Available online at www.sciencedirect.com
ScienceDirect
Chinese Chemical Letters 21 (2010) 175–178
CHINESE CHEMICAL LETTERS
www.elsevier.com/locate/cclet

An efficient chemoselective synthesis of O-vinylaryl systems using acetylenic esters and dihydroxybenzenes in the presence of triphenylphosphine or alkyl isocyanides

Robabeh Baharfar *, Mohammad Javad Taghizadeh, Majid Ahmadian, Seyed Meysam Baghbanian

Department of Chemistry, University of Mazandaran, Babolsar 47415, Iran

Received 6 July 2009

Abstract

The addition of 2,4-dihydroxyaceto(and benzo)phenone to propiolic ester is catalyzed by triphenylphosphine or *tert*-butyl isocyanide to form O-vinyl aryl derivatives in fairly good yields.

Keywords: 2,4-Dihydroxyaceto(and benzo)phenone; Triphenylphosphine; Propiolic ester; *tert*-Butyl isocyanide

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]. The O-alkylated phenols have numerous industrial applications, particularly in the production of dyes and agrochemicals [5–7].

We have already described the synthesis of O-vinyl, S-vinyl and N-vinyl systems from the reaction of triphenylphosphine with propiolic esters and enols or thiols (as an OH- or SH-acid) [8–10]. With the purpose of the study of chemoselectivity in bifunctional reagents, we selected 2,4-dihydroxy benzo(and aceto) phenones (**2**), which have two OH acidic groups.

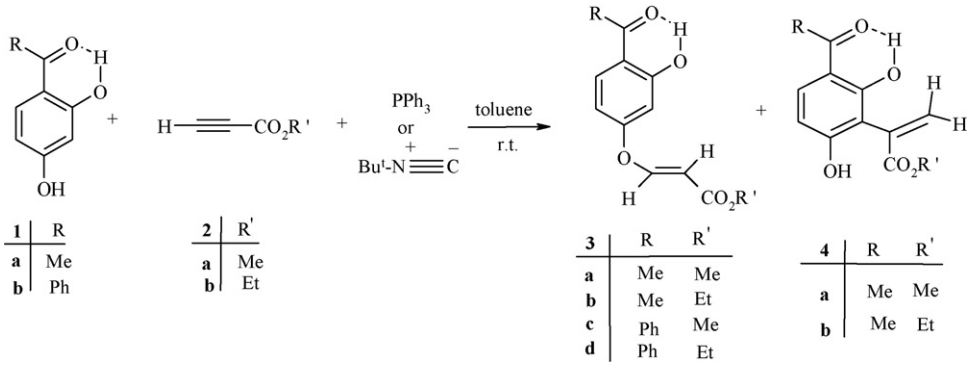
Therefore, the chemoselective reactions between OH-acids (**1a,b**) and propiolic esters in the presence of triphenylphosphine or *tert*-butyl isocyanide lead to the synthesis of O-vinyl systems (**3a–d**) and C-vinyl systems (**4a–b)** as by-products (Scheme 1).

1. Experimental

Melting points were measured on an Electrothermal 9100 apparatus. 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. 2,4-dihydroxy (aceto and benzo)phenone, propiolic esters,

* Corresponding author.
E-mail address: Baharfar@umz.ac.ir (R. Baharfar).

1001-8417/$ – see front matter
doi:10.1016/j.cclet.2009.10.007



Scheme 1. .

triphenylphosphine, *tert*-butyl isocyanide were obtained from Fluka (Buchs, Switzerland) and were used without further purification.

1.1. General procedure

To a magnetically stirred solution of 2,4-dihydroxy aceto (or benzo)phenone (2 mmol) and propiolic ester (2 mmol) in 10 mL of toluene was added dropwise at −10 °C over 10 min triphenylphosphine (1 mmol, 0.262 g) or *tert*-butyl isocyanide (1 mmol). The reaction mixture was then allowed to warm up to room temperature and stand for 24 h. The solvent was removed under reduced pressure and the residue was separated by silica gel column chromatography (Merck 230–400 mesh) using n-hexane: ethylacetate as eluent.

