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DBU-Catalyzed Rearrangement of Secondary Propargylic Alcohols: An Efficient and Cost-Effective Route to Chalcone Derivatives

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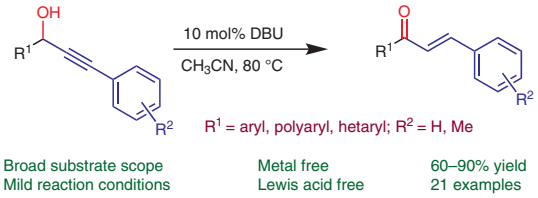

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Abstract A 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)-catalyzed rearrangement of diarylated secondary propargylic alcohols to give α,β-unsaturated carbonyl compounds has been developed. The typical 1,3-transposition of oxy functionality, characteristic of Mayer–Schuster rearrangements, is not observed in this case. A broad substrate scope, functional-group tolerance, operational simplicity, complete atom economy, and excellent yields are among the prominent features of the reaction. Additionally, the photophysical properties and crystal-structure-packing behavior of selected compounds were investigated and found to be of interest.

Key words rearrangement, propargylic alcohols, DBU, chalcones, allenols, organocatalysis

Chalcone compounds with a characteristic 1,3-diaryl-prop-2-en-1-one chemical scaffold are frequently found in naturally occurring substances, and have a widespread distribution in various plants and herbs.[1] Many of these naturally available compounds show numerous promising biological activities, including anticancer activity,[2a] cancer-preventive effects,[2b] antibacterial,[2c] antimalarial,[2d] antiinflammatory,[2e] antiviral,[2f] anti-HIV,[2g] antileishmanial,[2h] and neuroprotective effects[2i], among others. Even, a single chalcone derivative can demonstrate multiple types of bioactivity.[3] Some representative examples of bioactive chalcones (isoliquiritigenin and xanthohumol) and clinically approved chalcone-based drugs (metochalcone and sofalcone) are shown in Figure 1. Apart from their biological significance, chalcones and other related α,β-unsaturated carbonyl compounds are among the most sought-after synthetic intermediate in the area of synthetic organic chemistry, as they are extensively employed in syntheses of a variety of heterocyclic compounds, including pyridines,[4] pyrimidines,[5] imidazoles,[6] pyrazoles,[7] triazoles,[8] pyrazolines,[9] isooxazoles,[10] and many more.

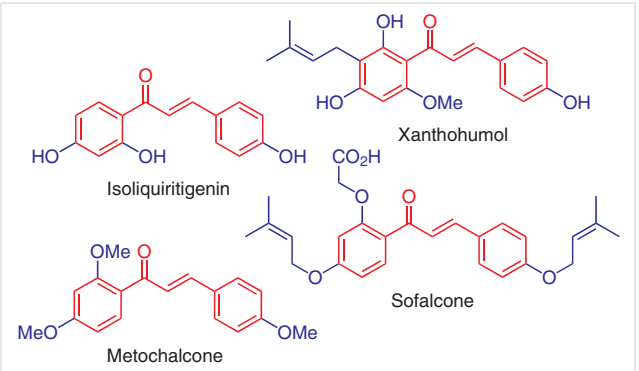

Figure 1 Bioactive chalcones and clinically approved chalcone-based marketed drugs

Because of their therapeutic potential and their versatility as organic synthons, chalcones and other related α,β-unsaturated carbonyl compounds have long been considered to be privileged structural units, and considerable efforts have been devoted to developing efficient methods for their synthesis. Conventionally, chalcones and related α,β-unsaturated carbonyl compounds are synthesized through Claisen–Schmidt condensations,[11] Wittig reactions,[12] Julia–Kocienski olefinations,[13] Friedel–Crafts acylations,[14] and

