOESY analysis (Figure 1). Notably, these 1,3-conjugated dienes are very important intermediates that have been frequently utilized as dienes in Diels−Alder reactions to construct various ring systems in organic synthesis.[5]

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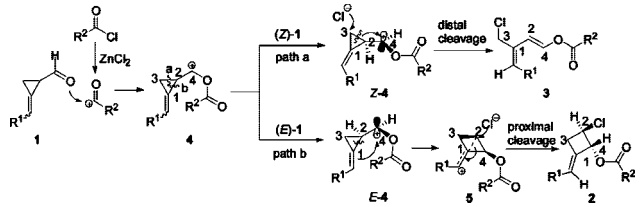
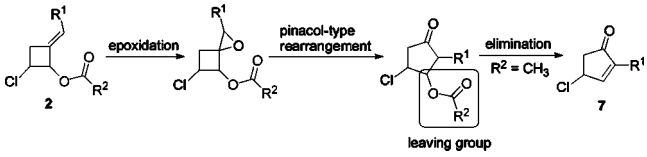
SCHEME 3. Proposed Mechanism for the Reaction



SCHEME 4. Possible Mode for the Formation of Cyclopentenones

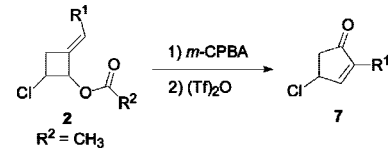


Therefore, our reaction to produce these analogues will be synthetically useful.

A possible mechanism for these reactions is proposed as depicted in Scheme 3. In the presence of $ZnCl_2$, the acyl chloride might first convert to an acyl cation.[6] Then a selective attack of acyl cation to carbonyl oxygen of MCPs **1** would produce a carbonium ion **4**. When (*Z*)-**4** was employed, a nucleophilic attack of chlorine anion at the less sterically hindered C_3 in the cyclopropyl ring might cause a distal cleavage to afford the thermodynamically stable product **3** (path a). When (*E*)-**4** was employed, as a result of the steric hindrance of the aromatic ring that blocks the nucleophilic attack of chlorine anion at C_3, an intramolecular nucleophilic attack might proceed first to produce a nonclassic carbocation-bicyclobutonium ion **5**.[7] Then the attack of chlorine anion from the back side at C_2 of intermediate **5** would finally give the product **2** stereoselectively via proximal cleavage (path b).

As a result of the inherent ring strain, MCBs have shown interesting reactivity in organic synthesis, and many reactions based on MCBs have been developed in the past for the synthesis of various acyclic and cyclic systems.[8] Considering the readily available bifuctional MCBs **2** with our protocol, we envisioned that a possible route to cyclopentenones **7** from **2** could be realized via a process of epoxidation, pinacol-type ring enlargement[9] and further elimination (Scheme 4). Therefore, we next investigated a new one-pot synthesis of cyclopentenones using MCBs **2** as starting materials. Here, it should be mentioned that cyclopentenones are not only important structural motifs in the synthesis of natural products but also key structural units in compounds with interesting biological activities.[10] Although a wide range of synthetic methods have been developed,[11] efficient and practical routes for the construction of these compounds are still required.

TABLE 3. Synthesis of Cyclopentanones Derivatives



entry	**2** (R^1)	yield (%)[a]
1	**2a** (C_6H_5)	**7a**, 65
2	**2e** (*p*-ClC_6H_4)	**7b**, 61
3	**2h** (*p*-BrC_6H_4)	**7c**, 53
4	**2j** (*p*-$MeOC_6H_4$)	**7d**, 42
5	**2m** (*p*-MeC_6H_4)	**7e**, 67
6	**2o** (*m*-ClC_6H_4)	**7f**, 72

[a] Isolated yields.

