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Lewis Acid Promoted Tandem Intermolecular Diels–Alder/ Intramolecular Allylation Reactions of Silyl-Substituted 1,3-Butadienes Leading to Multisubstituted 7-Norbornenones and Related Polycyclic Compounds

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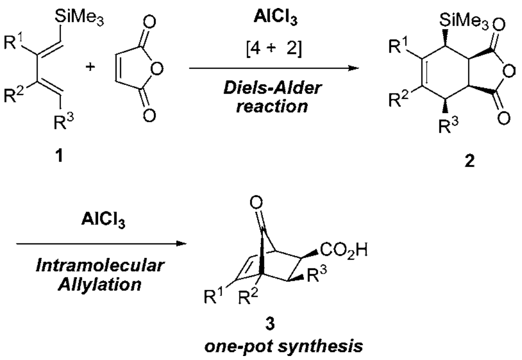
ABSTRACT



7-Norbornenones of exo,exo-disubstituted patterns were formed highly selectively in good yields from Lewis acid-promoted tandem intermolecular Diels–Alder/intramolecular allylation reactions. The intermolecular Diels–Alder reaction between 1,4-bis(trimethylsilyl)-1,3-butadienes or 1-trimethylsilyl-1,3-butadienes with maleic anhydride in the presence of newly sublimed $AlCl_3$ afforded their corresponding cycloaddition adducts, which underwent $AlCl_3$-mediated intramolecular allylation of the carbonyl group by the in situ generated allylsilane moiety affording 7-norbornenones of exo,exo-disubstituted patterns.

Vinylsilanes, especially the silyl-substituted conjugated dienes, have become versatile building blocks in organic synthesis.[1] One of the most promising applications of 1,4-bis(trimethylsilyl)-1,3-butadienes and 1-trimethylsilyl-1,3-butadienes is the Diels−Alder reaction to construct six-membered compounds.[2,3] On the other hand, allylsilanes have been widely used as allylation reagents in organic synthesis, and many interesting and complicated compounds including natural products have been prepared by applying the allylation reaction using allylsilanes.[4−6] The addition of trialkyl-

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(2) For a review on tandem Diels−Alder cycloadditions in organic synthesis, see: Winkler, J. D. *Chem. Rev.* **1996**, *96*, 167−176.

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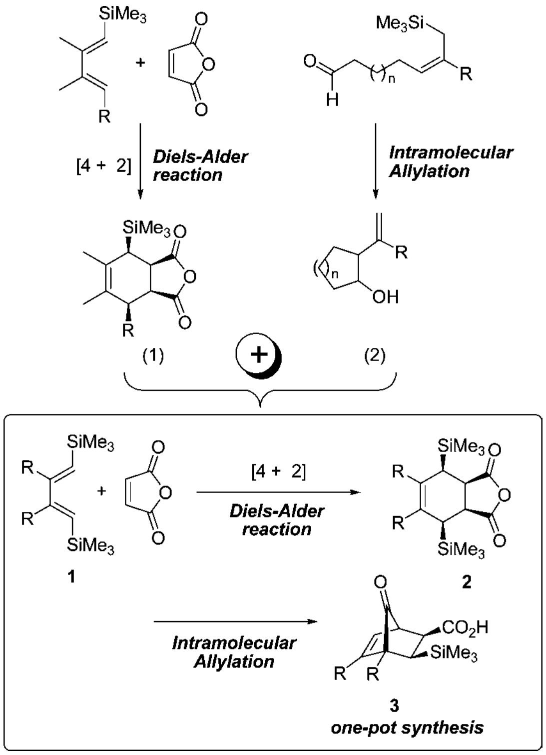
allylsilanes to carbonyl groups, both intermolecularly and intramolecularly, has been often used as a very useful method for construction of C−C bonds, normally mediated by stoichiometric amounts of Lewis acids or catalyzed by fluoride ions.[4−6]

We have recently studied the synthetic methodology and applications of multisubstituted 1,4-bis(trimethylsilyl)-1,3-butadienes **1** of well-defined stereochemistry.[7] During our continued research on this project, we found an interesting tandem process involving intermolecular Diels−Alder reaction followed by intramolecular allylation reaction affording multisubstituted 7-norbornenones (Scheme 1). Thus, a tandem process combining the well-known Diels−Alder reaction (eq 1, Scheme 1) and the intramolecular allylation (eq 2, Scheme 1) provides a new and convenient synthetic method for multi-substituted 7-norbornenones. As widely used as an important stereoelectronic probe in various organic reactions, 7-norbornenones have attracted much attention for their synthetic methods and applications.[8,9] In addition, 7-norbornenones of exo,exo-disubstituted patterns were obtained exclusively in this process, which is in sharp contrast to the well-known normal conformation of endo,endo-disubstitution.[10−12]

Scheme 1



To the best of our knowledge, this synthetically useful combination of Diels−Alder reaction with intramolecular allylation using in situ generated allylsilane moieties is unprecedented.[13] In this paper, we report the preliminary results.