Methyl-(E)-3-(4-acetyl-3-hydroxyphenoxy)-2- acrylate (***3a***)*:* Yellow powder, mp 91–95 °C, yield 70%; IR (KBr)($\upsilon_{max,}$ cm^{-1}): 1640 (C=O), 1735 (C=O), 3400–3500 (OH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.61 (s, 3 H, CH_3), 3.76 (s, 3 H, OCH_3), 5.73 (d, 1 H, $^3J_{HH}$ =12.1 Hz, =CH), 6.61(dd, 1 H, $^3J_{HH}$ = 8.8, $^4J_{HH}$ = 2.4 Hz, CH), 6.64 (d, 1 H, $^3J_{HH}$ = 2.4 Hz, CH), 7.75 (d,1 H, $^3J_{HH}$ = 8.8 Hz, CH), 7.81 (d, 1 H, $^3J_{HH}$ = 12.1 Hz, OCH), 12.57 (s, 1 H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.6 (CH_3), 51.5 (OCH_3), 104.3 (C=*C*H), 105.7, 108.5 and 132.8 (CH), 116.8, 161.4, 164.4 (3C), 156.1 (O*C*H=CH), 167.0 (C=O, ester), 203.0 (C=O, ketone); MS, (*m/z*, %): 236 (M^+, 57), 221 (M^+–Me, 100), 177 [M^+–($COCH_3$, Me, H), 34], 43 ($COCH_3^+$, 48).

Ethyl-(E)-3-(4-acetyl-3-hydroxyphenoxy)-2- acrylate (***3b***)*:* Yellow powder, mp 95–99 °C, yield 65%; IR (KBr)($\upsilon_{max,}$ cm^{-1}): 1625(C=O), 1765 (C=O), 3360–3480 (OH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.28 (t, 3 H, $^3J_{HH}$ = 7.1 Hz, CH_3), 2.56 (s, 3 H, CH_3), 4.20–4.28 (m, 2 H, OCH_2), 5.89 (d, 1 H, $^3J_{HH}$ = 12.1 Hz, =CH), 6.35(dd, 1 H, $^3J_{HH}$ = 8.8, $^4J_{HH}$ = 2.4 Hz, CH), 6.41 (d, 1 H, $^3J_{HH}$ = 2.4 Hz, CH), 7.64 (d, 1 H, $^3J_{HH}$ = 8.8 Hz, CH), 7.71 (d, 1 H, $^3J_{HH}$ = 12.1 Hz, OCH), 12.69 (s, 1 H, OH);^{13}C NMR (125 MHz, $CDCl_3$): δ 14.0 (CH_3), 26.2 (CH_3), 61.6 (OCH_2), 103.5 (C=*C*H), 103.6, 107.7 and 133.1 (CH), 114.3, 162.7, 165.1 (3C), 156.2 (OCH=CH), 165.9 (C=O, ester), 202.7 (C=O, ketone); MS, (*m/z*, %): 250 (M^+, 60), 221 (M^+–Et, 100), 177 [M^+–($COCH_3$, Et, H), 34], 43 ($COCH_3^+$, 50).

Methyl-(E)-3-(4-benzoyl-3-hydroxyphenoxy)-2-acrylate (***3c***)*:* Yellow powder, mp 91–93 °C, yield 80%; IR (KBr)($\upsilon_{max,}$ cm^{-1}): 1625 (C=O), 1765 (C=O), 3300–3500 (OH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.76 (s, 3 H, OCH_3), 5.75 (d, 1 H, $^3J_{HH}$ = 12.1 Hz, =CH), 6.58 (dd, 1 H, $^3J_{HH}$ = 8.8, $^4J_{HH}$ = 2.4 Hz, CH), 6.74 (d, 1 H, $^3J_{HH}$ = 2.4 Hz, CH), 7.50–7.64 (m, 5 H, CH), 7.65 (d, 1 H, $^3J_{HH}$ = 8.8 Hz, CH), 7.84 (d, 1 H, $^3J_{HH}$ = 12.1 Hz, OCH), 12.44 (s, 1 H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 51.5 (OCH_3), 104.5 (C=CH), 105.8, 108.2, 128.5, 129.0, 132.0, 135.8 (CH), 156.0 (OCH=CH), 116.1, 137.8, 161.4, 165.6 (4C), 167.0 (C=O, ester), 200.4 (C=O, ketone); MS, (*m/z*, %): 298 (M^+, 100), 105 (Ph–C=O^+, 92), 239 (M^+–CO_2Me, 35), 77 (ph^+, 45).

