Monatsh Chem (2011) 142:807–812
DOI 10.1007/s00706-011-0514-6

ORIGINAL PAPER

Stereoselective reaction between alkyl propiolates and phenols in the presence of sodium azide in *tert*-butyl alcohol

Farough Nasiri · Davood Malakutikhah

Received: 10 September 2009 / Accepted: 26 April 2011 / Published online: 31 May 2011

Abstract Stereoselective reaction of various substituted phenols with alkyl propiolates in the presence of a catalytic amount of sodium azide in *tert*-butyl alcohol at reflux temperature leads to alkyl (*Z*)-3-phenoxy-2-propenoates in good yields.

Keywords Activated alkynes · Alkyl propiolates · OH-acids · Phenols · Stereoselective addition

Introduction

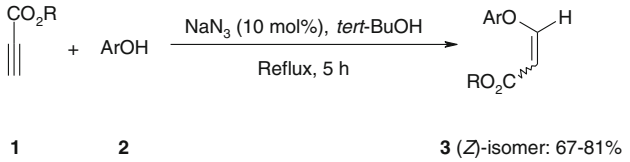
There are many studies on the reactions between OH-acids and acetylenic esters in the presence of various nucleophilic catalysts such as triphenylphosphine [1–5], trialkylphosphites [6], alkyl isocyanides [7–9], and tertiary amines [10, 11]. In most cases, the reaction was viewed as starting from the initial formation of a zwitterionic intermediate derived from the addition of a nucleophilic catalyst to an activated alkyne [1–11]. The azide anion usually reacts as a nucleophile in nucleophilic substitution reactions [12, 13] or reacts as a 1,3-dipole in 1,3-dipolar cycloaddition reactions [14–16]; however, to the best of our knowledge, there is not any report about the catalytic behavior of azide anions in the above reactions. Phenols react with alkyl propiolates to give a mixture of *E* and *Z* isomers, arising through a *cis* or *trans* mode of addition [17, 18]. In the above studies the *E* isomer is usually the major product. Recently, Liang and co-workers found [18] that phenols react smoothly with alkyl propiolates in the presence of a catalytic amount of 1,4-diazabicyclo[2.2.2]octane (DABCO) to produce O-vinylated products. On the other hand, Ramachandran et al. [19] found that alkyl propiolates couple with themselves in the presence of a catalytic amount of DABCO to provide a quantitative yield of (*E*)-hex-2-en-4-ynedioates. Accordingly, the reaction between phenols and alkyl propiolates in the presence of tertiary amines is limited to simple phenols [18]. As a part of our current studies on the development of new routes to stereoselective additions of phenols to acetylenic esters [20], we now report the stereoselective reaction between alkyl propiolates and various substituted phenols in the presence of a catalytic amount of sodium azide.

F. Nasiri (✉) · D. Malakutikhah
Department of Chemistry, Faculty of Sciences,
University of Kurdistan, P.O. Box 66315-416, Sanandaj, Iran
e-mail: fnasiri@uok.ac.ir; farough_na@yahoo.com

Results and discussion

The reaction of alkyl propiolates **1** and substituted phenols **2** in the presence of a catalytic amount of sodium azide in *tert*-butyl alcohol at reflux temperature leads to alkyl (*Z*)-3-phenoxy-2-propanoates **3** in good to high yields (Scheme 1 and Table 1).

The structures of the products were determined on the basis of their elemental analysis, mass spectrometry, ^{1}H NMR, ^{13}C NMR, and IR data. The ratio of *E*/*Z* isomers was determined by ^{1}H NMR spectroscopy. The ^{1}H NMR spectral data of the crude products exhibited two isomers and both of them displayed characteristic resonance patterns with appropriate chemical shift. The ^{1}H NMR spectra of *E* isomers displayed two doublets with $^{3}J_{HH} = 12.3$–12.5 Hz for the two olefinic protons, whereas the signals of the *Z* forms appeared with $^{3}J_{HH} = 6.7$–7.0 Hz; this was in agreement with the proposed *E* and *Z* isomers, respectively. For example, the ^{1}H NMR spectrum of **3a** showed one singlet at