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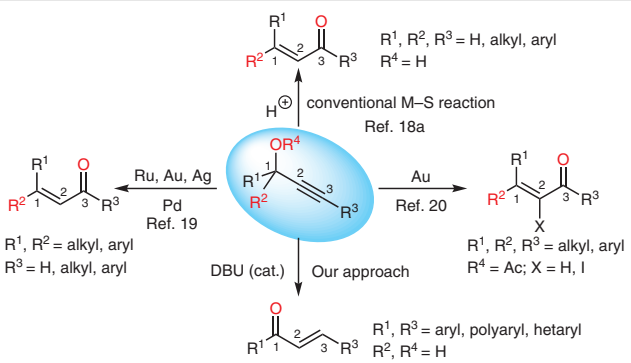
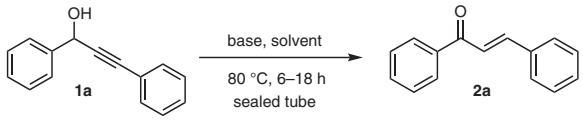
various C–C cross-coupling reactions, such as Suzuki–Miyaura[15] and Heck couplings.[16] Chalcone derivatives can also be prepared from propargylic alcohols, which can undergo molecular rearrangements under basic conditions to produce chalcones.[17] Probably, the most extensively used method for synthesizing chalcone derivatives is the Meyer–Schuster (M–S) rearrangement (Scheme 1),[18] an acid/transition-metal-catalyzed rearrangement of propargylic alcohols to chalcone derivatives. Although the M–S rearrangement was originally catalyzed by protic acids, several transition-metal-catalyzed variants have recently been developed (Scheme 1).[19] Even propargylic acetates have been shown to be excellent substrates for transition-metal-catalyzed M–S rearrangements[20] to produce chalcone and α-halochalcone derivatives (Scheme 1).



Scheme 1 Synthesis of (*E*)-chalcones from propargylic alcohols and acetates

However, transition-metal catalysts are expensive, and the related methods have their issues. Therefore, the development of a simple and cost-effective method for the synthesis of chalcone derivatives is required. Here, we report a simple DBU-catalyzed metal- and acid-free approach leading to chalcone derivatives from secondary propargylic alcohols. Unlike the M–S rearrangement, a 1,3-transposition of oxy functionality is not associated with this protocol. The newly developed method might be successfully employed to access many a range of substituted chalcones potentially useful for various purposes. For our preliminary studies, we selected 1,3-diphenylprop-2-yn-1-ol (**1a**) as our model substrate. Initially, a variety of organic bases (triethylamine, diisopropylamine, *N*,*N*-diisopropylethylamine, pyridine, and imidazole) were tested as promoters for the reaction in CH_3CN as the solvent. None of the desired product **2a** was detected, even after six hours of heating at 80 °C in a sealed tube (Table 1, entries 1–5). Next, we used DBU as a base, and we were delighted to find that all the starting material **1a** was consumed within six hours and that the desired chalcone **2a** was obtained in 85% yield (entry 6). DBU was further screened as the base in various solvent systems under heating conditions, but poorer results were obtained (entries 7 and 8). Again, Et_3N in THF proved totally ineffective (entry 9). Because DBU was found to be an efficient base for promoting the rearrangement reaction, we next examined the reaction with reduced amounts of DBU. We therefore examined the use of 50 and 20 mol% of the base under similar reaction conditions; in both cases, we obtained comparable yields, but the reaction time increased to 12 hours (entries 10 and 11). The amount of base could be reduced to less than 10 mol% without compromising the yield (entry 12), whereas increasing the amount of base did not have any beneficial effect (entry 13). Although the reaction time is increased, a reduction in the amount of organic base to 10 mol% is highly advantageous, as it reduces chemical waste considerably, making the method more compatible with environmental issues. We therefore consider the conditions shown in entry 12 as the optimal conditions for the reaction.

Table 1 Optimization of the Reaction Conditions



Entry	Base	mol%	Solvent	Yield (%)
1	Et_3N	100	CH_3CN	NR[a]
2	*i*-Pr_2NH	100	CH_3CN	NR
3	DIPEA	100	CH_3CN	NR
4	pyridine	100	CH_3CN	NR
5	imidazole	100	CH_3CN	NR
6	DBU	100	CH_3CN	85
7	DBU	100	CH_2Cl_2	50
8	DBU	100	THF	NR
9	Et_3N	100	THF	NR
10	DBU	50	CH_3CN	86
11	DBU	20	CH_3CN	84
12	**DBU**	**10**	**CH_3CN**	**85**
13	DBU	125	CH_3CN	85

[a] NR = no reaction.

