Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Catalysis A: Chemical 264 (2007) 313–317
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Ph_3P catalyzed efficient synthesis of ethyl 2-(acetylanilino)-acrylates and ethyl (*E*)-3-(acetylanilino)-2-propenoates by nucleophilic addition to ethyl propiolate

Issa Yavari [a,*], Norollah Hazeri [b], Malek T. Maghsoodlou [b], Sanaz Souri [a]

[a] *Department of Chemistry, Tarbiat Modarres University, PO Box 14115-175, Tehran, Iran*
[b] *Department of Chemistry, University of Sistan and Baluchestan, Zahedan, Iran*

Received 16 July 2006; received in revised form 23 September 2006; accepted 25 September 2006
Available online 29 September 2006

Abstract

The addition of acetanilides to ethyl propiolate proceeds under neutral conditions in the presence of triphenylphosphine to give the corresponding α-substituted alkyl acrylates together with variable amounts of the β-substituted isomer with (*E*) geometry. Addition of arylsulfonylanilides to alkyl propiolates under similar conditions, produced only the alkyl (*E*)-3-arylsulfonylanilino-2-propenoates.

Keywords: NH-acids; Arylsulfonylanilides; Acetanilides; Alkyl acrylates; Alkyl propiolates; Triphenylphosphine

1. Introduction

Organophosphorus compounds have been used in organic synthesis as useful reagents as well as ligands of a number of transition metal catalysts [1–3]. However, there are a few reactions in which organophosphorus(III) species work as catalysts [4–7]. The phosphine induced isomerization of alkynoates and addition to the α-position of these substrates indicated the possibility of a new reactivity pattern for alkynoates-nucleophilic addition at the α-position as a new source of α-substituted alkyl acrylates.

An important point is the ability of the nucleophile to undergo Michael addition in preference to the α-attack since phosphines could also serve as general base catalysts for conjugate additions [1–3]. Alkyl propiolates should be particularly prone to undergo such Michael additions.

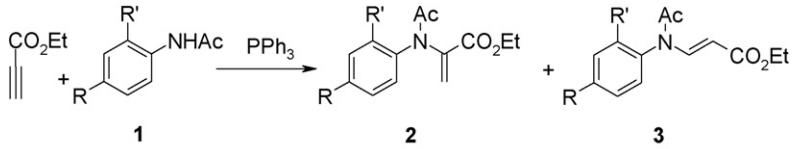
2. Results and discussion

The nucleophilic α-addition of acetanilides to ethyl propiolate was carried out under neutral conditions. Thus, ethyl propiolate undergoes a smooth reaction with the acetanilides in the presence of triphenylphosphine (Ph_3P) to produce α-substituted alkyl acrylates in good yields (Scheme 1).

The reaction of acetanilides with ethyl propiolate in the presence of Ph_3P proceeded spontaneously at room temperature in CH_2Cl_2 and was finished within 24 h. ^1H and ^{13}C NMR spectra of the reaction mixtures clearly indicated the presence of two types of products, namely the 1,1- and 1,2-enaminoesters. These products were separated by column chromatography and identified as **2a** and **3a** based on their elemental analyses and their IR, ^1H, and ^{13}C NMR spectral data. The mass spectra of these compounds displayed molecular ion peaks at appropriate *m/z* values. The ^1H NMR spectrum of **2a** exhibited a single sharp line for the methyl group at $\delta = 2.07$ ppm, together with characteristic A_2X_3 systems for the ethoxy groups at $\delta = 1.32$ and 4.32 ppm. Two singlets at $\delta = 6.17$ and 5.4 ppm are readily assigned to the C=CH_2 group. The ^{13}C NMR spectrum of **2a** showed 11 distinct resonances in agreement with the ethyl 2-(acetylanilino)-acrylate structure. The ^1H NMR of **3a** exhibited an AX system for the *trans*-olefinic protons at $\delta = 8.75$ and 4.75 ppm with $^3J = 18$ Hz. The ^1H and ^{13}C NMR spectra of **2b–2e** are similar to those of **2a**, and of **3b–3e** are similar to those of **3a** except for the substituted phenyl ring, which exhibited characteristic resonances with appropriate chemical shifts.