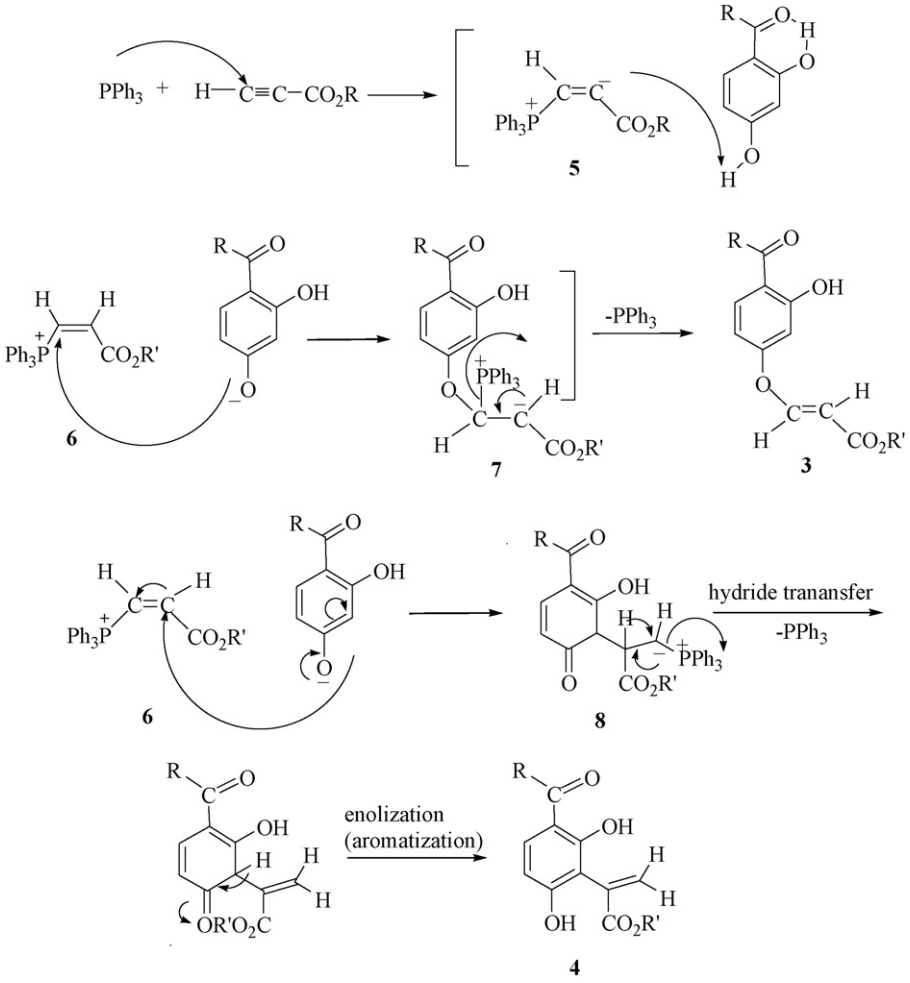
Ethyl-(E)-3-(4-benzoyl-3-hydroxyphenoxy)-2-acrylate (***3d***)*:* Yellow powder, mp 95–97 °C, yield 85%; IR (KBr)($\upsilon_{max,}$ cm^{-1}): 1625 (C=O), 1770 (C=O), 3350–3500 (OH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.31 (t, 3 H, $^3J_{HH}$ = 7.1 Hz, CH_3), 4.22 (q, 2 H, $^3J_{HH}$ = 7.1 Hz, OCH_2), 5.74 (d, 1 H, $^3J_{HH}$ = 12.1 Hz, =CH), 6.58 (dd, 1 H, $^3J_{HH}$ = 8.8, $^4J_{HH}$ = 2.4 Hz, CH), 6.74 (d, 1 H, $^3J_{HH}$ = 2.4 Hz, CH), 7.49–7.64 (m, 5 H, CH), 7.65 (d, 1 H, $^3J_{HH}$ = 8.8 Hz, CH), 7.82 (d, 1 H, $^3J_{HH}$ = 12.1 Hz, OCH), 12.44 (s, 1 H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3 (CH_3), 60.4 (OCH_2), 104.9 (C=*C*H), 105.8, 108.2, 128.4, 129.0, 132.0, 135.8 (CH), 155.9 (OCH=*C*H), 116.1, 137.8, 161.5, 165.6 (4C), 166.6 (C=O, ester), 200.4 (C=O, ketone); MS, (*m/z*, %): 312 (M^+, 100), 105 (Ph–C=O^+, 96), 239 (M^+–CO_2Et, 40), 77 (ph^+, 39).

