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An efficient and green approach for the synthesis of vinyl aryl ethers in the presence of guanidine hydrochloride

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A stereoselective procedure for vinyl aryl ether bond formation by direct coupling of dialkyl acetylenedicarboxylates and substituted phenols or naphthols under mild reaction conditions has been developed. Using guanidine hydrochloride as a new catalyst and water-acetone as green solvent, dialkyl acetylenedicarboxylates were reacted with substituted phenols or naphthols in room temperature to produce vinyl aryl ethers in good to excellent yields.

Key Words: Guanidine hydrochloride, dialkyl acetylenedicarboxylates, vinyl aryl ether, O-vinylation, water solvent

Introduction

Vinyl ethers of alcohols and phenols are well established monomers, building blocks and auxiliaries in organic synthesis, steadily expanding their scope of applications.[1−4] These compounds are important raw materials as practical chemicals for the production of glutaraldehyde[5,6] as well as vinyl polymer materials[7−9] containing oxygen, which are expected to degrade easily in nature. Methods for their synthesis include alcohol addition to acetylene under high pressure (20∼50 atm) and high temperature (180∼200 °C), Michael-type addition–elimination processes,[10] transition metal catalyzed vinyl transfer,[11] and elimination of the alcohol moiety or HBr from acetals or α-bromo ethers, respectively.[12,13] Moreover, there are many studies on the reaction between acetylenic esters and phenols in organic solvents or under solvent-free conditions to produce fumarate or maleate isomer as the major product.[14−19]

In the last decade, green chemistry has been recognized as a new approach in environmental protection.[20] Thus demands for substitutes for toxic and/or volatile molecular solvents are increasing.

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In this paper we wish to report a stereoselective synthesis of dialkyl (Z)- aryloxy butenedioates from the reaction of a wide range of functionalized phenols or naphthols and dialkyl acetylenedicarboxylates in water-acetone solution as a green solvent using guanidine hydrochloride as a novel and effective catalyst. Guanidines can be categorized as organic superbases[21,22] owing to the resonance stabilization of their conjugated acids[23] and are therefore expected to catalyze various types of base-mediated organic reactions.

Experimental

General

Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHN–O-Rapid analyzer. IR spectra were measured on a Shimadzu IR-460 spectrometer. ^{1}H- and ^{13}C-NMR spectra were measured with a Bruker DRX-500 AVANCE instrument with $CDCl_3$ as solvent at 500.1 and 125.7 MHz, respectively. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. Guanidine hydrochloride, dialkyl acetylenedicarboxylates, and phenol or naphthol derivatives were obtained from Fluka (Buchs, Switzerland) and were used without further purification.

General procedure

A water-acetone (6:4 v/v) solution (10 mL) of phenol or naphthol derivatives (2 mmol) and the dialkyl acetylenedicarboxylates (2 mmol) was mixed with solid guanidine hydrochloride (10 mol%). The mixture was stirred for 2 h under room temperature. The products were isolated by filtration (for solid products) or the organic layer was separated, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (Merck 230-400 mesh) using n-hexane–ethyl acetate as eluent (for liquid products) to yield the highly pure vinyl aryl ether derivatives. Compounds **3a** and **3b**[25], **3c**, **3f** and **3g**[14], **3e**[26], **3h**[25], **3i**[14], **3j**[27], **3k** and **3l**[25], **3s** and **3t**[14] are known compounds.

Dimethyl (Z)-2-(2-hydroxyphenoxy)-2-butenedioate (3d)

Yellow Oil, yield 68%. IR (KBr) (ν_{max} /cm^{-1}): 3460 (OH), 1675-1712 (C=O), 1195 (CO) cm^{-1} MS, *m/z (%)* = 252 (M^+, 78), 193 (76), 161 (100), 110 (24). Anal. Calcd for $C_{12}H_{12}O_6$ (252.2): C, 57.09; H, 4.76%; Found: C, 57.00; H, 4.79%. ^{1}H-NMR (500.13 MHz, $CDCl_3$): δ = 3.71 (s, OCH_3, 3H), 3.85 (s, OCH_3, 3H), 6.77 (s, CH, 1H), 6.83-6.97 (m, CH, 4H). ^{13}C-NMR (125.77 MHz, $CDCl_3$): δ = 52.3, 53.4, 109.0, 109.6, 115.4, 121.0, 122.3, 133.7, 143.8, 146.3, 166.3, 168.2.