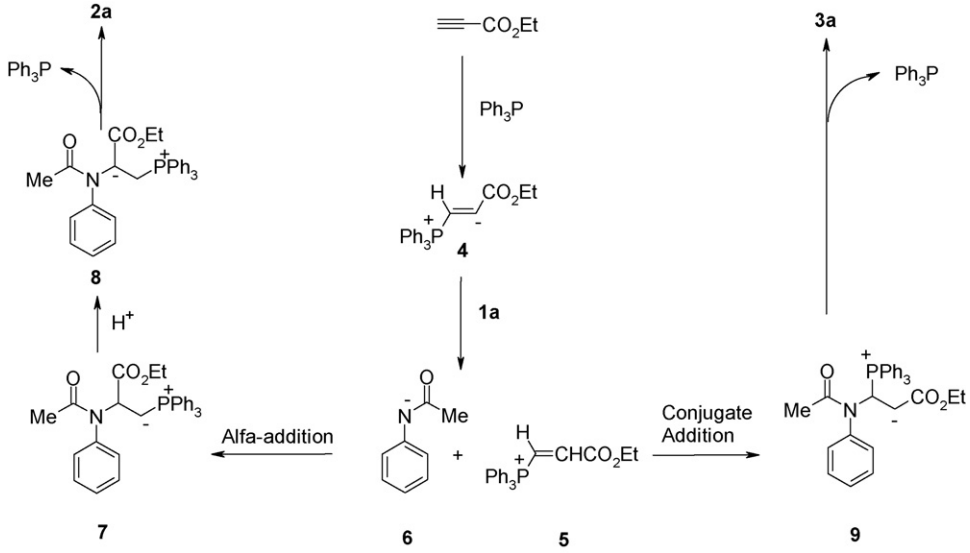
* Corresponding author. Tel.: +98 21 88011001; fax: +98 21 88006544.
E-mail address: yavarisa@modares.ac.ir (I. Yavari).

1381-1169/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2006.09.042



1, 2, 3	R	R'	Yield (%) of 2	Yield (%) of 3
a	H	H	70	22
b	H	Me	65	28
c	Me	H	64	30
d	OMe	H	72	25
e	Br	H	65	32

Scheme 1.



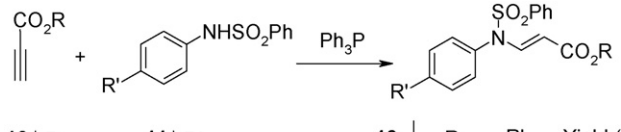
Scheme 2.

On the basis of the chemistry of trivalent phosphorus nucleophiles [8], it is reasonable to assume that compounds **2** and **3** result from initial addition of Ph_3P to ethyl propiolate and subsequent protonation of the 1:1 adduct by the N–H acid. Then, the positively charged ion is attacked by the nitrogen atom of the conjugate base of the NH-acid at the α-position. Compound **2a** is formed by elimination of Ph_3P. Attack of the conjugate base to the β-position leads to **3a**.

Under similar conditions described for the reaction of acetanilides and ethyl propiolate in the presence of Ph_3P, arylsulfanilides undergo a smooth reaction with alky propiolates to produce alkyl (*E*)-3-arylsulfonylanilino-2-propenoates (**12**) in excellent yields (Scheme 3). Compound **12** is formed by a mechanism similar to that given for ethyl (*E*)-3-(acetylanilino)-2-propenoates **3** in Scheme 2.

Why the acetanilides give a mixture of α- and β-alkenyl products, whereas the arylsulfonylanilides lead exclusively to the latter products? This marked switch in regioselectivity can be explained on the basis of the reactivity of the conjugate base of the acetanilides. Acetanilides [9] are weaker N–H acids compared to arylsulfonanilides [10], thus, the conjugate base of the former is less stable (more reactive) and leads to the kinetically preferred α-alkenyls as major product (Scheme 3).