We were initially trying to functionalize those bis(trimethylsilyl) butadiene derivatives via Lewis acid-mediated desilylation−carbonylation process. During the course of survey of different carbonylation reagents, we were surprised to find that, when bis(trimethylsilyl)butadiene **1a** was treated with 2 equiv of maleic anhydride in the presence of newly sublimed $AlCl_3$, an unexpected product was formed (Scheme 2). Optimization of reaction condition afforded **3a** in 75% isolated yield.

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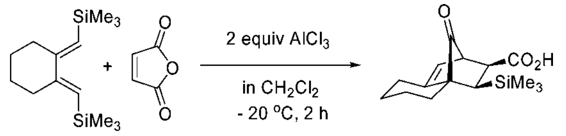
Scheme 2



1a

3a
75% isolated yield

Single crystals which were suitable for X-ray analysis were obtained. The X-ray structure for **3a** is shown in Figure 1.

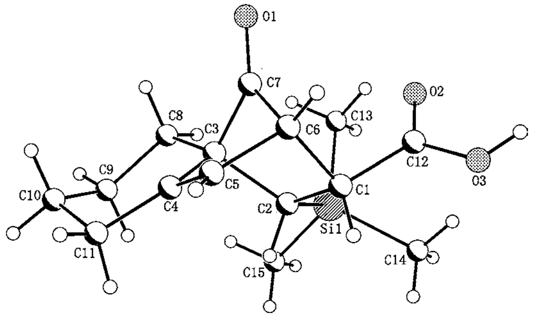
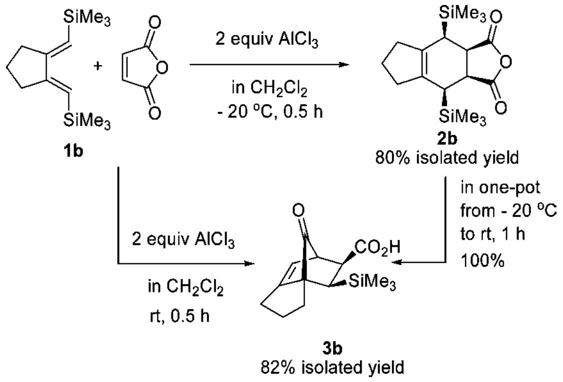


Figure 1. X-ray structure for **3a**. Selected bond lengths (Å): C(1)−C(6) 1.562(3), C(6)−C(7) 1.507(3), C(7)−C(3) 1.524(3), C(3)−C(4) 1.522(3), C(4)−C(5) 1.318(3), C(5)−C(6) 1.499(3), C(1)−C(2) 1.564(3), C(2)−C(3) 1.585(3), O(1)−C(7) 1.212(2).

7-Norbornenone **3a** of exo,exo-disubstituted pattern was obtained exclusively, which is in sharp contrast to the well-known normal conformation of endo,endo-disubstitution.

When we applied bis(trimethylsilyl) butadiene derivative **1b** (Scheme 3), we found the reaction was very temperature-dependent, affording the product **2b** in 80% isolated yield when the reaction was carried out at −20 °C for 30 min. This product **2b** was obviously the Diels−Alder cycloaddition adduct. No product **3b** was obtained under this reaction condition. However, surprisingly, when the reaction temperature increased to room temperature, **2b** disappeared completely after 1 h, affording the multisubstituted 7-norbornenone **3b** in quantitative conversion. We then carried out the above reaction directly at room temperature. The 7-norbornenone **3b** was obtained in 82% isolated yield. This experimental observation is very useful for understanding the mechanism for the formation of 7-norbornenone derivatives.