Having established the optimal reaction conditions, we turned our focus on exploring the substrate scope of the reaction. For this purpose, we synthesized a series of secondary propargylic alcohols **1a–w** from various aromatic aldehydes and lithiated phenylacetylene by employing slightly modified version of the reported procedure.[21] Propargylic alcohols **1b–g**, prepared from alkyl-substituted benzaldehydes, when subjected to the optimal reaction conditions, gave the corresponding chalcone **2b–g** in excellent yields (Scheme 2). Moreover, propargylic alcohols **1h–k**, prepared from various methoxylated benzaldehydes proved to be excellent substrates for the present reaction, giving the corresponding chalcone derivatives **2h–k**. Chloro- and bromo-

substituted propargylic alcohols **1l** and **1m**, respectively, were smoothly transformed into the corresponding chalcones **2l** and **2m**, albeit with slightly inferior yields. Heterocycle-containing propargylic alcohols **1n** and **1o** readily reacted under the optimized conditions to afford chalcones **2n** and **2o**, both in 88% yield. As expected, propargylic alcohols with polycyclic aryl or benzyloxy substituents **1p–s** afforded the corresponding chalcones **2p–s** in good to excellent yields. Propargylic alcohols **1t** and **1u** prepared from 1-ethynyl-4-methylbenzene were found to be excellent substrates, affording the correspond chalcones **2t** and **2u** in yields of 86 and 67%, respectively. Unfortunately, propargylic alcohols **1v** and **1w**, prepared from isobutyraldehyde and acetaldehyde, respectively, were found to be unresponsive under the standard reaction conditions, and chalcones **2v** and **2w** were not detected.

Most of the chalcone derivatives were solid, and we attempted to obtain crystal structures of some of the products for structural confirmation and to obtain mechanistic insight. Compound **2s** crystallized from 20% ethyl acetate–hexane as white crystals suitable for X-ray analysis (Figure 2).[22] Crystal-structure determination of **2s** not only confirmed its structure unambiguously, but also confirmed that the reaction did not follow the usual M–S pathway, as the typical 1,3-transposition of oxy- functionality was not observed.

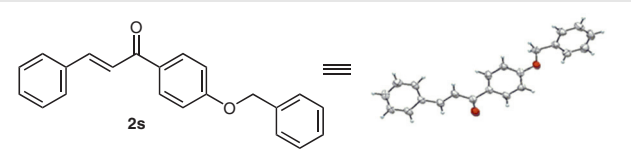
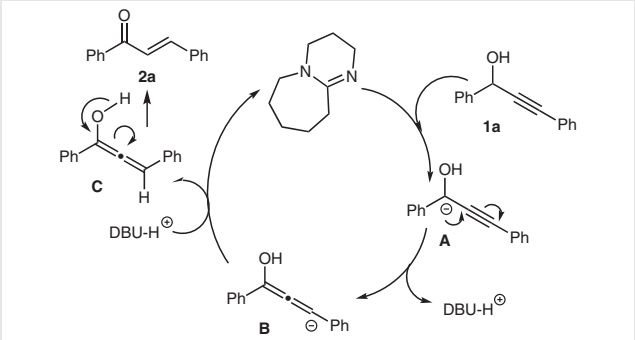


Figure 2 ORTEP diagram of compound **2s** (CCDC 1998081)[22]