In conclusion, we have described a convenient route to ethyl 2-(acetylanilino)-acrylates and ethyl (*E*)-3-(acetylanilino)-2-propenoates through nucleophilic addition to ethyl propiolate. Addition of sulfanilides to alkyl propiolates under similar conditions produced only alkyl (*E*)-3-arylsulfonylanilino-2-propenoates. These functionalized acrylates and propenoates may be considered as potentially useful synthetic intermediates because they possess atoms with different oxidation states. The present method has the advantages that not only are the reaction performed under neutral conditions, but also the substances



10	R
a	Me
b	Et

11	R'
a	H
b	4-Me
c	4-OMe

12	R	R'	Yield (%)
a	Me	H	96
b	Et	H	98
c	Me	4-Me	93
d	Et	4-Me	95
e	Me	4-OMe	91
f	Et	4-OMe	97

Scheme 3.

can be mixed without any modification. The simplicity of the present procedure makes it an interesting alternative to other approaches.

3. Experimental

3.1. General

Elemental analyses for C, H, and N were performed using a *Heraeus CHN-O-Rapid* analyzer. The experimental data were in good agreement with the calculated values. M.p.: *Electrothermal-9100* apparatus; uncorrected. IR Spectra: *Shimadzu IR-460* spectrometer; ^{1}H and ^{13}C NMR spectra: *JEOL* instrument; in $CDCl_3$ at 90 and 22.6 MHz, respectively; δ in ppm, J in Hz. EI-MS (70 eV): *Finnigan-MAT-8430* mass spectrometer, in *m/z*. Alkyl propiolates, acetanilides, Ph_3P and arylsulfanilides were obtained from Fluka and were used without further purification.

3.2. Typical procedure for preparation of ethyl 2-(acetylanilino)-acrylate (**2a**) and ethyl (E)-3-(acetylanilino)-2-propenoate (**3a**)

To a stirred solution of 0.05 g of Ph_3P (0.2 mmol) and 0.27 g of acetanilide (2 mmol) in 10 mL of CH_2Cl_2 was added, drop wise, a mixture of 0.20 g of ethyl propiolate in 4 mL of CH_2Cl_2 at −5 °C over 10 min. 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–EtOAc as eluent to give **2a** and **3a**.

3.2.1. Ethyl 2-(acetylanilino)-acrylate (**2a**)

Yellow oil, yield 0.16 g (35%). IR (KBr) (ν_{max}/cm^{-1}): 1774 and 1723 (C=O), 1629 and 1607 (C=C). ^{1}H NMR: 1.32 (t, ^3J = 7.2, CH_3), 2.07 (s, Me), 4.32 (q, ^3J = 7.2, OCH_2), 5.4 (d, ^2J = 1.2, CH), 6.17 (d, ^2J = 1.2, CH), 7.20–7.52 (m, C_6H_5). ^{13}C NMR: 14.1 (CH_3), 22.5 (CH_3), 61.5 (OCH_2), 120.2 (=CH_2), 127.7 (CH), 128.0 (CH), 129.6 (CH), 141.8 (C), 142.6 (C), 164.0 (C=O), 170.4 (C=O). EI-MS: 233 (M^+, 5), 191 (80), 117 (100). Anal. Calcd for $C_{13}H_{15}NO_3$ (233.2): C, 66.94; H, 6.48; N, 6.00; Found: C, 66.82; H, 6.45; N, 6.10%.

