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Geminal Difunctionalization of Vinylarenes: Concise Synthesis of 1,3-Dioxolan-4-ones

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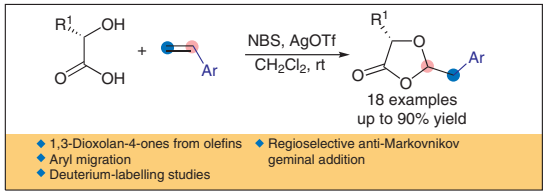

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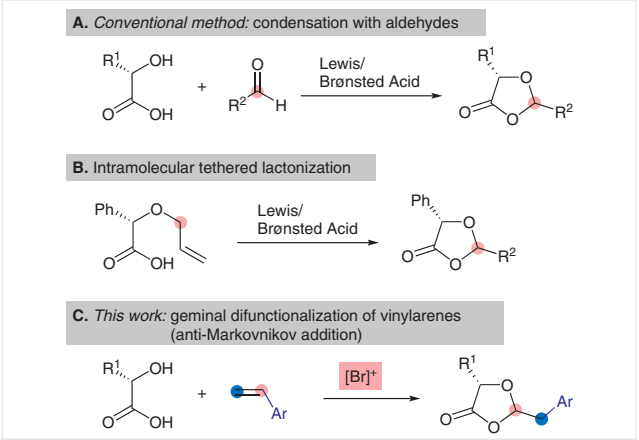
Abstract We report a straightforward method for the synthesis of five-membered 1,3-dioxolan-4-ones by an unprecedented oxidative alkene geminal difunctionalization strategy using α-hydroxy carboxylic acids. Under the geminal oxidative addition conditions, various substituted α-hydroxy carboxylic acids and styrenes containing a variety of substituents, including β-substituted styrenes, were effectively coupled regioselectively (anti-Markovnikov) with an isobutyl-substituted chiral α-hydroxy carboxylic acid, providing an annulation with excellent diastereoselectivity. An aryl migration in the semipinacol rearrangement leading to geminal oxidative addition of the α-hydroxy carboxylic acids was confirmed by deuterium-labelling and control studies.

Key words dioxolanones, geminal difunctionalization, regioselectivity, rearrangement, aryl migration

Installation of new chiral centers or stereoselective transformation using a chiral auxiliary (the chiral pool approach) remains an attractive and powerful strategy in organic synthesis. Because of its effectiveness in stereocontrol and its broad applicability, the chiral pool approach has been routinely employed in stereoselective syntheses of enantiopure compounds, despite the emergence of efficient catalytic asymmetric synthetic methods. The five-membered chiral 1,3-dioxolan-4-one unit is among the most highly privileged and most widely used chiral scaffolds in asymmetric synthesis.[1] The remarkable work of Seebach and co-workers, illustrating the power of self-regeneration of stereoisomers has popularized the use of dioxolanones as chiral auxiliaries in asymmetric synthesis.[2,3] Due to their effectiveness in generating new stereogenic centers, chiral 1,3-dioxolan-4-ones are widely used in syntheses of a variety of chiral building blocks, especially through α-functionalizations of carbonyl groups,[2a,b,4] the Petasis–Ferrier rearrangement,[5] cycloadditions,[6] and radical reactions.[7] These have been used as powerful tools in syntheses of complex natural products and in stereocontrolled polymerizations.[8,9] Moreover the 1,3-dioxolan-4-one moiety is also found as a key structural motif in many bioactive natural products.[10]

Five-membered 1,3-dioxolan-4-ones are conventionally synthesized by Lewis or Brønsted acid mediated condensation of α-hydroxy carboxylic acids with aldehydes.[1c,2] Owing to the importance of 1,3-dioxolan-4-ones as useful synthons, various methods have been developed for their synthesis by using such Lewis or Brønsted acids as $Bi(NO_3)_2$, $BF_3{\cdot}OEt_2$, I_2, TsOH, TfOH, or MsOH, or dehydrating agents, such as P_2O_5, under microwave conditions (Scheme 1A).[11] Yamamoto and co-workers have developed a highly efficient and diastereoselective $Sc(OTf)_3$/$Sc(NTf)_3$-catalyzed condensation of chiral α-hydroxy carboxylic acids with aldehydes or ketones.[12] Senanayake and co-workers investigated in detail the factors that control the diastereoselectivity of the condensation, and they developed a multikilogram protocol for the synthesis of (*S*)-cyclohexyl-



Scheme 1 Approaches to the synthesis of 1,3-dioxolan-4-ones

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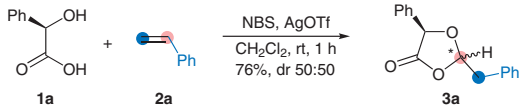
(phenyl)glycolic acid.[13] Although variety of efficient methods has been reported for the synthesis of 1,3-dioxolan-4-ones, most of them rely on a dehydrative acetal-type condensation between an aldehyde and an α-hydroxy carboxylic acid mediated either by activation of the carbonyl group or by dehydration.