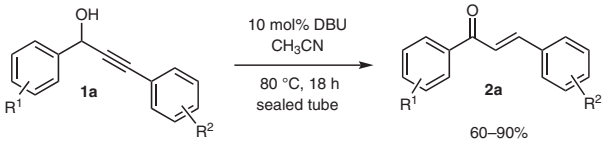
Mechanistically the current isomerization/rearrangement reaction is quite interesting. The propargylic alcohol–enone isomerization reaction proceeds through three elementary steps.[23a] Slow deprotonation of propargylic alcohol **1a** produces propargylic carbanion **A** which is transformed into the allenol intermediate **C** via intermediate **B** (Scheme 3). Finally, a keto–enol tautomerism of **C** produces enone **2a**, and DBU is regenerated to initiate another catalytic cycle (Scheme 2). If the proposed mechanism is acceptable, an allenol derivative might be expected to form as an end-product from an appropriately protected propargylic alcohol. In fact, a silyloxyallene derivative has been identified in a similar base-catalyzed reaction,[23b] further validating our mechanistic proposal. Aliphatic propargylic alcohols such as **1v** and **1w** were found to be incompatible under the standard reaction condition. There are two possible reasons for this: either a corresponding propargylic carbanion similar to **A** is not generated from **1v** or **1w**, or the carbanion is unstable due to the absence of a resonance effect from the aromatic ring (as present in **A**). Therefore, the ineffectiveness of **1v** and **1w** as potential substrates indirectly supports the mechanistic proposal shown in Scheme 2.



Scheme 3 A plausible mechanism of the rearrangement reaction

Among all the various products, **2r** and **2u** contain large-π-surface-area aromatic pyrene groups. Pyrene-based compounds often self-assemble through strong π–π stacking interactions.[24] It was therefore interesting to examine the self-assembly of these chalcone derivatives in the solid and solution states. The self-assembly behavior of **2u** in the solid state was examined by single-crystal X-ray analysis by using a suitable crystal obtained by slow evaporation in a pentanol medium.[22] Detailed crystallographic information is presented in Table S2 of the Supporting Information (SI). Chalcone **2u** crystallizes in a triclinic crystal system with a *P*1 space group. In single packing (Figure S1, SI), two monomers are present, and the pyrene rings interact through aromatic–aromatic interactions in antiparallel fashion. In a higher-order assembly (Figure 3), we also noticed an aromatic–aromatic interaction of the phenyl rings, which is responsible for the antiparallel arrangement. Here, the pyrene–pyrene and phenyl–phenyl ring distances are 4.321 and 4.272 Å, respectively. Moreover, the CH–π interaction (3.178 Å) between the pyrene ring surface and the H-22 hydrogen of the phenyl ring brings the two aromatic surfaces close to one another. Additional two hydrogen-bonding interactions (C–H···O) were observed involving a pyrene hydrogen [H8···O1] and a phenyl-ring hydrogen [H25···O1] with distances of 2.372 Å and 2.499 Å, respectively. Here the aromatic–aromatic interaction mainly helps growth in one dimension, whereas the hydrogen-bonding interaction helps growth in a plane.

We had then studied the photophysical properties of the large-π-surface-containing pyrene-based chalcone **2u** by means of UV-visible absorption spectroscopy and fluorescence spectroscopy. The absorption and emission spectra of **2u** were investigated in two common organic solvents (MeOH and DMSO). In the absorption spectra (Figure 4a), shorter-wavelength (250–300 nm) and longer-wavelength (350–440 nm) peaks are attributed to π–π* transitions of



Substrate	Product	Substrate	Product
1a	2a, 85%	1b	2b, 86%
1c	2c, 78%	1d	2d, 82%
1e	2e, 87%	1f	2f, 86%
1g	2g, 85%	1h	2h, 88%
1i	2i, 85%	1j	2j, 87%
1k	2k, 89%	1l	2l, 71 %
1m	2m, 75 %	1n	2n, 88%
1o	2o 88%	1p	2p, 82%
1q	2q, 86%	1r	2r, 60%
1s	2s, 91%	1t	2t, 86%
1u	2u 67%	1v	2v, 0%
1w	2w, 0%		

Scheme 2 Substrate scope of the reaction

the phenyl ring and pyrene ring, respectively.[25] In the emission spectra, a strong emission band of **2u** was observed in both solvents.