Dimethyl (Z)-2-(4-acetyl-3-hydroxyphenoxy)-2-butenedioate (3m)

Yellow powder, yield 80%, mp 85-86 °C. IR (KBr) (ν_{max} /cm^{-1}): 3300-3464 (OH), 1650-1732 (C=O), 1135 (CO) cm^{-1}. MS, *m/z (%)* = 294 (M^+, 68), 279 (39), 235 (100), 193 (55), 151 (32), 43 (47). Anal. Calcd for $C_{14}H_{14}O_7$ (294.3): C, 57.09; H, 4.76%; Found: C, 57.01; H, 4.72%. ^{1}H-NMR (500.13 MHz, $CDCl_3$): δ = 2.57 (s, CH_3, 3H), 3.71 (s, OCH_3, 3H), 3.78 (s, OCH_3, 3H), 6.41 (d, $^4J_{HH}$ = 2.4 Hz, CH, 1H), 6.54 (dd,

$^3J_{HH}$ = 8.8, $^4J_{HH}$ = 2.4 Hz, CH, 1H), 6.73 (s, CH, 1H), 7.70 (d,$^3J_{HH}$ = 8.8 Hz, CH, 1H), 12.61 (s, OH, 1H). ^{13}C-NMR (125.77 MHz, $CDCl_3$): δ = 26.5, 52.2, 53.3, 103.8, 107.8, 117.1, 132.8, 115.8, 148.5, 161.9, 162.6, 163.3, 164.7, 203.1.

Diethyl (Z)-2-(4-acetyl-3-hydroxyphenoxy)-2-butenedioate (3n)

Yellow oil, yield 60%. IR (KBr) (ν_{max} /cm^{-1}): 3310-3520 (OH), 1640-1738 (C=O), 1128 (CO) cm^{-1}. MS, *m/z (%)* = 322 (M^+, 80), 277 (32), 249 (100), 221 (56), 153 (70), 43 (88). Anal. Calcd for $C_{16}H_{18}O_7$ (322.3): C, 59.57; H, 5.58%; Found: C, 59.52; H, 5.50%. ^{1}H-NMR (500.13 MHz, $CDCl_3$): δ = 1.18(t,$^3J_{HH}$ = 7.1 Hz, CH_3, 3H), 1.23 (t, $^3J_{HH}$ = 7.1 Hz, CH_3, 3H), 2.55 (s, 3H, CH_3), 4.15 (q, $^3J_{HH}$ = 7.1 Hz, OCH_2, 2H), 4.20 (q, $^3J_{HH}$ = 7.1 Hz, OCH_2, 2H), 6.41 (d, $^4J_{HH}$ = 2.4 Hz, CH, 1H), 6.53 (dd, $^3J_{HH}$ = 8.8, $^4J_{HH}$ = 2.4 Hz, CH, 1H), 6.71 (s, CH, 1H), 7.69 (d,$^3J_{HH}$ = 8.8 Hz, CH, 1H), 12.60 (s, OH, 1H). ^{13}C-NMR (125.77 MHz, $CDCl_3$): δ = 13.9, 14.0, 26.4, 61.2, 62.6, 103.8, 107.8, 117.3, 132.7, 115.7, 148.5, 161.4, 162.7, 162, 164.7, 203.2.

Dimethyl (Z)-2-(3-acetyl-4-hydroxyphenoxy)-2-butenedioate (3o)

White powder, yield 85%, mp 93-94 °C. IR (KBr) (ν_{max} /cm^{-1}): 3348-3438 (OH), 1662-1737 (C=O), 1179 (CO) cm^{-1}. MS, *m/z (%)* = 294 (M^+, 66), 279 (40), 235 (100), 193 (56), 151 (32), 43 (49). Anal. Calcd for $C_{14}H_{14}O_7$ (294.3): C, 57.09; H, 4.76%; Found: C, 57.00; H, 4.70%. ^{1}H-NMR (500.13 MHz, $CDCl_3$): δ = 2.61 (s, CH_3, 3H), 3.75 (s, OCH_3, 3H), 3.77 (s, OCH_3, 3H), 6.59 (s, CH, 1H), 6.93 (d, $^3J_{HH}$ = 9.0 Hz, CH, 1H), 7.14 (dd, $^3J_{HH}$ = 9.0, $^4J_{HH}$ = 2.9 Hz, CH, 1H), 7.36 (d,$^3J_{HH}$ = 2.9 Hz, CH, 1H), 11.99 (s, OH, 1H). ^{13}C-NMR (125.77 MHz, $CDCl_3$): δ = 26.8, 52.1, 53.2, 114.9, 117.6, 119.5, 125.4, 119.3, 148.2, 149.8, 158.6, 162.4, 163.9, 203.9.