3.2.2. Ethyl 2-(acetyl-2-methylanilino)-acrylate (**2b**)

Yellow oil, yield 0.19 g (40%). IR (KBr) (ν_{max}/cm^{-1}): 1720 (C=O), 1610, 1705 (C=O), 1240, 1151 (C–O), 1099. ^{1}H NMR: 1.35 (t, ^3J = 7.0, CH_3), 1.87 (s, CH_3), 2.32 (s, Me), 4.31 (q, ^3J = 7.0, CH_2), 4.89 (s, CH), 5.66 (s, CH), 7.20–7.30 (m, 4CH). ^{13}C NMR: 14.1 (CH_3), 22.4 (CH_3), 29.7 (CH_3), 61.5 (CH_2), 114.3 (CH), 127.4 (CH), 128.8 (CH), 129.0 (CH), 132.1 (CH), 135.9 (CH), 140.4 (CH), 141.2 (CH), 164.3 (C=O), 170.4 (C=O). EI-MS: 247 (M^+, 11), 233 (54), 116 (45), 92 (100), 77 (52). Anal. Calcd for $C_{14}H_{17}NO_3$ (247.3): C, 68.00; H, 6.93; N, 5.66; Found: C, 68.12; H, 6.98; N, 5.68%.

3.2.3. Ethyl 2-(acetyl-4-methylanilino)-acrylate (**2c**)

Yellow oil, yield 0.25 g (52%). IR (KBr) (ν_{max}/cm^{-1}): 1723 and 1671 (C=O). ^{1}H NMR: 1.85 (t, ^3J = 7.2, CH_3), 1.97 (s, Me), 2.38 (s, Me), 4.30 (q, ^3J = 7.2, OCH_2), 5.30 (d, ^2J = 1.2, CH), 6.05 (d, ^2J = 1.2, CH), 7.20–7.52 (m, C_6H_4). ^{13}C NMR: 14.1 (CH_3), 21.0 (CH_3), 22.4 (CH_3), 61.5 (OCH_2), 119.5 (=CH_2), 127.5 (CH), 130.2 (CH), 138.0 (C), 140.1 (C), 141.8 (C), 164.1 (C=O), 170.7 (C=O). EI-MS: 247 (M^+, 6), 233 (41), 116 (34), 92 (100), 77 (52). Anal. Calcd for $C_{14}H_{17}NO_3$ (247.3): C, 68.00; H, 6.93; N, 5.66; Found: C, 67.82; H, 6.89; N, 5.78%.

3.2.4. Ethyl 2-(acetyl-4-methoxyanilino)-acrylate (**2d**)

Yellow oil, yield 0.42 g (80%). IR (KBr) (ν_{max}/cm^{-1}): 1710 and 1666 (C=O). ^{1}H NMR: 1.39 (t, $^3J_{HH}$ = 7.2, CH_3), 1.96 (s, Me), 3.84 (s, OMe), 4.30 (q, ^3J = 7.2, OCH_2), 5.31 (d, ^2J = 1.0, CH), 5.97 (d, ^2J = 1.0, CH), 6.41 (d, ^3J = 8.3, 2CH), 7.53 (d, ^3J = 8.3, 2CH). ^{13}C NMR: 14.2 (CH_3), 22.5 (CH_3), 55.5 (OCH_3), 61.6 (OCH_2), 119.2 (=CH_2), 114.8 (CH), 130.2 (CH), 139.1 (C), 142.0 (C), 142.4 (C), 159.2 (C=O), 170.9 (C=O). EI-MS: 263 (M^+, 10), 233 (34), 116 (54), 92 (100), 77 (41). Anal. Calcd for $C_{14}H_{17}NO_4$ (263.3): C, 63.87; H, 6.51; N, 5.32; Found: C, 63.79; H, 6.53; N, 5.28%.