Methyl-2-(3-acetyl-2,6-dihydroxyphenyl)acrylate (***4a***)*:* Yellow powder, mp 120–122 °C, yield 15%; IR (KBr)(υ_{max}, cm^{-1}): 1625 (C=O), 1765 (C=O), 3400–3480 (OH); ^1H NMR (500 MHz, $CDCl_3$): δ 2.68 (s, 3 H, CH_3), 3.80 (s, 3 H, OCH_3), 6.11 (s, 1 H, OH), 6.47(s, 1 H, =CH), 6.88 (d, 1 H, $^3J_{HH}$ = 9.0 Hz, CH), 7.96 (d, 1 H, $^3J_{HH}$ = 9.0 Hz, CH), 8.18 (s, 1 H, =CH), 13.51 (s, 1 H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.7 (CH_3), 52.4 (OCH_3), 107.7 and 133.8 (CH), 109.2, 115.3, 158.6 and 160.7 (4 C), 129.6 ($C=CH_2$), 135.8 ($=CH_2$), 165.8 (C=O, ester), 203.6 (C=O, ketone); MS, (*m/z*, %): 236 (M^+, 60), 221 (M^+–Me, 100), 177 [M^+–($COCH_3$, Me, H), 37], 43 ($COCH_3^+$, 40).

Ethyl-2-(3-acetyl-2,6-dihydroxyphenyl)acrylate (***4b***)*:* Yellow powder, mp 140–145 °C, yield 20%; IR (KBr)(υ_{max}, cm^{-1}): 1625 (C=O), 1765 (C=O), 3400–3450 (OH); ^1H NMR (500 MHz, $CDCl_3$): δ 1.32 (t, 3 H, $^3J_{HH}$ = 7.1 Hz, CH_3), 2.67 (s, 3 H, CH_3), 4.29 (q, 2 H, $^3J_{HH}$ = 7.1 Hz, OCH_2), 6.10 (s, 1 H, OH), 6.50 (s, 1 H, =CH), 6.86 (d,1 H, $^3J_{HH}$ = 8.9 Hz, CH), 7.87 (d, 1 H, $^3J_{HH}$ = 8.9 Hz, CH), 8.18 (s, 1 H, =CH), 13.50 (s, 1 H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1 (CH_3), 26.7 (CH_3), 61.5 (OCH_2), 107.7 and 133.5 (CH), 109.5, 115.3, 158.8 and 161.2 (4C), 129.4 ($C=CH_2$), 135.7 ($=CH_2$), 165.4 (C=O, ester), 203.6 (C=O, ketone); MS, (*m/z*, %): 250 (M^+, 60), 221 (M^+–Et, 100), 177 [M^+–($COCH_3$, Et, H), 35], 43 ($COCH_3^+$, 43).