We examined the reaction of MCB **2a** (0.2 mmol) with *m*-CPBA (0.5 mmol) in CH_2Cl_2. After stirring overnight and subsequent treatment with $(Tf)_2O$ (0.2 mmol), the reaction gave the expected cyclopentenone **7a** in 65% yield. The results, summarized in Table 3, show that various cyclopentenones **7** could be obtained smoothly in moderate yields using the current protocol.

In conclusion, we have disclosed a novel Lewis acid mediated reaction of formyl-substituted MCPs with acyl chloride. The reaction features a substrate-controlled cleavage of the C−C bond, leading to a facile synthesis of bifunctional MCBs **2** and 1,3-conjugated dienes **3** with high stereoselectivities. We also demonstrated that the obtained MCBs could be applied to the synthesis of cyclopentanones **7**. Further studies on this transformation are being carried out in our laboratory.

Experimental Section

General Procedure for Synthesis of MCBs 2 and 1,3-Conjugated Dienes 3. Under an atmosphere of dry nitrogen, 1.0 equiv of $ZnCl_2$ (0.5 mmol) was added to a solution of 2-(arylmethylene)cyclopropylaldehyde **1** (0.5 mmol) in 5 mL of dry CH_2Cl_2 at 0 °C. Then 1.5 equiv of acyl chloride (0.75 mmol) was injected. After being stirred for 10−40 min (monitored by TLC), the mixture was quenched with 5 mL of water and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$. After filtration and removal of the solvent in vacuo, the residues were purified with flash silica chromatography (petroleum ether/ethyl acetate 15:1 v/v) to afford **2** or **3**.

***trans*-Acetic Acid-(*E*)-2-benzylidene-4-chloro-cyclobutyl Ester (2a).** Oil, ^1H NMR (400 Hz, $CDCl_3$) δ 7.29−7.36 (m, 2H), 7.17−7.27 (m, 3H), 6.41−6.45 (m, 1H), 5.76−5.81 (m, 1H), 4.28−4.35 (m, 1H), 3.36−3.45 (m, 1H), 2.90−3.00 (m, 1H), 2.17 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 20.7, 37.1, 52.4, 79.9, 124.4, 127.5, 127.8, 128.5, 132.7, 135.7, 169.9; IR (neat) 3057, 3027, 2931, 1740, 1599, 1493, 1224, 1052, 695, 511 cm^{-1}; MS (70 eV, EI) *m*/*z* 236 (M^+); HRMS (EI) *m*/*z* calcd for $C_{13}H_{13}O_2Cl$ (M^+) 236.0604, found 236.0607.

General Procedure for Synthesis of Cyclopentanones 7. To a stirred solution of MCBs **2** (0.2 mmol) in CH_2Cl_2 (2 mL) was added *m*-CPBA (0.5 mmol) at room temperature. The mixture was stirred overnight, and then $(Tf)_2O$ (0.2 mmol) was injected. After the reaction was complete (1 h), the mixture was quenched with 5 mL

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of water and extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$. After filtration and removal of the solvent in vacuo, the residues were purified with flash silica chromatography (petroleum ether/ethyl acetate 15:1 v/v) to afford **7**.

4-Chloro-2-phenylcyclopent-2-enone (7a). Oil, ^{1}H NMR (400 Hz, $CDCl_3$) δ 7.70−7.76 (m, 2H), 7.64 (d, J = 2.8 Hz 1H), 7.38−7.44 (m, 3H), 5.12−5.18 (m, 1H), 3.20 (dd, J_1 = 6.0, J_2 = 19.6 Hz, 1H), 2.85 (dd, J_1 = 2.0, J_2 = 19.2 Hz, 1H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 46.2, 52.6, 127.5, 128.6, 129.5, 129.8, 144.3, 154.5, 202.5; IR (neat) 1712, 1126, 933, 762, 692 cm^{-1}; MS (70 eV, EI) *m*/*z* 192 (M^+); HRMS (EI) *m*/*z* calcd for $C_{11}H_9OCl$ (M^+) 192.0342, found 192.0350.

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Supporting Information Available: General experimental procedures and spectroscopic data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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