3.2.5. Ethyl 2-(acetyl-4-bromoanilino)-acrylate (**2e**)

Yellow oil, yield 0.21 g (35%). IR (KBr) (ν_{max}/cm^{-1}): 1717 (C=O), 1673 (C=O), 1153 (C–O). ^{1}H NMR: 1.32 (t, ^3J = 6.8, CH_3), 1.97 (s, CH_3), 4.27 (q, ^3J = 6.8, CH_2), 5.35 (s, CH), 6.04 (s, CH), 7.22 (d, ^3J = 7.8, 2CH), 7.5 (d, ^3J = 7.8, 2CH). ^{13}C NMR: 14.1 (CH_3), 29.6 (CH_3), 61.7 (OCH_2), 120.5 (=CH_2), 129.5 (C), 130.9 (2CH), 133.0 (2CH), 137.4 (C), 141.7 (C), 163.8 (C=O), 170.2 (C=O). EI-MS: 312 (M^+, 12), 310 (13), 252 (10), 250 (18), 231 (52), 200 (100), 156 (51), 60 (18), 45 (32). Anal. Calcd for $C_{13}H_{14}BrNO_3$ (312.2): C, 50.02; H, 4.52; N, 4.49; Found: C, 50.09; H, 4.55; N, 4.52%.

3.2.6. Ethyl (E)-3-(acetylanilino)-2-propenoate (**3a**)

Yellow oil, yield 0.3 g (65%). IR (KBr) (ν_{max}/cm^{-1}): 1715 and 1626 (C=O), 1593 and 1491 (C=C). ^{1}H NMR: 1.28 (t, ^3J = 7.2, CH_3), 2.01 (s, Me), 4.17 (q, ^3J = 7.2, CH_3), 4.75 (d, ^3J = 17.2, CH), 7.12–7.82 (m, C_6H_5), 8.75 (d, ^3J = 17.2, CH). ^{13}C NMR: 14.2 (CH_3), 23.1 (CH_3), 59.9 (OCH_2), 102.3 (CH), 128.1 (2CH), 129.3 (CH), 130.3 (2CH), 138.3 (CH), 141.8 (C), 167.1 (C=O), 169.3 (C=O). EI-MS: 233 (M^+, 9), 205 (60), 159 (100). Anal. Calcd for $C_{13}H_{15}NO_3$ (233.2): C, 66.94; H, 6.48; N, 6.00; Found: C, 66.88; H, 6.45; N, 6.06%.

3.2.7. Ethyl (E)-3-(acetyl-2-methylanilino)-2-propenoate (**3b**)

Yellow oil, yield 0.22 g (45%). IR (KBr) (ν_{max}/cm^{-1}): 1720 (C=O), 1673 (C=O), 1152 (C–O). ^{1}H NMR: 1.27 (t, ^3J = 7.3, CH_3), 1.35 (s, CH_3), 2.16 (s, Me), 4.17 (q, ^3J = 7.3, CH_2), 4.62 (d, ^3J = 14.1, CH), 7.09–7.39 (m, 4CH), 8.71 (d, ^3J = 14.1, CH). ^{13}C NMR: 14.3 (CH_3), 17.0 (CH_3), 29.7 (CH_3), 60.1 (CH_2), 101.9 (CH), 128.1 (CH), 128.4 (CH), 129.7 (CH), 131.9 (CH), 134.2 (C), 136.1 (CH), 140.6 (C), 167.4 (C=O), 169.6 (C=O). EI-MS: 247 (M^+, 8), 233 (65), 116 (18), 92 (100), 77 (34). Anal. Calcd

for $C_{14}H_{17}NO_3$ (247.3): C, 68.00; H, 6.93; N, 5.66; Found: C, 68.19; H, 6.99; N, 5.70%.

