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Unusual Formal [4 + 2] Cycloaddition of Ethyl Allenoate with Arylidenoxindoles: Synthesis of Dihydropyran-Fused Indoles

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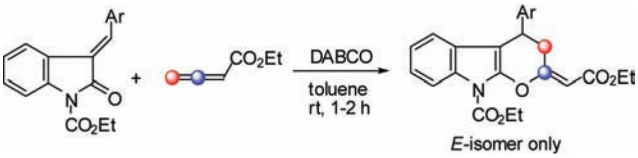
ABSTRACT



An unusual DABCO-catalyzed formal [4 + 2] cycloaddition of ethyl allenoate, as a surrogate of a "1,2-dipole", with various arylidenoxindoles has been developed for the synthesis of dihydropyran-fused indoles. The DFT mechanistic study indicates that the cycloaddition takes place stepwise and the essential role of the catalyst is to raise the HOMO of allenoate.

Allenes, due to their unique reactivity, have become one of the most powerful reagents in organic synthesis,[1] particularly in cycloaddition reactions for cyclic compounds that are present in many natural products and biologically active molecules.[2]

The Lewis base catalyzed reaction of allenoates can be traced back to the early 1990s, when Trost et al. and Lu et al. independently reported the phosphine-catalyzed reactions of alkynes.[3] In 1995, Lu et al. published their pioneering phosphine-catalyzed [3 + 2] cycloaddition reaction of allenoates, as a surrogate of "1,3-dipole", with alkenes (Scheme 1, reaction a).[4] Since then, a series of phosphine-catalyzed [3 + 2] cycloaddition of allenoates was developed, by Lu[2d,5] and other groups,[2f,6] for a variety of carbocycles and heterocycles. In 2003, Kwon et al. reported a novel [4 + 2] annulation of α-alkylallenoates, as a surrogate of "1,4-dipole", with imines,[7,8] which was then expanded to the reactions with electron-deficient olefins[9] and trifluoromethyl ketones[10] (reaction b). In addition, several other reactions, such as Kwon's [3 + 3]

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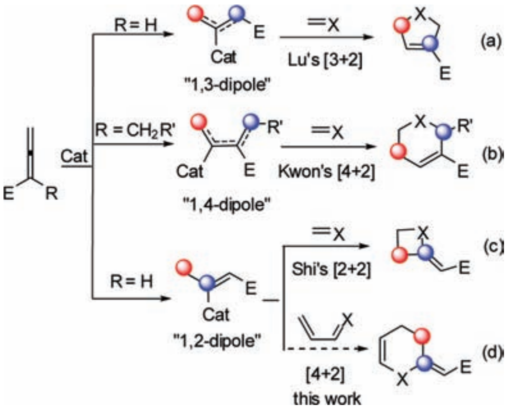
Scheme 1. Lewis Base Catalyzed Formal Cycloaddition Reactions of Allenoates



annulations of aziridines and Tong's [4 + *n*], [3 + *n*] annulations, have also been reported.[11]

In 2003, Shi reported the DABCO-catalyzed [2 + 2] annulation reaction of allenoates, as a surrogate of a "1,2-dipole", with imines (reaction c).[12,13] Later, the dimerization of allenic ketone in a [4 + 2] annulation mode was reported.[14] However, to the best of our knowledge, the [4 + 2] cycloaddition of allenoates as a "1,2-dipole" with dienes or heterodienes has not been reported (reaction d).[15,16] We envisioned that the [4 + 2] formal cycloaddition may be achieved if the proper catalyst and (hetero)diene are introduced. In this letter, we report a DABCO-catalyzed formal [4 + 2] cycloaddition of allenoates with 3-arylidenoxindole for the synthesis of dihydropyran-fused indoles.