Scheme 1

3.75 ppm for the methoxy group and two doublets with $^{3}J_{HH} = 7.0$ Hz at 5.17 and 6.85 ppm for the olefinic protons in the *Z* isomer and one singlet at 3.73 ppm for the methoxy group and two doublets with $^{3}J_{HH} = 12.3$ Hz at 5.56 and 7.81 ppm for the olefinic protons in the *E* isomer. These data were in agreement with the values reported in the literature [18]. Table 1 shows that this addition reaction tolerates a wide range of functional groups on the phenol including alkyls, alkoxyls, aldehydes, halides, and nitro groups.

Although the mechanism of the reaction between alkyl propiolates and phenols in the presence of sodium azide is unknown, a proposed mechanism for this reaction is outlined in Scheme 2 based on the previous reports [1–11]. Initially, the azide anion reacts with the electron-deficient acetylenic esters to generate the conjugate ionic systems **4**, which deprotonate the OH-acid to give the corresponding intermediates **5** and **6**. Subsequent Michael addition of **6** to **5** forms the intermediates **7**, which then eliminates azide anion to afford the desired product (Scheme 2).

Further comparative studies demonstrate that sodium azide in *tert*-butyl alcohol at reflux temperature was the optimal catalyst for the stereoselective *syn* addition of phenols to alkyl propiolates. Results of these studies are summarized in Table 2. DABCO, triphenylphosphine, and sodium azide in CH_2Cl_2, as Table 2 shows, were particularly effective in producing *E* isomers. The stereoselectivity/conversion of this reaction was influenced by the nature of the solvent. When the reaction of 2-methoxyphenol and methyl propiolate was carried out in THF/H_2O, the *syn* addition was dominant; however, the yield of the reaction was low (entry 21). When this reaction was carried out in acetonitrile, a polar aprotic solvent, the stereoselectivity was inversed (entry 23). These results show that the protic solvent can prompt *syn* addition of phenols to alkyl propiolates. In methanol, the reaction afforded a complex mixture of products as a result of the high nucleophilicity of methanol (entry 22). Thus *tert*-butyl alcohol, a protic solvent with weak nucleophilicity, could lead to stereoselective *syn* addition of phenols to alkyl propiolates (Table 2).

In conclusion, we have described a convenient route to alkyl (*Z*)-3-phenoxy-2-propenoates through nucleophilic *syn* addition of phenols to alkyl propiolates in *tert*-butyl alcohol. In this procedure the catalyst can be removed by filtration. The simplicity of this procedure makes it an interesting alternative to other approaches.

Experimental

Alkyl propiolates and phenols were obtained from Fluka (Buchs, Switzerland) and were used without further purification. Melting points were measured with an Electrothermal 9100 apparatus. Elemental analyses (C, H,

Table 1 Stereoselectivity of the addition of phenols to alkyl acetylenecarboxylate in the presence of sodium azide (10 mol%) in *tert*-BuOH at reflux temperature

Entry	Ar	R	Product	Yield of **3** (%)[a]	Isomer (%)[b]	
					E	*Z*
1	Phenyl	Me	**3a**	96	26	74
2	4-Chlorophenyl	Me	**3b**	76	30	70
3	2,4-Dichlorophenyl	Me	**3c**	95	22	78
4	2,4-Dichlorophenyl	Et	**3d**	96	23	77
5	4-Formylphenyl	Me	**3e**	96	30	70
6	2-Methoxyphenyl	Me	**3f**	97	28	72
7	4-Formyl-2-methoxyphenyl	Me	**3g**	60	19	81
8	1-Naphthyl	Me	**3h**	97	26	74
9	2-Naphthyl	Me	**3i**	80	24	76
10	2-Nitrophenyl	Me	**3j**	90	21	79
11	3-Nitrophenyl	Me	**3k**	97	33	67
12	2,6-Dimethylphenyl	Me	**3l**	80	29	71
13	2,6-Dimethylphenyl	Et	**3m**	96	33	67