Intriguingly, however, only a few methods are available based on other approaches. 1,3-Dioxolan-4-ones have also been obtained by protic-acid-mediated or $Cu(OTf)_2$- or $Al(OTf)_2$-catalyzed intramolecular lactonization through addition of a tethered carboxylic acid to an alkene, and also by aldol-type addition of a carbonyl group to an akene through tethered lactonization of a carboxylic acid (Scheme 1B).[14] Dixneuf and co-workers reported an elegant and highly diastereoselective Ru(II)-catalyzed addition of α-hydroxy carboxylic acids to terminal alkynes for the synthesis of 1,3-dioxolan-4-ones.[15] Despite the high utility of 1,3-dioxolan-4-ones in organic synthesis, there are few alternative methods to the condensation reaction for the synthesis. In this context, we report a concise method for the synthesis of 1,3-dioxolan-4-ones through oxidative difunctionalization of olefins, mediated by bromonium ion, in a highly regioselective manner (Scheme 1C).

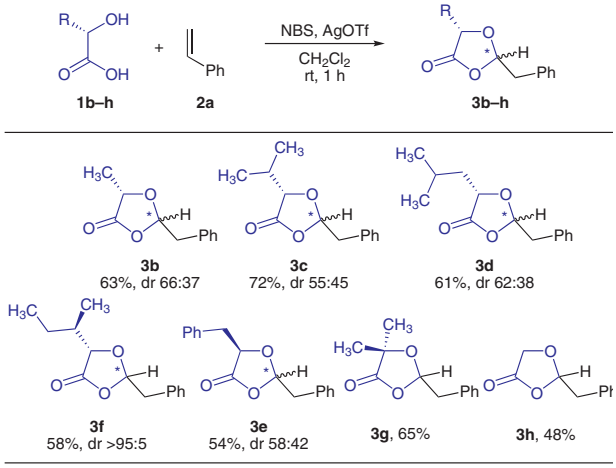
We recently reported that vinylarenes can be oxidatively difunctionalized in a stereoselective manner by halonium-mediated methods, providing straightforward access to nitrogen- or oxygen-containing heterocycles.[16] With our continued interest in oxidative geminal difunctionalization of alkenes, and with the scarcity of available methods for the synthesis of 1,3-dioxolan-4-ones, we surmised that successful geminal addition of α-hydroxy carboxylic acids to alkenes might provide a concise access to 1,3-dioxolan-4-ones directly from alkenes. Accordingly, when we treated (*R*)-(−)-mandelic acid (**1a**), an α-hydroxy carboxylic acid, with styrene (**2a**) under our prototype bromonium ion mediated conditions (NBS, AgOTf, CH_2Cl_2, 1 h, rt),[16a] we were pleased to observe that the 1,3-dioxolan-4-one product **3a** was obtained in a good yield through geminal addition, albeit as a mixture of diastereomers (Scheme 2)



Scheme 2 Synthesis of a 1,3-dioxolan-4-one through a geminal addition to styrene (**2a**)

Encouraged by these results, which demonstrated the feasibility of a straightforward synthesis of 1,3-dioxolan-4-ones from styrene through geminal addition, we decided to study the scope of the reaction further. First, we studied the effects on the geminal addition of substituents on the α-hydroxy carboxylic acid (Table 1). The α-hydroxy carboxylic acids **1b–e**, containing various substituents at the α-position, reacted smoothly with styrene (**2a**) (NBS, AgOTf, CH_2Cl_2, 1 h, rt) to give good yields of the corresponding 1,3-dioxolan-4-ones **3b–e**. Interestingly, the chiral α-hydroxy carboxylic acid **1f** containing a 2-butyl group derived from L-isoleucine, on reaction with styrene, afforded a single diastereomer of the 1,3-dioxolan-4-one **3f** exclusively and in a good yield. The disubstituted and unsubstituted α-hydroxy carboxylic acids **1g** and **1h**, respectively, also underwent efficient geminal addition reactions with styrene to furnish the corresponding 1,3-dioxolan-4-ones **3g** and **3h** as sole products with good regioselectivity.