Indole is regarded as a privileged structure in many bioactive natural products.[17,18] In the meantime, dihyropyrans are also featured in a number of biologically active compounds.[19] The general methodology for dihydropyrans includes the intramolecular Sakurai reaction,[20] ring-closing olefin metathesis,[21] and the inverse-electron-demanded hetero-Diels–Alder (HDA) reaction of oxodienes and electron-rich alkenes.[22] However, the direct HDA of oxodienes with electron-deficient alkenes is often unfavorable in spite of the formal [4 + 2] feature, which limits the access to highly functionalized dihydropyrans. Recently, we developed an N-heterocyclic carbene (NHC)-catalyzed formal [4 + 2] cycloaddition of alkylenyloxindole with ketenes, which involves the electron-riched enolate generated from the electron-deficient ketenes by nucleophilic addition of NHC.[23] We reasoned that the addition of a Lewis base to allenoate may also raise the HOMO of allenoate and, thus, facilitate the HDA reaction of allenoate with oxodienes.

In accord with the reasoning, the reaction of benzylidenoxindole **1a** and ethyl allenoate (**2**) was carried out in the

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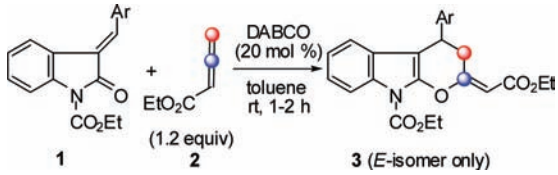
presence of Lewis base catalysts (nucleophilic catalysts). We were happy to find that the formal [4 + 2] cycloaddition reaction of oxodiene **1a** and allenoate **2** went smoothly in the presence of 20 mol % DABCO, affording the corresponding dihydropyran-fused indole **3a** in 79% yield with exclusive regio- and diastereoselectivity. Interestingly, during the preparation of the manuscript, Marinetti reported that a [3 + 2] cycloadduct resulted for the same reaction but using phosphine as the catalyst.[24]

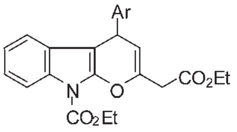
Table 1. DABCO-Catalyzed Formal [4 + 2] Cycloaddition of Arylidenoxindoles with Ethyl Allenoate



1 **2** **3** (*E*-isomer only)

entry	1	Ar	3	yield (%)[a,b]
1	**1a**	Ph	**3a**	79
2	**1b**	4-MeC_6H_4	**3b**	91
3	**1c**	4-ClC_6H_4	**3c**	94
4	**1d**	4-BrC_6H_4	**3d**	95
5	**1e**	4-CNC_6H_4	**3e**	89
6	**1f**	3-$NO_2C_6H_4$	**3f**	67 (8)[c]
7	**1g**	2- $NO_2C_6H_4$	**3g**	65 (7)[c]
8	**1h**	3-ClC_6H_4	**3h**	83
9	**1i**	2-ClC_6H_4	**3i**	85
10	**1j**	2-BrC_6H_4	**3j**	68
11	**1k**	2,4-$Cl_2C_6H_3$	**3k**	83
12	**1l**	2-pyridyl	**3l**	70
13	**1m**	1-naphthyl	**3m**	89

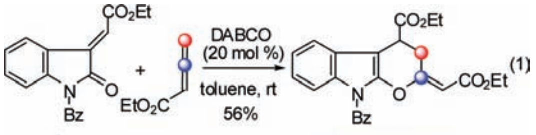
[a] Isolated yield. [b] No *Z*-isomer of cycloadduct **3** was detected for all the reactions (entries 1−13). [c] The isolated yield of the double-bond migrated isomers **4f** or **4g** is showed in parentheses (entries 6 and 7). None or only trace amounts of double bond migrated isomers **4** were observed for other entries.