[a] Isolated yields

[b] Determined by ^{1}H NMR spectroscopy

Scheme 2

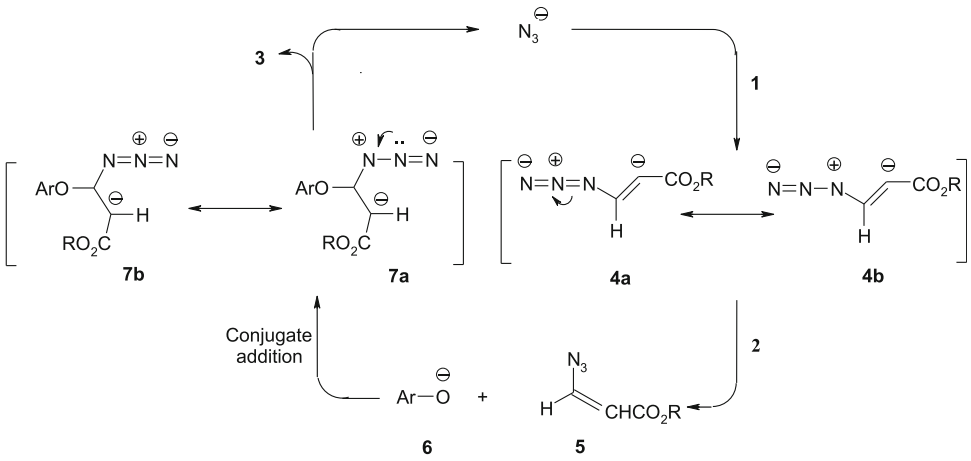


Table 2 Stereoselectivity of the addition of phenols to alkyl propiolates to produce alkyl 3-phenoxy-2-propanoates in the presence of different catalysts and reaction conditions

Entry	Ar	R	Product	Catalyst	Solvent	Yield of 3 (%)[a]	*E*/*Z* [Ref.]
1	Phenyl	Me	**3a**	DABCO	CH_2Cl_2	95	85:15 [18]
2	1-Naphthyl	Me	**3h**	DABCO	CH_2Cl_2	97	95:5 [18]
3	2-Naphthyl	Me	**3i**	DABCO	CH_2Cl_2	90	*E* [18]
4	2-Nitrophenyl	Me	–[b]	DABCO	CH_2Cl_2	–	–[c]
5	Phenyl	*t*-Bu	**3n**	Ph_3P	CH_2Cl_2	90	*E* [17]
6	1-Naphthyl	*t*-Bu	**3o**	Ph_3P	CH_2Cl_2	45	*E* [17]
7	2-Naphthyl	*t*-Bu	**3p**	Ph_3P	CH_2Cl_2	55	*E* [17]
8	4-Formyl-2-methoxyphenyl	*t*-Bu	**3q**	Ph_3P	CH_2Cl_2	95	*E* [17]
9	8-Quinolyl	Me	**3r**	Ph_3P	CH_2Cl_2	85	*E* [18]
10	Phenyl	Me	**3a**	Et_3N	CH_2Cl_2	73	99:1 [18]
11	Phenyl	Me	–[b]	Me_3N	CH_2Cl_2	–	–[c]
12	2-Nitrophenyl	Me	–[b]	Me_3N	CH_2Cl_2	–	–[c]
13	4-Formylphenyl	Me	**3e**	Me_3N	CH_2Cl_2	75	*E*[c]
14	2-Methoxyphenyl	Me	**3f**	NaN_3	CH_2Cl_2	66	74:26[c]
15	2,6-Dimethylphenyl	Me	**3l**	NaN_3	CH_2Cl_2	50	82:18[c]
16	1-Naphthyl	Me	**3h**	NaN_3	CH_2Cl_2	45	84:16[c]
17	2-Naphthyl	Me	**3i**	NaN_3	CH_2Cl_2	36	86:14[c]
18	3-Nitrophenyl	Me	–	NaN_3	CH_2Cl_2	No reaction	–[c]
19	4-Nitrophenyl	Me	–	NaN_3	CH_2Cl_2	No reaction	–[c]
20	4-Formylphenyl	Me	–	NaN_3	CH_2Cl_2	No reaction	–[c]
21	2-Methoxyphenyl	Me	**3f**	NaN_3	H_2O/THF	55	12:88[c]
22	2-Methoxyphenyl	Me	**3f**	NaN_3	CH_3OH	–[d]	–[c]
23	2-Methoxyphenyl	Me	**3f**	NaN_3	CH_3CN	55	85:15[c]