3.2.8. Ethyl (E)-3-(acetyl-4-methylanilino)-2-propenoate (**3c**)

Yellow oil, yield 0.25 g (52%). IR (KBr) (ν_{max}/cm^{-1}): 1709 and 1625 (C=O). ^{1}H NMR: 1.18 (t, ^3J = 7.2, CH_3), 1.90 (s, Me), 2.30 (s, Me), 4.05 (q, ^3J = 7.2, OCH_2), 4.65 (d, ^3J = 16.5, CH), 6.86 (d, ^3J = 8.4, 2CH), 7.40 (d, ^3J = 8.4, 2CH), 8.60 (d, ^3J = 16.5, CH). ^{13}C NMR: 14.1 (CH_3), 21.0 (CH_3), 22.4 (CH_3), 61.5 (OCH_2), 102.4 (CH), 127.9 (2CH), 130.9 (2CH), 135.8 (C), 139.5 (CH), 142.0 (C), 167.3 (C=O), 169.6 (C=O). EI-MS: 247 (M^+, 6), 221 (100), 147 (65), 132 (35). Anal. Calcd for $C_{14}H_{17}NO_3$ (247.3): C, 68.00; H, 6.93; N, 5.76; Found: C, 67.92; H, 6.89; N, 5.72%.

3.2.9. Ethyl (E)-3-(acetyl-4-methoxyanilino)-2-propenoate (**3d**)

Yellow oil, yield 0.42 g (80%). IR (KBr) (ν_{max}/cm^{-1}): 1700 and 1617 (C=O). ^{1}H NMR: 1.22 (t, ^3J = 7.2, CH_3), 1.95 (s, Me), 3.85 (s, OCH_3), 4.15 (q, ^3J = 7.2, OCH_2), 4.75 (d, ^3J = 16.4, CH), 6.81 (d, ^3J = 8.5, 2CH), 7.38 (d, ^3J = 8.5, 2CH), 8.70 (d, ^3J = 16.4, CH). ^{13}C NMR: 14.3 (CH_3), 23.3 (CH_3), 55.6 (OCH_3), 60.1 (OCH_2), 102.5 (CH), 115.6 (2CH), 129.3 (2CH), 131.0 (CH), 142.3 (C), 160.1 (C), 167.4 (C=O), 169.7 (C=O). EI-MS: 263 (M^+, 8), 233 (54), 116 (42), 92 (100), 77 (39). Anal. Calcd for $C_{14}H_{17}NO_4$ (263.3): C, 63.87; H, 6.51; N, 5.32; Found: C, 63.39; H, 6.56; N, 5.23%.

3.2.10. Ethyl (E)-3-(acetyl-4-bromoanilin)-2-propenoate (**3e**)

Yellow solid, mp 107–111 °C, yield 0.37 g (60%). IR (KBr) (ν_{max}/cm^{-1}): 1698 (C=O), 1690 (C=O), 1119 (C–O). ^{1}H NMR: 1.24 (t, ^3J = 7.1, CH_3), 1.98 (s, CH_3), 4.14 (q, ^3J = 7.1, CH_2), 4.67 (d, ^3J = 14.1, CH), 7.06 (d, ^3J = 8.4, 2CH), 7.66 (d, ^3J = 8.4, 2CH), 8.59 (d, ^3J = 14.14, CH). ^{13}C NMR 14.3 (CH_3), 23.2 (CH_3), 60.2 (OCH_2), 102.7 (CH), 123.6 (CH), 130.0 (2CH), 133.8 (2CH), 137.4 (C), 141.7 (C), 167.0 (C=O), 169.0 (C=O). EI-MS: 312 (M^+, 10), 310 (11), 252 (23), 250 (20). Anal. Calcd for $C_{13}H_{14}BrNO_3$ (312.2): C, 50.02; H, 4.52; N, 4.49; Found: C, 50.21; H, 4.57; N, 4.52%.

3.2.11. Methyl (E)-3-[(phenylsulfonyl)anilino]-2-propenoate (**12a**)

Yellow oil, yield 0.49 g (78%). IR (KBr) (ν_{max}/cm^{-1}): 1710 (C=O), 1621 (C=C), 1360 and 1168 (N–SO_2). ^{1}H NMR: 3.68 (s, CH_3), 4.64 (d, ^3J = 14, =CH), 6.80–8.30 (10 H, m, aromatic), 8.38 (d, ^3J = 14, =CH–N). ^{13}C NMR: 53.0 (OCH_3) 101.4 (CH), 123.4 (CH), 127.0 (CH), 128.8 (CH), 129.4 (2CH), 130.9 (CH), 131.3 (CH), 135.5 (C), 139.3 (C), 145.6 (CH), 169.1 (C=O). EI-MS: 317 (M^+, 12), 233 (65), 116 (51), 92 (100), 77 (44). Anal. Calcd for $C_{16}H_{15}NO_4S$ (317.3): C, 60.55; H, 4.76; N, 4.41; Found: C, 60.68; H, 4.78; N, 4.46%.

