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DMAP catalysed vinylogous Rauhut–Currier reaction of allenoates with *para*-quinone methides

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ABSTRACT

The hitherto unknown, organocatalysed (DMAP) vinylogous Rauhut-Currier reaction of 2,3-butadienoates with *para*-quinone methides has been achieved. The products, diarylmethane substituted allenoates, are formed in high to excellent yields under mild reaction conditions.

Introduction

Zwitterionic intermediates, generated by the addition of nucleophiles to activated carbon-carbon multiple bonds, are highly versatile three-carbon reactive intermediates in organic chemistry.[1] There are two patterns of reactivity in such transformations. In one class, the nucleophile, which initially triggers the reaction, can become part of the product. Such transformations require stoichiometric amounts of the nucleophile to drive the reaction to completion. In the second category, only a substoichiometric amount of the nucleophilic "initiator" is required as it is regenerated at the end of the reaction cycle.[2] While the addition of isocyanides to activated alkynes and subsequent trapping of the zwitterionic intermediate with different electrophiles falls into the former class, reactions triggered by the addition of triphenylphosphine as well as tertiary amines fall into the latter class. The zwitterionic intermediate is usually generated by nucleophilic addition to an activated alkene, alkyne or allene.

Allenes are excellent three carbon synthons in organic synthesis.[3] The reactive species generated by the addition of nucleophiles to the β-carbon of allenes, often undergo addition cyclization reactions with suitable electrophiles resulting in cyclic structures.[4] A less often encountered reaction pathway of zwitterions generated from allenoates involves the trapping of electrophiles without cyclization forming open-chain adducts. The allenoate Baylis–Hillman reaction,[5] the 1,2-addition of an allenoate anion to electrophiles and the Rauhut–Currier (R–C) reaction,[6] the 1,4-addition to electrophiles, have precedence in the literature, albeit, limited to isolated examples (Scheme 1). However, to the best of our knowledge, the nucleophile-catalysed 1,6-addition (vinylogous R–C) reaction of an allenoate zwitterion to electrophiles is hitherto unknown despite the fact that the notion of vinylogy has been used as a powerful tool for remote functionalization in organic synthesis.[7] *para*-Quinone methides (*p*-QM) are highly reactive scaffolds, exhibiting a wide variety of reactivity patterns.[8] Their ready participation as vinylogous Michael acceptors make them ideally suited for the study of a vinylogous R–C reaction of allenoate zwitterionic species generated by the addition of nucleophilic catalysts such as phosphines or tertiary amines to allenes. The known instances of vinylogous R–C reactions involve the chiral phosphine-catalysed intermolecular addition of vinyl ketones[9] and the intramolecular addition of vinyl esters/amides[10] to *p*-quinone methides. Thus, the unique nature of *p*-QM to act as a 1,6-acceptor, coupled with the unprecedented nature of the transformation, prompted us to study the addition of allenoate anions to *p*-QM.