All reactions were carried out at room temperature

[a] Isolated yields

[b] Quantitative self-coupling of alkyl propiolate occurs

[c] Considered in this research

[d] The reaction afforded a complex mixture

and N) were performed using a Heraeus CHN-O-Rapid analyzer. The results agreed favorably with the calculated values. IR spectra were measured with a Shimadzu IR-460 spectrometer. NMR spectra were recorded with a Bruker DRX-250 AVANCE instrument (250.1 MHz for ^1H and 62.9 MHz for ^{13}C) with $CDCl_3$ as solvent. Chemical shifts (δ) are given in ppm relative to internal TMS, and coupling constants (J) are reported in hertz (Hz). Mass spectra were

recorded with a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV.

Typical procedure for preparation of methyl 3-phenoxy-2-propenoate (**3a**)

To a stirred solution of 0.02 g of NaN_3 (10 mol%) and 0.29 g of phenol (3 mmol) in 10 cm^3 of *tert*-butyl alcohol was added dropwise a mixture of 0.26 g of methyl propiolate (3 mmol) in 2 cm^3 of *tert*-butyl alcohol at room temperature over 10 min. The reaction mixture was then refluxed for 5 h. Sodium azide was separated by filtration, the solvent was removed under reduced pressure, and the residue was separated by silica gel column chromatography (Merck 230–400 mesh) using *n*-hexane–EtOAc as eluent to give **3a**. Compounds **3a**, **3 h**, and **3i** are known compounds [18].

Methyl 3-(4-chlorophenoxy)-2-propenoate
(**3b**, $C_{10}H_9ClO_3$)
Brown oil; IR (KBr): $\bar{\nu}$ = 1,713 (C=O), 1,646 and 1,585 (C=C) cm^{-1}.

Major isomer (*Z*)-**3b**: 70%; ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 3.75 (s, OCH_3), 5.20 (d, $^3J_{HH}$ = 7.0 Hz, O–C=C*H*), 6.79 (d, $^3J_{HH}$ = 7.0 Hz, CH), 6.98 and 7.32 (2d, $^3J_{HH}$ = 9.0 Hz, 4CH) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 51.2 (OCH_3), 100.2 (O–C=*C*H), 119.0 and 129.8 (4CH), 130.3 and 153.5 (2C), 157.2 (O–CH), 166.3 (C=O) ppm.

Minor isomer (*E*)-**3b**: 30%; ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 3.73 (s, OCH_3), 5.56 (d, $^3J_{HH}$ = 12.3 Hz, O–C=*C*H), 6.98 and 7.32 (2d, $^3J_{HH}$ = 9.0 Hz, 4CH), 7.74 (d, $^3J_{HH}$ = 12.3 Hz, O–CH) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 51.4 (OCH_3), 102.4 (O–C=*C*H), 119.3 and 130.0 (4CH), 130.2 and 154.3 (2C-Ar), 158.5 (O–*C*=CH), 167.3 (C=O) ppm.

Methyl 3-(2,4-dichlorophenoxy)-2-propenoate
(**3c**, $C_{10}H_8Cl_2O_3$)
Brown oil; IR (KBr): $\bar{\nu}$ = 1,713 (C=O), 1,647 and 1,575 (C=C) cm^{-1}.