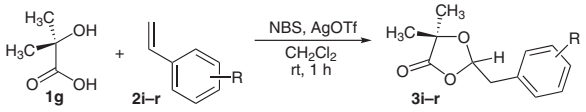
Table 1 Geminal Addition of Substituted α-Hydroxy Carboxylic Acids to Styrene (**2a**)



Reaction conditions: 1 equiv (0.50 mmol) of corresponding α-hydroxy acid **1a–h**, 1.5 equiv of **2a**, 1.2 equiv of NBS, 1.4 equiv of AgOTf, 5 mL of CH_2Cl_2. Isolated yields

We then examined the effects of substituents on the styrene on the geminal oxidative addition reaction (Table 2). Styrenes **2i–l** containing alkyl substituents at the *ortho*-, *meta*- or *para*-positions, on reaction with the α-hydroxy carboxylic acid **1g**, afforded good yields of the corresponding 1,3-dioxolan-4-ones **3i–l** through geminal addition (Table 2, entries 1–4). Interestingly, styrenes **2m** and **2n**, containing electron-withdrawing substituents, also reacted effectively with the α-hydroxy carboxylic acid **1g** to furnish the 1,3-dioxolan-4-ones **3m** and **3n**, respectively, under the same oxidative conditions (NBS, AgOTf, CH_2Cl_2, rt, 1 h) (entries 5 and 6). The β-substituted styrenes, *cis*- and *trans*-stilbenes **2o** and **2p**, respectively, on reaction with α-hydroxy carboxylic acid **1g** both gave the 1,3-dioxolan-4-one **3o** as the sole product (entries 7 and 8). Similarly, the *cis*- and *trans*- β-methyl styrenes **2q** and **2r**, on reaction with α-hydroxy carboxylic acid **1g**, also both gave the single 1,3-dioxolan-4-one **3q** as the sole product (entries 9 and 10).

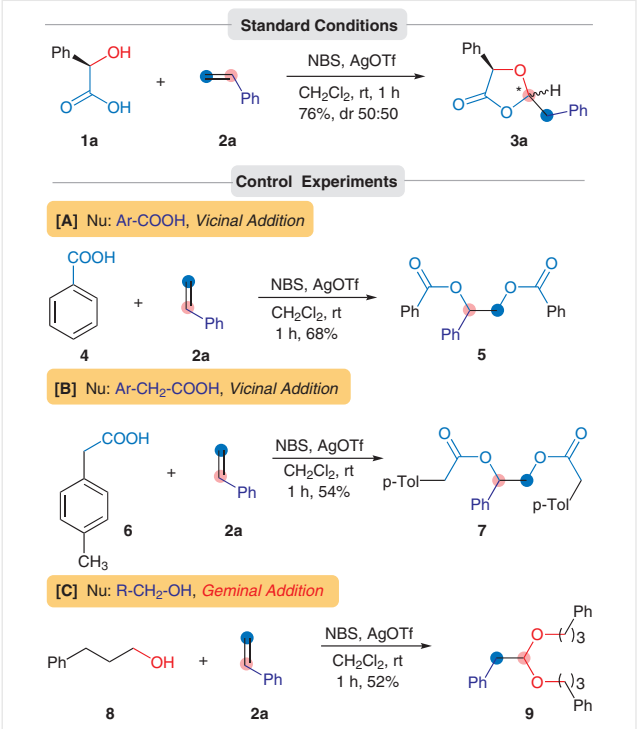
Table 2 Geminal Addition of α-Hydroxy Carboxylic Acid **1g** to Substituted Styrenes



Entry	Styrene	Product	Yield (%)[b]
1	**2i**	**3i**	58
2	**2j**	**3j**	61
3	**2k**	**3k**	57
4	**2l**	**3l**	67
5	**2m**	**3m**	62
6	**2n**	**3n**	60
7	**2o**	**3o**	65
8	**2p**	**3o**	86
9	**2q**	**3q**	72
10	**2r**	**3q**	90

[a] Reaction conditions: same as **Table 1**. [b] Isolated yields.