2. Results and discussion

On the basis of the chemistry of trivalent phosphorus nucleophiles, it is reasonable to assume that O-vinyl and C-vinyl 2,4-dihydroxyaceto(and benzo)phenone derivatives **3** and **4** result from the initial attack of triphenylphosphine at the β–carbon atom of the propiolic ester to form dipolar intermediate (**5**). Then, concomitant protonation of



Scheme 2. .

this 1:1 adduct by the OH-acid (**1**) leads to the corresponding phosphonium salt (**6**). The addition of the anion of (**1**) (from O-head or C-head) to the (- or (-position of triphenylphosphonium acrylate counterpart (**6**) followed by elimination of the triphenylphosphine to be recycled as a catalyst would lead to the O-vinyl and C-vinyl systems **3** and **4**, respectively, Scheme 2. Tert-butyl isocyanide also catalyze this reaction *via* similar mechanism to produce the same products.

The chemoselectivity of this reaction is explained by the deactivation of the hydroxy group by an intramolecular hydrogen bonding with the neighboring carbonyl group. The structures of final products **(3a–d)** and by-products **(4a–b)** were assigned to the isolated adducts on the basis of their elemental analysis, IR, ^{1}H NMR, ^{13}C NMR and mass spectral data. Observation of two characteristic doublets with $^{3}J_{HH}$ of about 12 Hz in the ^{1}H NMR spectra of (**3a–d)** is consistent with O-vinylation of the aromatic ring and formation of alkyl (E)-aryloxy propenoates (**3a–d**). ^{1}H NMR spectra of (**4a–b**) revealed in each case, two single peaks at about *(* = 6.50 and 8.18 ppm in agreement with the diastereotopic protons in olefin moiety. The ^{13}C NMR spectra of (**3a–d**) and (**4a–b**) show distinct resonances in agreement with the proposed structures. Partial assignments of these resonances are given in the experimental section.

3. Conclusions

We have found a tri-component synthetic method for the preparation of some O-vinyl aryl derivatives of potential synthetic interest. The present method carries the advantage that not only is the reaction performed under neutral conditions, but also the starting materials and reagents can be mixed without any activation or modification.

References

[1] W. Reppe, Neue Entwicklungen auf dem Gebiete der Chimie des Acetylens und Kohlenoxyds, Springer, Berlin, 1949.
[2] M.F. Shostakovsky, Vinyl Ethers, Akademie Nauk SSSR, Moscow, 1952 (in Russian).
[3] B.A. Trofimov, Heteroatomic Derivatives of Acetylene: New Polyfunctional Monomers, Reagents, and Intermediates, Nauka, Moscow, 1981 (in Russian).
[4] R.J. Tedeschi, Acetylene-Based Chemicals from Coal and Other Natural Resources, Marcel Dekker, New York, 1982.
[5] K. Weissermel, H.J. Arfe, Industrial Organic Chemistry, third ed., Wiley VCH, Weinheim, 1997, p. 358.
[6] L.D. Quin, A Guide to Organophosphorus Chemistry, Wiley-Interscience, New York, 2000.
[7] (a) I. Yavari, A. Ramazani, Synth. Commun. 27 (1997) 1449;
(b) I. Yavari, H. Norouzi-Arasi, Phosphorus, Sulfur Silicon 177 (2002) 87;
(c) I. Yavari, S. Souri, M. Sirouspour, et al. Synthesis (2005) 1761.
[8] R. Baharfar, A. Ostadzadeh, A.J. Abbasi, J. Chem. Res. (S) (2004) 37.
[9] R. Baharfar, S.M. Baghbanian, R. Hosseinnia, Lett. Organ. Chem. 4 (2007) 567–570.
[10] R. Baharfar, M. Tajbakhsh, A. Hamedaninejad, et al. Chin. Chem. Lett. 19 (2008) 175.