Major isomer (*Z*)-**3c**: 78%; ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 3.74 (s, OCH_3), 5.22 (d, $^3J_{HH}$ = 7.0 Hz, O–C=C*H*), 6.68 (d, $^3J_{HH}$ = 7.0 Hz, O–CH), 7.03–7.44 (m, 3CH) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 51.3 (OCH_3), 101.0 (O–C=*C*H), 120.0 (CH), 125.9 (C), 128.1 and 130.6 (2CH), 131.1 (C), 151.6 (O–C_{ipso}), 153.9 (O–CH), 166.4 (C=O) ppm.

Minor isomer (*E*)-**3c**: 22%; ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 3.71 (s, OCH_3), 5.45 (d, $^3J_{HH}$ = 12.3 Hz, O–C=C*H*), 7.03–7.44 (m, 3CH), 7.65 (d, $^3J_{HH}$ = 12.3 Hz, O–CH) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 51.5 (OCH_3), 102.5 (O–C=*C*H), 121.1 (CH), 126.2 (C), 128.3 and 130.7 (2CH), 131.2 (C), 149.9 (O–C_{ipso}), 158.6 (O–CH), 167.0 (C=O) ppm.

Ethyl 3-(2,4-dichlorophenoxy)-2-propenoate
(**3d**, $C_{11}H_{10}Cl_2O_3$)
Brown oil; IR (KBr): $\bar{\nu}$ = 1,710 (C=O), 1,645 (C=C) cm^{-1}.

Major isomer (*Z*)-**3d**: 77%; ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 1.29 (t, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3), 4.20 (q, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3), 5.21 (d, $^3J_{HH}$ = 6.8 Hz, O–C=C*H*), 6.68 (d, $^3J_{HH}$ = 6.8 Hz, O–CH), 6.94–7.44 (m, 3CH) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.3 (OCH_2CH_3), 60.2 (OCH_2CH_3), 101.5 (O–C=*C*H), 119.7 (CH), 125.8 (C), 128.1 (CH), 130.4 (C), 130.5 (CH), 151.6 (O–C_{ipso}), 153.1 (O–*C*=CH), 164.3 (C=O) ppm.

Minor isomer (*E*)-**3d**: 23%; ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 1.23 (t, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3), 4.16 (q, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3), 5.43 (d, $^3J_{HH}$ = 12.3 Hz, O–C=C*H*), 6.93–7.44 (m, 3CH), 7.65 (d, $^3J_{HH}$ = 12.3 Hz, O–CH) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.3 (OCH_2CH_3), 60.3 (OCH_2CH_3), 102.8 (O–C=*C*H), 121.1 (CH), 126.2 (C), 128.3 and 130.6 (2CH), 131.1 (C), 149.8 (O–C_{ipso}), 158.6 (O–CH), 166.7 (C=O) ppm.

Methyl 3-(4-formylphenoxy)-2-propenoate
(**3e**, $C_{11}H_{10}O_4$)
Brown oil; IR (KBr): $\bar{\nu}$ = 1,714 and 1,713 (C=O), 1,649 (C=C) cm^{-1}.

Major isomer (*Z*)-**3e**: 70%; ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 3.72 (s, OCH_3), 5.28 (d, $^3J_{HH}$ = 7.3 Hz, O–C=C*H*), 6.92 (d, $^3J_{HH}$ = 7.3 Hz, O–CH), 7.21 and 7.88 (2d, $^3J_{HH}$ = 8.5 Hz, 4CH), 9.92 (s, CHO) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 51.3 (OCH_3), 101.9 (O–C=*C*H), 117.6 and 131.9 (4CH), 132.8 (C), 151.7 (O–CH), 160.9 (O–C_{ipso}), 164.6 (C=O), 190.6 (CHO) ppm.

Minor isomer (*E*)-**3e**: 30%; ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 3.72 (s, OCH_3), 5.70 (d, $^3J_{HH}$ = 12.3 Hz, O–C=C*H*), 7.18 (d, $^3J_{HH}$ = 8.5 Hz, 2CH), 7.80 (d, $^3J_{HH}$ = 12.3 Hz, O–CH), 7.89 (d, $^3J_{HH}$ = 8.5 Hz, 2CH), 9.92 (s, CHO) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 51.5 (OCH_3), 104.1 (O–C=*C*H), 117.7 and 132.0 (4CH), 132.9 (C), 156.6 (O–CH), 160.1 (O–C_{ipso}), 167.1 (C=O, ester), 190.6 (CHO) ppm.