To gain some mechanistic insights into the geminal oxidative addition of α-hydroxy carboxylic acids to vinylarenes, we conducted control experiments using carboxylic acids and an alcohol as mononucleophiles (Scheme 3). The alkyl and the aryl carboxylic acids **4** and **6**, on reaction with styrene (**2a**) (NBS, AgOTf, CH_2Cl_2, rt, 1 h), formed only the vicinal addition products **5** and **7**, respectively (Scheme 3, A and B), and did not give geminal addition products, whereas alcohol **8**, under the same reaction conditions, formed the geminal addition product **9** exclusively (Scheme 3C), showing that the regioselectivity is dependent on the nature of the nucleophile being added.

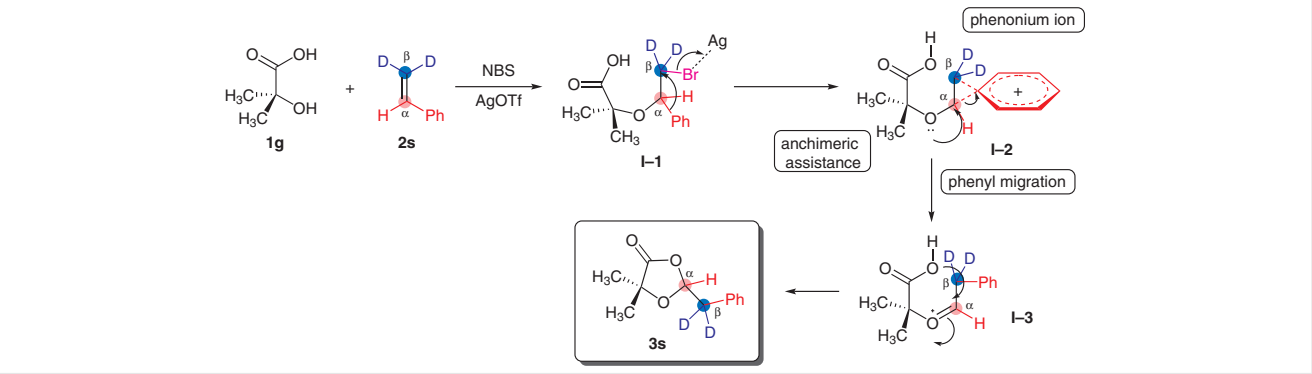


Scheme 3 Control experiments

The reaction of β,β-dideuterostyrene (**2s**) with α-hydroxy carboxylic acid **1g** provided the dideuterobenzyl-substituted 1,3-dioxolan-4-one **3s** as the sole product in good yield (Scheme 4).

Scheme 4 Deuterium-labelling studies

A plausible mechanism for the geminal oxidative addition reaction, based on the control studies and the deuterium-labelling study, is presented in Scheme 5. Activation of alkene **2s** by formation of bromonium ion, followed by the regioselective ring-opening addition of the hydroxy group of **1g** provides the β-bromo benzylic ether **I-1**. The formation of the dideuterobenzyl-substituted 1,3-dioxolan-4-one **3s** (see Scheme 4) as the only product in the addition reaction of β,β-dideuterostyrene (**2s**) clearly demonstrates that



Scheme 5 Plausible pathway for the geminal addition of α-hydroxy carboxylic acids to a vinylarene

the reaction follows a single pathway involving the formation of phenonium ion **I-2** and subsequent migration of the phenyl group from the benzylic (α-position) to the methylene (β-position) driven by the formation of the oxonium ion intermediate **I-3** (Scheme 5). Furthermore, this is in accordance with the observed dependence of the regioselectivity on the nature of the nucleophile being added (cf. Scheme 3, B and C). This indicates the essential role of the functional group in the formation of a favorable carbocation through neighboring-group participation, thereby controlling the regioselectivity of the addition process. Eventually, the tethered carboxylic acid adds to the oxonium ion **I-3** to form the 1,3-dioxolan-4-one **3s** in an overall geminal addition process.