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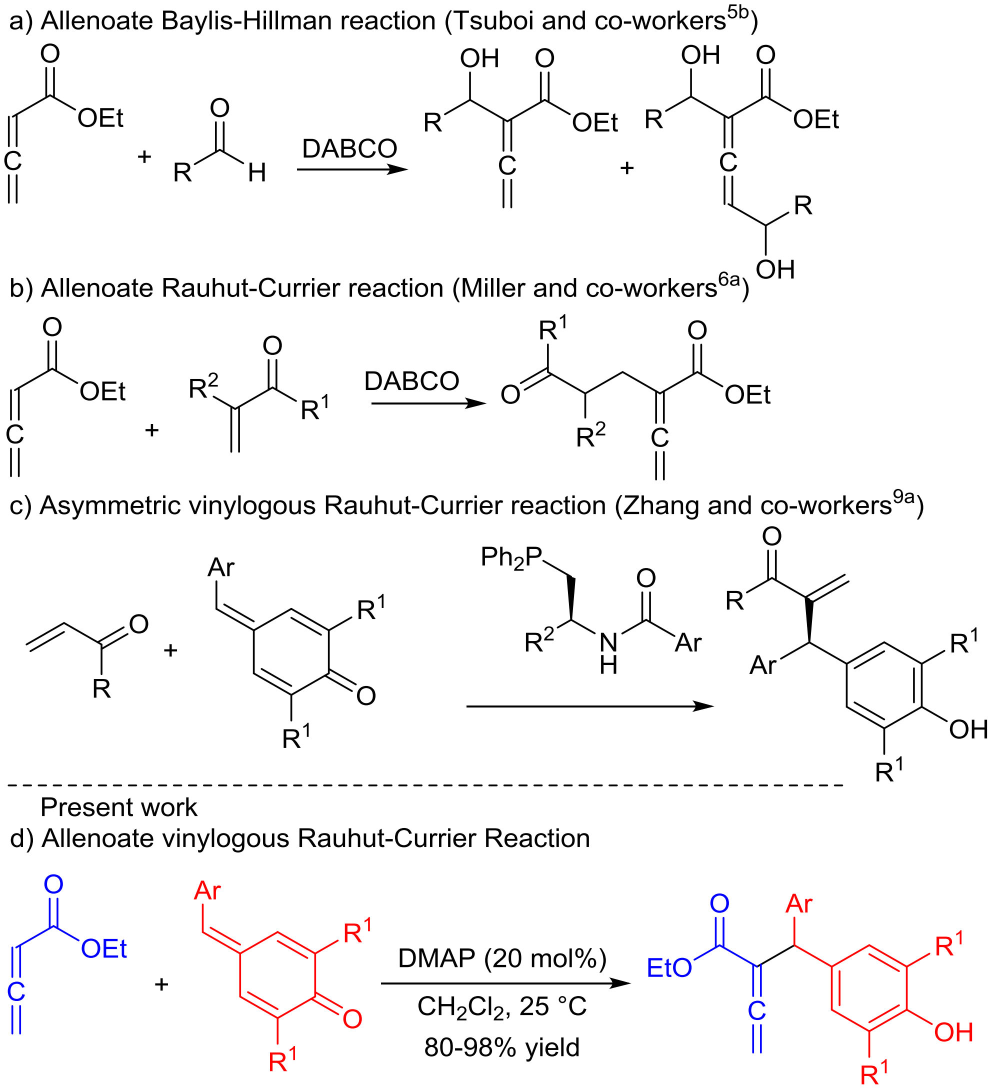
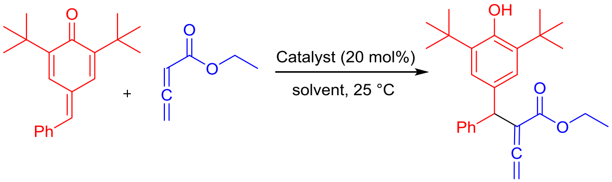


Scheme 1. Activated alkene addition to electrophilic acceptors under nucleophilic catalysis: (a–c) literature precedence and (d) present work.

Table 1
Preliminary studies.[a]



1a **2a** **3a**

Entry	Catalyst	Solvent	Time (h)	Yield **3a** (%)[b]
1	–	CH_2Cl_2	24	–
2	PPh_3	CH_2Cl_2	24	–
3	PBu_3	CH_2Cl_2	24	–
4	DABCO	CH_2Cl_2	24	60
5	DBU	CH_2Cl_2	24	50
6	Et_3N	CH_2Cl_2	24	–
7	Imidazole	CH_2Cl_2	24	–
8	DMAP	CH_2Cl_2	12	98
9	Na_2CO_3	CH_2Cl_2	24	–
10	DMAP	$CHCl_3$	12	96
11	DMAP	DCE	18	90
12	DMAP	DCE	6	86[c]
13	DMAP	Toluene	24	80
14	DMAP	THF	16	95