Methyl 3-(2-methoxyphenoxy)-2-propenoate
(**3f**, $C_{11}H_{12}O_4$)
Orange oil; IR (KBr): $\bar{\nu}$ = 1,712 (C=O), 1,644 (C=C) cm^{-1}.

Major isomer (*Z*)-**3f**: 72%; ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 3.73 and 3.84 (2 s, $2OCH_3$), 5.08 (d, $^3J_{HH}$ = 7.5 Hz, O–C=C*H*), 6.73 (d, $^3J_{HH}$ = 7.5 Hz, O–CH), 6.78–7.26 (m, 4CH) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 51.1 and 56.1 ($2OCH_3$), 98.3 (O–C=*C*H), 113.1, 119.8, 120.9, and 125.9 (4CH), 146.3 and 150.3 (2C), 156.6 (O–CH), 165.3 (C=O) ppm.

Minor isomer (*E*)-**3f**: 28%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.69$ and 3.85 (2 s, $2OCH_3$), 5.41 (d, $^3J_{HH} = 12.3$ Hz, O–C=C*H*), 6.78–7.26 (m, 4CH), 7.71 (d, $^3J_{HH} = 12.3$, Hz, O–CH) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 51.2$ and 55.9 ($2OCH_3$), 100.5 (O–C=*C*H), 112.8, 120.4, 121.0, and 126.3 (4CH), 144.2 and 150.4 (2C), 161.0 (O–CH), 167.7 (C=O) ppm.

Methyl 3-(4-formyl-2-methoxyphenoxy)-2-propenoate (**3g**, $C_{12}H_{12}O_5$)

Yellow oil; IR (KBr): $\bar{\nu} = 1{,}713$ and 1,686 (C=O), 1,649 (C=C) cm^{-1}.

Major isomer (*Z*)-**3g**: 81%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.73$ and 3.91 (2 s, $2OCH_3$), 5.21 (d, $^3J_{HH} = 6.8$ Hz, O–C=C*H*), 6.79 (d, $^3J_{HH} = 6.8$ Hz, O–CH), 7.18 and 7.42 (2d, $^3J_{HH} = 7.5$ Hz, 2CH), 7.45 (s, CH), 9.82 (CHO) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 51.3$ and 56.3 ($2OCH_3$), 100.5 (O–C=*C*H), 111.3, 118.9, and 125.1 (3CH–Ar), 133.9 (C), 153.9 and 154.9 (2 O–C_{ipso}), 158.6 (O–CH), 164.8 (C=O, ester), 190.7 (CHO) ppm.

Minor isomer (*E*)-**3g**: 19%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.70$ and 3.91 (2 s, $2OCH_3$), 5.62 (d, $^3J_{HH} = 12.3$ Hz, O–C=C*H*), 7.18 and 7.42 (2d, $^3J_{HH} = 7.5$ Hz, 2CH), 7.45 (s, CH), 7.72 (d, $^3J_{HH} = 12.3$, Hz, O–CH), 9.91 (CHO) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 51.2$ and 56.2 ($2OCH_3$), 102.7 (O–C=*C*H), 111.1, 119.3, and 125.2 (3CH), 134.2 (C), 149.4 and 150.9 (2O–C_{ipso}), 158.7 (O–CH), 167.2 (C=O, ester), 190.7 (CHO) ppm.

Methyl 3-(2-nitrophenoxy)-2-propenoate (**3j**, $C_{10}H_9NO_5$)

Brown oil; IR (KBr): $\bar{\nu} = 1{,}718$ (C=O), 1,650 (C=C) cm^{-1}.