4f Ar = 3-$NO_2C_6H_4$
4g Ar = 2-$NO_2C_6H_4$

With the optimized reaction conditions in hand,[25] a variety of arylidenoxindoles were then examined for the [4 + 2] cycloaddition reaction (Table 1). It was found that a range of substituents in arylidenoxindoles (4-Me, 4-Cl, 4-Br, and 4-CNC_6H_4) were tolerated to afford the corresponding cycloadducts in high yield with exclusive regio- and diastereoselectivity (entries 2−5). Unexpectedly, when strong electron-withdrawing groups (3-NO_2, 2-NO_2) were introduced, the double bond migrated isomers **4f**−**4g** (see Table 1) were also produced along with normal products **3f**−**3g** (entries 6 and 7). It was also observed that more double bond migrated isomer **4g** (42%) and less **3g** (16%) were isolated when the reaction time was prolonged to 30 h. Arylidenoxindoles with a *meta*- or *ortho*-substituent (3-Cl, 2-Cl, 2-BrC_6H_4) or an *ortho*,*para*-disubstituent (2,4-$Cl_2C_6H_3$) also worked well (entries 8−11). The reaction of 2-pyridylmethenoxindole (**1l**) and 1-naphthylmethylenoxindole (**1m**) gave the corresponding [4 + 2] cycloadducts in 70% and 89% yield, respectively (entries 12−13).

To further explore the scope of the new [4 + 2] cycloaddition, the reaction of (*E*)-ethyl 2-(1-benzoyl-2-oxoindolin-3-ylidene)acetate (**1n**) was also investigated, which gave the cycloadduct **3n** in 56% yield (eq 1).



1n **3n** (*E*-isomer only)

The structure of dihydropyran-fused indole (**3a**) was unambiguously established by X-ray analysis of its crystal (Figure 1).[26]

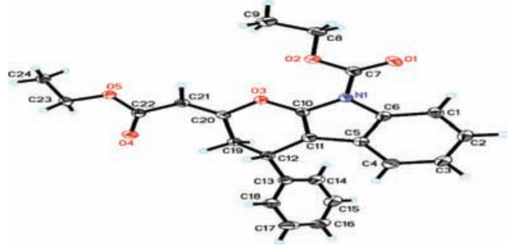


Figure 1. X-ray structure of dihydropyran-fused indole **3a**.

To gain insight into the reaction mechanism, the DABCO-catalyzed reaction of **1a** and **2** was studied by means of DFT calculations.[27] All the structures were optimized and characterized to be energy minima or transition states in the gas phase at the M05-2X/6-31G* level. The energies were further refined by M05-2X/6-311++G**//M05-2X/6-31G*[28] single-point calculations in toluene solvent. The solvation effects were accounted for by the polarizable continumm solvent model (PCM).[29] The M05-2X/6-31G* harmonic frequencies were used for the thermal and entropic corrections (298.15 K and 1 atm) to the single-point energies. The reliability of the computational levels have been calibrated in our previous studies.[30] The free energies were discussed in the following.

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(26) See Supporting Information for details.

(27) The DFT calculations were carried out by using the Gaussian 03 program (Frisch, M. J.; et al. *Gaussian03*; revision E.01 ed.; Gaussian, Inc.: Wallingford, CT, 2004). See Supporting Information for full reference.