Diethyl (Z)-2-(3-acetyl-4-hydroxyphenoxy)-2-butenedioate (3p)

White powder, yield 75%, mp 96-97 °C. IR (KBr) (ν_{max} /cm^{-1}): 3380-3555 (OH), 1653-1734 (C=O), 1203 (CO) cm^{-1}. MS, *m/z (%)* = 322 (M^+, 82), 277 (33), 249 (100), 221 (56), 153 (72), 43 (88). Anal. Calcd for $C_{16}H_{18}O_7$ (322.3): C, 59.57; H, 5.58%; Found: C, 59.50; H, 5.51%. ^{1}H-NMR (500.13 MHz, $CDCl_3$): δ = 1.21 (t, $^3J_{HH}$ = 7.1 Hz, CH_3, 3H), 1.26 (t, $^3J_{HH}$ = 7.1 Hz, CH_3, 3H), 2.60 (s, CH_3, 3H), 4.20 (q, $^3J_{HH}$ = 7.1 Hz, OCH_2, 4H), 6.57 (s, CH, 1 H), 6.93 (d, $^3J_{HH}$ = 9.0 Hz, CH, 1H), 7.15 (dd, $^3J_{HH}$ = 9.0, $^4J_{HH}$ = 2.9 Hz, CH, 1H), 7.36 (d,$^3J_{HH}$ = 2.9 Hz, CH, 1H), 11.99 (s, OH, 1H). ^{13}C-NMR (125.77 MHz, $CDCl_3$): δ = 14.0, 14.1, 26.8, 61.1, 62.4, 115.0, 117.6, 119.4, 125.6, 119.3, 148.3, 150.0, 158.5, 161.9, 163.5, 203.9.

Dimethyl (Z)-2-(4-benzoyl-3-hydroxyphenoxy)-2-butenedioate (3q)

White powder, yield 85%, mp 104-105 °C. IR (KBr) ($\nu_{\max}$/cm^{-1}): 3310-3438 (OH), 1633-1729 (C=O), 1158 (CO) cm^{-1}. MS, *m/z (%)* = 356 (M^+, 65), 297 (61), 105 (100), 77 (32). Anal. Calcd for $C_{19}H_{16}O_7$ (356.3): C, 63.99; H, 4.49%; Found: C, 63.90; H, 4.41%. ^{1}H-NMR (500.13 MHz, $CDCl_3$): δ = 3.73 (s, CH_3, 3H), 3.83 (s, OCH_3, 3H), 6.53 (m, CH, 2H), 6.76 (s, CH, 1H), 7.47-7.52 (m, CH, 2H), 7.56-7.60 (m, CH, 2H), 7.63-7.66

(m, CH, 2H), 12.52 (s,OH, 1H). ^{13}C-NMR (125.77 MHz, $CDCl_3$): δ = 52.2, 53.3, 104.0, 107.6, 117.3, 128.4, 128.9, 135.7, 138.0, 115.2, 131.8, 148.4, 161.9, 162.6, 163.3, 165.7, 200.4.

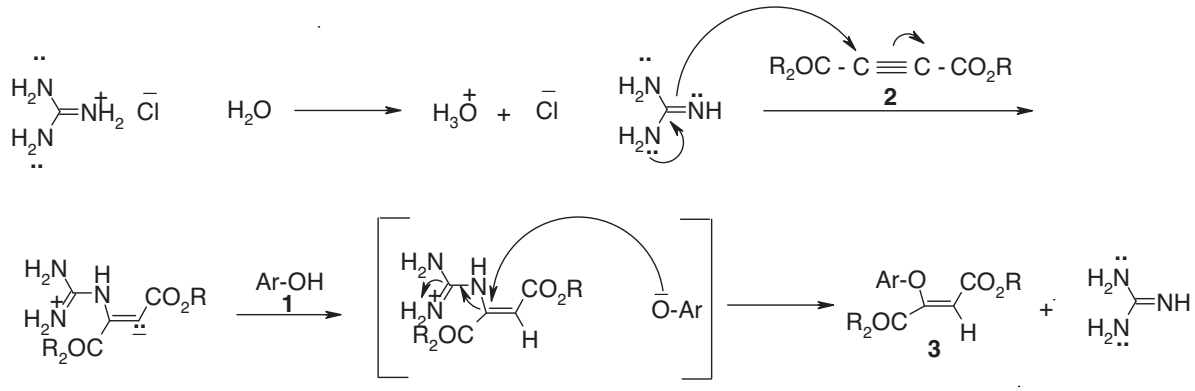
Diethyl (Z)-2-(4-benzoyl-3-hydroxyphenoxy)-2-butenedioate (3r)