Major isomer (*Z*)-**3j**: 79%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.75$ (s, OCH_3), 5.31 (d, $^3J_{HH} = 6.8$ Hz, O–C=C*H*), 6.77 (d, $^3J_{HH} = 6.8$ Hz, O–CH), 7.22–7.98 (4CH) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 51.4$ (OCH_3), 102.4 (O–C=*C*H), 120.2, 125.1, 125.8, and 134.5 (4CH), 141.0 (C–Ar), 152.2 (O–CH), 157.9 (O–C_{ipso}), 164.4 (C=O) ppm.

Minor isomer (*E*)-**3j**: 21%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.73$ (3H, s, OCH_3), 5.58 (d, $^3J_{HH} = 12.3$ Hz, O–C=C*H*), 7.22–7.98 (4CH), 7.72 (d, $^3J_{HH} = 12.3$ Hz, O–CH) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 51.5$ (OCH_3), 103.9 (O–C=*C*H), 121.0, 125.6, 125.9, and 134.6 (4CH), 141.1 (C–Ar), 149.7 (O–CH), 155.1 (O–C_{ipso}), 164.4 (C=O) ppm.

Methyl 3-(3-nitrophenoxy)-2-propenoate (**3k**, $C_{10}H_9NO_5$)

Pale yellow solid; m.p.: 80–81 °C; IR (KBr): $\bar{\nu} = 1{,}714$ (C=O), 1,650 (C=C) cm^{-1}.

Major isomer (*Z*)-**3k**: 67%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.76$ (s, OCH_3), 5.33 (d, $^3J_{HH} = 6.8$ Hz, O–C=C*H*), 6.89 (d, $^3J_{HH} = 6.8$ Hz, O–CH), 7.26–8.07 (4CH) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 51.4$ (OCH_3), 102.2 (O–C=*C*H), 112.4, 119.4, 123.9, and 130.7 (4CH), 149.2 and 151.9 (2C), 156.1 (O–CH), 166.9 (C=O) ppm.

Minor isomer (*E*)-**3k**: 33%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 3.75$ (s, OCH_3), 5.69 (d, $^3J_{HH} = 12.3$ Hz, O–C=C*H*), 7.26-8.07 (4CH), 7.79 (d, $^3J_{HH} = 12.3$ Hz, O–CH) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 51.6$ (OCH_3), 104.1 (O–C=*C*H), 112.9, 119.7, 124.0, and 130.8 (4CH),149.2 and 151.9 (2C), 157.0 (O–CH), 166.9 (C=O) ppm.

Methyl 3-(2,6-dimethylphenoxy)-2-propenoate (**3l**, $C_{12}H_{14}O_3$)

Brown oil; IR (KBr): $\bar{\nu} = 1{,}712$ (C=O), 1,644 (C=C) cm^{-1}.

Major isomer (*Z*)-**3l**: 71%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 2.25$ (s, $2CH_3$), 5.05 (d, $^3J_{HH} = 7.0$ Hz, O–C=C*H*), 6.48 (d, $^3J_{HH} = 7.0$ Hz, O–CH), 7.03–7.08 (m, 3CH) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 16.1$ ($2CH_3$), 51.1 (OCH_3), 97.5 (O–C=*C*H), 125.7 and 128.9 (3CH), 130.0 (2C), 157.5 (O–CH), 160.7 (O–C_{ipso}), 165.3 (C=O) ppm.

Minor isomer (*E*)-**3l**: 29%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 2.17$ (s, $2CH_3$), 5.01 (d, $^3J_{HH} = 12.5$ Hz, O–C=C*H*), 7.03–7.08 (3CH), 7.75 (d, $^3J_{HH} = 12.5$ Hz, O–CH) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 16.0$ ($2CH_3$), 51.2 (OCH_3), 98.4 (O–C=*C*H), 125.9 and 129.1 (3CH), 129.8 (2C), 154.6 (O–CH), 161.5 (O–C_{ipso}), 165.4 (C=O) ppm.

Ethyl 3-(2,6-dimethylphenoxy)-2-propenoate (**3m**, $C_{13}H_{16}O_3$)

Brown oil; IR (KBr): $\bar{\nu} = 1{,}712$ (C=O), 1,644 (C=C) cm^{-1}.