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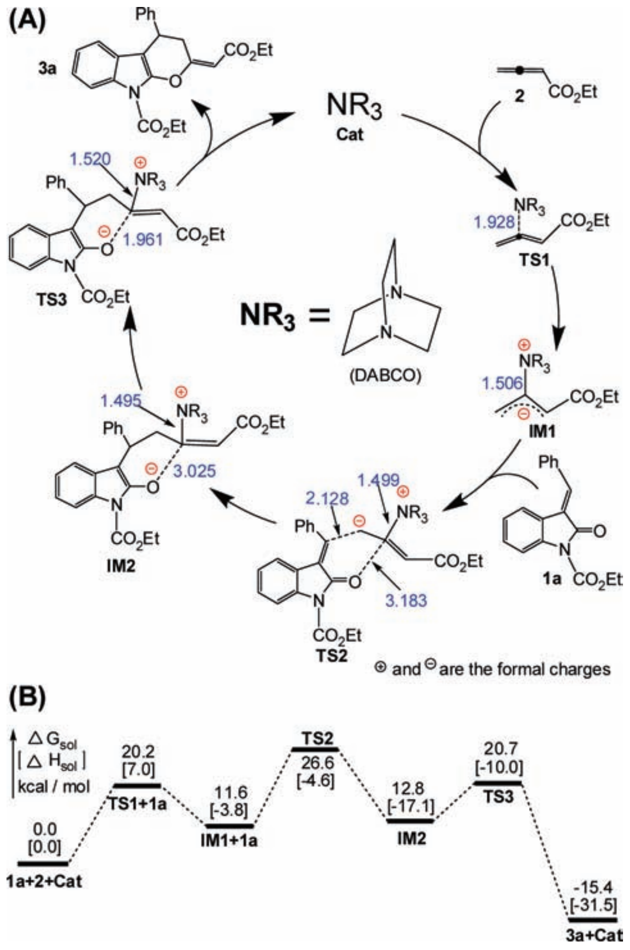
Scheme 2[a]



[a] (**A**) Reaction mechanism of the DABCO-catalyzed "1,-2 dipole" [4 + 2] cycloaddition. (**B**) Energy profile corresponding to (**A**).

The DFT study allows us to construct the catalytic cycle of the reaction in Scheme 2A. The catalyst (DABCO) first attacks allenoate (**2**) at the middle carbon to activate allenoate by passing a barrier (**TS1**) of 20.2 kcal/mol (Scheme 2B). The resultant intermediate (**IM1**) is 11.6 kcal/mol less stable than DABCO + **2**. Unlike the regular concerted mechanism for the Diels–Alder reaction but similar to the "1,2-dipole" [2 + 2] annulation,[12] the addition of **IM1** to **1a**, forming new C–C and C–O bonds, takes place stepwise. After crossing the barrier (**TS2**), a new C–C bond is first formed to give the intermediate (**IM2**). Relative to **IM1** + **2**, the barrier (**TS2**) for the C–C bond forming is 15.0 kcal/mol. Subsequently, the C–O bond is formed by passing another barrier (**TS3**) of 7.9 kcal/mol. The C–O bond formation closes the six-membered ring to yield the product **3a** and liberates the catalyst simultaneously. The final product **3a** is 15.4 kcal/mol more stable than **1a** + **2**.

To understand the role of the catalyst, the direct reaction of **1a** with **2** was also investigated. The HOMO orbital energy of allenoate (**1a**) is −9.0 eV, 7.7 eV below the LUMO of **2**. In comparison, under the influence of the DABCO catalyst, the HOMO energy of **IM1** is −5.2 eV, 3.9 eV below that of the LUMO of **2**. Therefore, the HOMO of **IM1** interacts with the LUMO of **2** more efficiently than the HOMO of **1a**. Consistently, the direct addition barrier of **2** to **1a**, 41.1 kcal/mol, is much higher than the 15.0 kcal/mol for the reaction of **1a** with **IM2**. It can be concluded that the essential role of the DABCO catalyst is to raise the HOMO of allenoate, which facilitates the orbital interations between substrates. In addition to the energetic difference, the direct [4 + 2] cycloaddition of **1a** and **2** takes place concertedly rather than stepwise.

In conclusion, a DABCO-catalyzed formal [4 + 2] cycloaddition of arylidenoxindole and allenoates was developed, which provides a new route to access dihydropyran-fused indoles in good yields with excellent regio- and diastereoselectivities. To our knowledge, this is the first example of a formal [4 + 2] cycloaddition, where allenoates act as a surrogate of "1,2-dipole". The DFT mechanistic study further characterizes a stepwise mechanism for the addition. The new organocatalytic cycloaddition mode and the potential usage of the resulting dihydropyran-fused indoles may find applications in organic synthesis.

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Supporting Information Available. Experimental procedures, compound characterization, and computational data (PDF); the crystal information file of indole **3a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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