Scheme 3



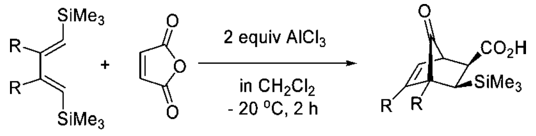
1b

2b
80% isolated yield

3b
82% isolated yield

1,4-Bis(trimethylsilyl)-2,3-dihexyl-1,3-butadiene **1c** and 1,4-bis(trimethylsilyl)-2,3-dibutyl-1,3-butadiene **1d** could also undergo similar reactions affording their corresponding structurally interesting exo,exo-disubstituted 7-norbornenones **3c** and **3d**, in 64% and 68% isolated yields, respectively (Scheme 4). The structure of **3d** was also determined by single-crystal X-ray structural analysis (Figure 2).

Scheme 4



1c: R = Hex
1d: R = Bu

3c: R = Hex
64% isolated yield
3d: R = Bu
68% isolated yield

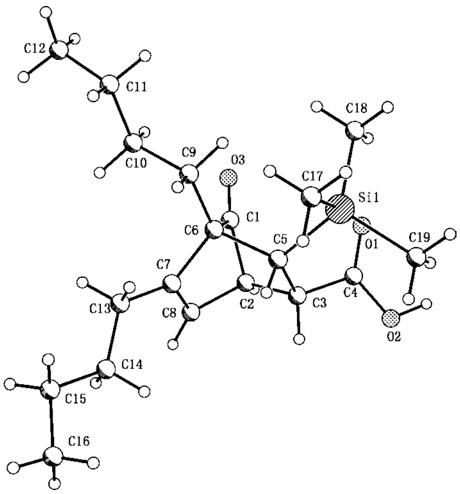
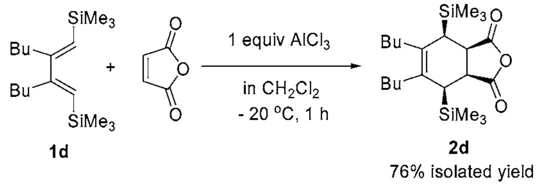


Figure 2. X-ray structure for **3d**. Selected bond lengths (Å): C(1)−C(6) 1.522(3), C(1)−C(2) 1.521(3), C(6)−C(7) 1.518(3), C(7)−C(8) 1.324(3), C(8)−C(2) 1.512(3), C(2)−C(3) 1.560(3), C(3)−C(5) 1.578(3), C(5)−C(6) 1.592(3), O(3)−C(1) 1.193 (3).

$EtAlCl_2$ worked similarly as Lewis acid for the above reaction. Other common Lewis acids such as $TiCl_4$, $FeCl_3$, VCl_3, BF_3, CuCl, and $MgBr_2$ did not work well for this reaction.

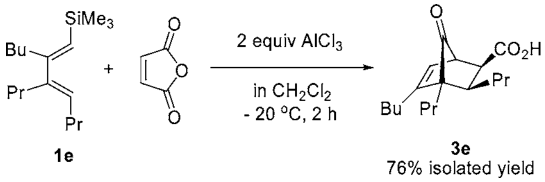
When 1 equiv of $AlCl_3$ instead of 2 equiv of $AlCl_3$ were used for the case of **1d**, the Diels−Alder cycloaddition product **2d**, instead of the 7-norbornenones **3d**, was obtained in 76% isolated yield (Scheme 5).

Scheme 5



In addition to those 1,4-bis(trimethylsilyl)-1,3-butadienes **1a**−**d**, 1-trimethylsilyl-1,3-butadiene such as **1e** was found to undergo the tandem process similarly. Thus, when **1e** was treated with maleric anhydride in the presence of two equivalents of $AlCl_3$, the 7-norbornenone derivative **3e** was obtained as the sole product in 76% isolated yield (Scheme 6).

Scheme 6



For the formation of 7-norbornenone derivatives from 1,4-bis(trimethylsilyl)-1,3-butadienes or 1-trimethylsilyl-1,3-butadienes and maleic anhydride in the presence of $AlCl_3$, a proposed key intermediate is shown in Figure 3.

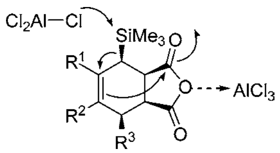


Figure 3. Proposed key step.

In summary, we have developed an unprecedented and synthetically useful one-pot process for the preparation of multisubstituted 7-norbornenones of well-defined exo,exo-disubstituted patterns. This new synthetic strategy involving intermolecular Diels−Alder reaction followed by intramolecular allylation reaction is of general interest for preparation of cyclic compounds. Further application of this strategy for construction of various cyclic compounds is in progress.

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Supporting Information Available: Experimental details, characterization data, copies of ^{1}H and ^{13}C NMR spectra for all isolated compounds, and crystallographic data for **3a** and **3d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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