Major isomer (*Z*)-**3m**: 67%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 1.34$ (t, $^3J_{HH} = 7.0$ Hz, OCH_2CH_3), 2.26 (6H, s, $2CH_3$), 4.22 (q, $^3J_{HH} = 7.0$ Hz, OCH_2CH_3), 5.03 (d, $^3J_{HH} = 6.8$ Hz, O–C=C*H*), 6.47 (d, $^3J_{HH} = 6.8$ Hz, O–CH), 7.03–7.08 (3CH) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.4$ (OCH_2CH_3), 16.1 ($2CH_3$), 59.7 (OCH_2CH_3), 97.9 (O–C=*C*H), 125.6 and 128.9 (3CH), 130.0 (2C–Ar), 157.3 (O–CH), 160.6 (O–C_{ipso}), 164.9 (C=O) ppm.

Minor isomer (*E*)-**3m**: 33%; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 1.25$ (t, $^3J_{HH} = 7.0$ Hz, OCH_2CH_3), 2.17 (s, $2CH_3$), 4.14 (q, $^3J_{HH} = 7.0$ Hz, OCH_2CH_3), 5.00 (d, $^3J_{HH} = 12.5$ Hz, O–C=C*H*), 7.03–7.08 (3CH), 7.75 (1H, d, $^3J_{HH} = 12.5$ Hz, O–CH) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.3$ (OCH_2CH_3), 16.0 ($2CH_3$), 60.0 (OCH_2CH_3), 98.7 (O–C=*C*H), 125.9 and 129.1 (3CH), 129.8 (2C), 154.7 (O–CH), 161.6 (O–C_{ipso}), 167.5 (C=O) ppm.

References

1. Yavari I, Adib M, Hojabri L (2002) Tetrahedron 58:6895
2. Yavari I, Nourmohammadian F, Bijanzadeh HR (2002) Phosphorus Sulfur Silicon 177:1147
3. Evans LA, Griffiths KE, Guthmann H (2002) Tetrahedron Lett 43:299
4. Ramazani A, Kazemzadeh AR, Ahmadi E (2005) Phosphorus Sulfur Silicon 180:2373
5. Ramazani A, Amini I, Massoudi A (2006) Phosphorus Sulfur Silicon 181:2373
6. Yavari I, Anary-Abbasinejad M, Hossaini Z (2003) Org Biomol Chem 1:560
7. Nair V, Deepthi A (2006) Tetrahedron Lett 47:2037
8. Yavari I, Djahaniani H, Nasiri F (2003) Tetrahedron 59:9409
9. Yavari I, Alizadeh A, Anary-Abbasinejad M, Hossaini Z (2003) Tetrahedron 59:1289
10. Fan MJ, Li GQ, Liang YM (2006) Tetrahedron 62:6782
11. Stoermer MJ, Fairlie DP (1995) Aust J Chem 48:677
12. Matteson DS, Maliakal D, Fabry-Asztalos L (2008) J Organomet Chem 693:2258
13. Tiecco M, Testaferri L, Santi C, Tomassini C, Santoro S, Marini F, Bagnoli L, Temperini A (2007) Tetrahedron 63:12373
14. Lakshmi Kantam M, Swarna Jaya V, Sreedhar B, Mohan Rao M, Choudary BM (2006) J Mol Cat A Chem 256:273
15. Yadav JS, Subba Reddy BV, Madhusudhan Reddy G, Narasimha Chary D (2007) Tetrahedron Lett 48:8773
16. Chafin A, Irvin DJ, Mason MH, Mason SL (2008) Tetrahedron Lett 49:3823
17. Yavari I, Souri S, Sirouspour M, Djahaniani H, Nasiri F (2005) Synthesis 1761
18. Fan MJ, Li GQ, Li LH, Yang SD, Liang YM (2006) Synthesis 2286
19. Ramachandran PV, Rudd MT, Reddy MVR (2005) Tetrahedron Lett 46:2547
20. Nasiri F, Atashkar B (2008) Monatsh Chem 139:1223