In summary, a, bromonium-ion-mediated, straightforward synthesis of 1,3-dioxolan-4-ones has been developed through highly regioselective (anti-Markovnikov) geminal addition of α-hydroxy carboxylic acids to vinylarenes.[17] In this unprecedented approach, the reaction proceeds through geminal oxidative dioxygenation of a hydrocarbon (olefin) facilitated by NBS and AgOTf, in which two new C–O bonds are formed. This geminal addition works efficiently with various substituted α-hydroxy carboxylic acids to provide 1,3-dioxolan-4-ones in good yields. Moreover, a chiral α-hydroxy carboxylic acid derived from isoleucine, which contained a 2-butyl substituent at the α-position, formed the corresponding annulation product with excellent diastereoselectivity. The α-hydroxy carboxylic acids added effectively to variety of substituted styrenes with complete regioselectivity. Control studies using carboxylic acids and alcohols as nucleophiles exclusively gave vicinal and geminal addition products, respectively. This supports the essential role of neighboring-group-participation-facilitated formation of an oxonium ion in achieving selective geminal addition in a highly regioselective manner. The involvement of aryl-group migration leading to geminal oxidative addition was confirmed by deuterium-labelling studies.

Acknowledgment

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1690250.

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(17) Because the observed diastereoselectivities in Table 1 (including **3f**) are essentially highly substrate controlled, a more robust and comprehensive catalyst-controlled protocol for the highly enantio- and diastereoselective synthesis of 1,3-dioxolan-4-ones through geminal dioxygenation of alkenes is being currently pursued in the authors' laboratory, the results of which will be disclosed in a separate article in the future.
(18) **1,3-Dioxolan-4-ones 3a–s; General Procedure**
NBS (0.60 mmol) and AgOTf (0.70 mmol) were added to a well-stirred colorless solution of the appropriate α-hydroxy carboxylic acid **1** (0.50 mmol) and the appropriate styrene **2** (0.75 mmol) in CH_2Cl_2 (5 mL) at rt (25 °C) under argon in a dry Schlenk flask. The mixture initially changed from colorless to cloudy white, then to colorless with a pale-yellow suspension, and finally to colorless with a pale-gray precipitate after 1 h. The progress of the reaction was monitored by TLC. The mixture was stirred for 1 h at rt, then H_2O (3 mL), sat. aq $NaHCO_3$ (4 mL), and sat. aq $Na_2S_2O_3$ (4 mL) were added successively. The mixture was extracted with CH_2Cl_2 (3 × 5 mL), and the combined organic layers were dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude product was purified by flash chromatography [silica gel, pentane–Et_2O (25:1)].
(5*R*)-2-Benzyl-5-phenyl-1,3-dioxolan-4-one (3a)
Yield: 97 mg (76%).
Diastereomer A: white solid; mp 82–84 °C; $[\alpha]_D^{24}$ –89.7 (*c* 1.0, $CHCl_3$). IR (thin film): 3032, 2924, 1796, 1496, 1454, 1401, 1274, 1214 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.21 (m, 10 H), 5.86 (t, *J* = 4.5 Hz, 1 H), 5.19 (s, 1 H), 3.30–3.20 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.3, 133.5, 133.0, 130.2, 129.2, 128.6, 128.5, 127.3, 127.0, 103.9, 76.8, 40.5. HRMS (ESI-QTOF): *m/z* [M + Na]$^+$ calcd for $C_{16}H_{14}NaO_3$: 277.0841; found: 277.0843.
Diastereomer B: white solid; mp 53–54 °C; $[\alpha]_D^{24}$ –38.2 (*c* 1.0, $CHCl_3$). IR (thin film): 3031, 2924, 1797, 1495, 1454, 1215, 1177, 1109, 992, 934 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.25 (m, 10 H), 6.02 (t, *J* = 3.9 Hz, 1 H), 5.11 (s, 1 H), 3.21 (d, *J* = 4.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.1, 126.6, 126.0, 123.2, 122.0, 121.9, 121.6, 120.4, 118.9, 97.9, 68.3, 34.3. HRMS (ESI-QTOF): *m/z* [M + Na]$^+$ calcd for $C_{16}H_{14}NaO_3$: 277.0841; found: 277.0850.
2-Benzyl-5,5-dimethyl-1,3-dioxolan-4-one-*d*$_2$ (3s)
Colorless oil; yield: 66 mg (63%). IR (thin film): 2984, 2926, 1798, 1387, 1281, 1183, 1008, 986 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.25 (m, 5 H), 5.72 (s, 1 H, *H*CCD_2Ph), 1.38 (s, 3 H), 1.34 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.4, 133.3, 130.1, 128.4, 127.2, 101.9, 77.2, 40.4 (quint, $^3J_{C-D}$ = 19.6 Hz), 24.4, 21.8. HRMS (ESI-QTOF): *m/z* [M + Na]$^+$ calcd for $C_{12}H_{12}D_2NaO_3$: 231.0966; found: 231.0969.