Yellow oil, yield 65%. IR (KBr) (ν_{max} /cm^{-1}): 3300-3423 (OH), 1658-1734 (C=O), 1123 (CO) cm^{-1}. MS, *m/z (%)* = 384 (M^+, 60), 311 (75), 105 (100), 77 (48). Anal. Calcd for $C_{21}H_{20}O_7$ (384.4): C, 65.56; H, 5.20%; Found: C, 65.50; H, 5.22%. ^{1}H-NMR (500.13 MHz, $CDCl_3$): δ = 1.19 (t, $^3J_{HH}$ = 7.1 Hz, CH_3, 3H), 1.24 (t, $^3J_{HH}$ = 7.1 Hz, CH_3, 3H), 4.15 (q, $^3J_{HH}$ = 7.1 Hz, OCH_2, 2H), 4.22 (q, $^3J_{HH}$ = 7.1 Hz, OCH_2, 2H), 6.51 (m, CH, 2H), 6.73 (s, CH, 1H), 7.42-7.61 (m, CH, 6H), 12.50 (s, OH, 1 H). ^{13}C-NMR (125.77 MHz, $CDCl_3$): δ = 13.8, 14.0, 61.2, 62.5, 104.0, 107.6, 117.5, 128.5, 129.0, 135.6, 137.9, 116.7, 131.8, 148.4, 161.4, 162.8, 162.9, 165

Results and discussion

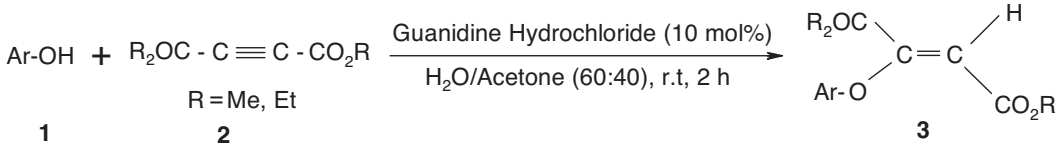
The chemoselective reaction of OH-acids **1** with dialkyl acetylenedicarboxylates **2** in the presence of guanidine hydrochloride as the vinylation agent led to the synthesis of vinyl aryl ethers **3a-t**. In this paper, we introduce guanidine hydrochloride as an excellent catalyst for the stereoselective synthesis of various (Z)-O-vinyl aryl ethers. This catalyst is completely soluble in water and the products **3a-t** are more easily worked up. The reactions were carried out by mixing the OH-acids **1** with acetylenic esters **2** and then guanidine hydrochloride (10 mol%) was added to the mixture. The reactions proceeded spontaneously in water/acetone (60:40) at room temperature for 2 h to afford the ether products **3a-t** in 55%-85% isolated yield (Table).

The structures of compounds **3a-t** were determined on the basis of their elemental analyses, mass spectra, ^{1}H- and ^{13}C-NMR, and IR spectroscopic data. Observation of a single peak at about δ = 6.70 in the ^{1}H-NMR spectra is consistent with O-vinylation of the aromatic ring and formation of dialkyl (Z)-aryloxy butenedioates **3a-t** as major products. The assignment of the Z configuration of **3a-t** is based on the chemical shift of the vinylic proton.[24] The ^{13}C-NMR spectra of **3a-t** show distinct resonances in agreement with the proposed structures. Partial assignments of these resonances are given in the Experimental section. A possible mechanism for the formation of products **3a-t** is proposed in the Scheme.



Scheme. The formation mechanism for vinyl aryl ethers.

Table. O-Vinylation of aryl alcohols with dialkyl acetylenedicarboxylates in the presence of guanidine hydrochloride.



1 **2** **3**

Entry	Ar	R	(Z) - Isolated yields%
3a	phenyl	Me	72
3b	4-chlorophenyl	Me	58
3c	2,4-dichlorophenyl	Me	55
3d	2-hydroxyphenyl	Me	68
3e	4-hydroxyphenyl	Me	85
3f	2-nitrophenyl	Me	60
3g	3-nitrophenyl	Me	78
3h	4-nitrophenyl	Me	85
3i	2-acetylphenyl	Me	68
3j	2-formylphenyl	Me	75
3k	2-methoxyphenyl	Me	78
3l	2-methoxy-4-formylphenyl	Me	72
3m	4-acetyl-3-hydroxyphenyl	Me	80
3n	4-acetyl-3-hydroxyphenyl	Et	60
3o	3-acetyl-4-hydroxyphenyl	Me	85
3p	3-acetyl-4-hydroxyphenyl	Et	75
3q	4-benzoyl-3-hydroxyphenyl	Me	85
3r	4-benzoyl-3-hydroxyphenyl	Et	65
3s	1-naphthyl	Me	60
3t	2-naphthyl	Me	65

Conclusion

We have developed a stereoselective, simple and efficient method for the synthesis of a new family of stable and safe in handling O-vinyl aryl ethers. This method has several advantages such as mild conditions, easy work up, and good to excellent yields for products, which make it attractive for researchers.

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