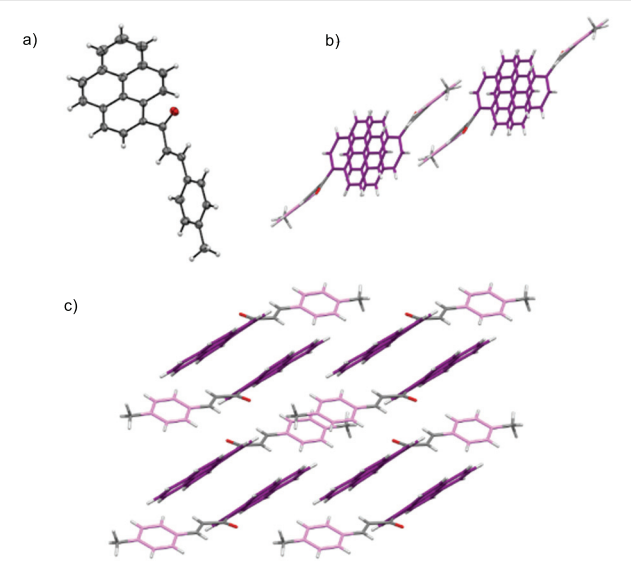


Figure 3 (a) ORTEP diagram of compound **2u** (CCDC1998036),[22] (b) aromatic–aromatic pyrene–pyrene and phenyl–phenyl interactions, and (c) higher-order packing of **2u**.

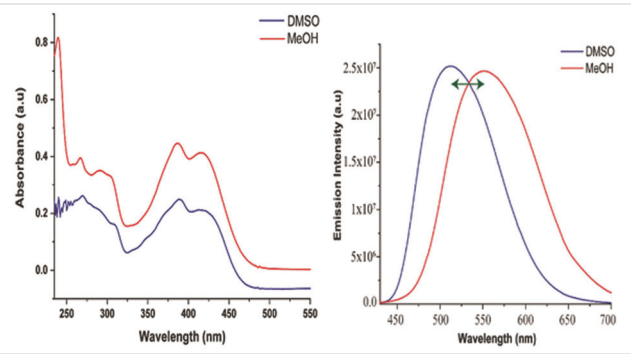


Figure 4 (a) Absorption spectra of **2u** (25 μM) in DMSO and MeOH. (b) Emission spectra of **2u** on excitation at 387 nm in DMSO and MeOH as solvents (25 μM).

In DMSO, the emission band of compound **2u** appeared at a wavelength of 512 nm, whereas in MeOH, the emission peak shifted toward a higher wavelength of 550 nm (Figure 4b). It is interesting to note that the emission of **2u** is dependent on the solvent polarity (polarity MeOH > DMSO).[26] This red shift is due to the stabilization of an excited state in the more-polar solvent.

In summary, we have developed a mild and efficient method for the direct generation of chalcones from secondary propargylic alcohols.[27] The amount of base necessary to complete the reaction can be reduced to just 10 mol%. This fully atom-economical process can be used to prepare many chalcone derivatives with complex molecular architectures. The photophysical properties and molecular arrangement in the crystal state of a few selected compounds were examined successfully. Moreover, the complete atom economy, mild reaction conditions, operational simplicity, and broad functional-group tolerance make this method attractive.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1707909.

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(27) **Chalcones 2a–u; General Procedure**
DBU (10 mol%) was added to a solution of the appropriate propargylic alcohol **1** (1.0 equiv) in dry MeCN (0.2 M) in a sealed tube, and the solution was mixed well by manual shaking. N_2 gas was flashed into the tube, and the cap was quickly closed. The sealed tube was placed in an oil bath at 80 °C, and the mixture was stirred for 18 h until the substrate was completely consumed (TLC). The mixture was then allowed to cool to r.t. and the reaction was quenched with H_2O (10 mL). The product was extracted with Et_2O (3 × 20 mL), and the combined organic layers were washed with brine (10 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified by column chromatography [silica gel (100–200 mesh), PE–EtOAc (10:1)].
(2*E*)-1,3-Diphenylprop-2-en-1-one (**2a**)
White solid; yield: 43.2 mg (86%); mp 54–56 °C. IR (ATR): 3059 (=CH), 1658 (C=O), 1598 (C=C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ =8.02 (d, *J* = 8.0 Hz, 2 H), 7.81 (d, *J* = 16.0 Hz, 1 H), 7.63 (dd, *J* = 8.0, 4.0 Hz, 2 H), 7.59–7.48 (m, 4 H), 7.42–7.40 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 144.9, 138.2, 134.9, 132.9, 130.6, 129.0, 128.7, 128.6, 128.5, 122.2.