3.2.12. Ethyl (E)-3-[(phenylsulfonyl)anilino]-2-propenoate (**12b**)

Yellow oil, yield 0.47 g (71%). IR (KBr) (ν_{max}/cm^{-1}): 1704 (C=O), 1683 (C=C), 1363 and 1165 (N–SO_2). ^{1}H NMR: 1.20 (t, ^3J = 7.2, CH_3), 4.17 (q, ^3J = 7.2, CH_2), 4.7 (d, ^3J = 17, CH), 6.8–8 (10 H, m, aromatic), 8.5 (d, ^3J = 17, CH). ^{13}C NMR: 14.3 (CH_3), 60.4 (O–CH_2), 100.1 (CH), 121.5–139.2 (12C, 2C_6H_5), 143.8 (2CH), 167.2 (C=O). EI-MS: 331 (M^+, 9), 233 (54), 116 (54), 92 (100), 77 (65). Anal. Calcd for $C_{17}H_{17}NO_4S$ (331.4): C, 61.61; H, 5.17; N, 4.23; Found: C, 61.55; H, 5.20; N, 4.26%.

3.2.13. Methyl (E)-3-[4-methyl (phenylsulfonyl)anilino]- 2-propenoate (**12c**)

Yellow oil, yield 0.53 g (80%). IR (KBr) (ν_{max}/cm^{-1}): 1716 (C=O), 1600 (C=C), 1359 and 1166 (N–SO_2). ^{1}H NMR: 2.36 (s, CH_3), 3.97 (s, OCH_3), 4.64 (d, ^3J = 14, CH), 6.78 and 7.25 (dd, ^3J = 8, C_4H_6), 7.4–7.9 (m, C_6H_5), 8.35 (d, ^3J = 14, CH). ^{13}C NMR: 21.2 (CH_3), 51.3 (OCH_3), 99.7 (CH), 122.5, 127.7, 129.2, 130.5, 132.1, 133.7, 137.7, and 140.1 (12C, aromatic), 144.0 (CH), 167.5 (C=O). EI-MS: 331 (M^+, 8), 233 (69), 116 (47), 92 (100), 77 (32). Anal. Calcd for $C_{17}H_{17}NO_4S$ (331.4): C, 61.62; H, 5.17; N, 4.23; Found: C, 61.48; H, 5.22; N, 4.18%.

3.2.14. Ethyl (E)-3-(4-methyl (phenylsulfonyl)anilino)-2-propenoate (**12d**)

Yellow oil, yield 0.57 g (83%). IR (KBr) (ν_{max}/cm^{-1}): 1706 (C=O), 1622 (C=C), 1365 and 1167 (N–SO_2). ^{1}H NMR: 1.22 (t, ^3J = 7.0, CH_3), 2.4 (s, CH_3), 4.18 (q, ^3J = 7.0, OCH_2), 4.7 (d, ^3J = 16, CH), 6.82 and 7.18 (dd, ^3J = 9 Hz, C_6H_4), 8.4 (d, ^3J = 16, CH). ^{13}C NMR: 13.8 (CH_3), 20.6 (CH_3), 59.5 (O–CH_2), 99.5 (CH), 121.7, 126.7, 127.2, 130.1, 131.8, 134.0, 137.8 and 139.7 (12C, aromatic), 143.4 (CH), 166.8 (C=O). EI-MS: 345 (M^+, 9), 233 (60), 116 (42), 92 (100), 77 (34). Anal. Calcd for $C_{18}H_{19}NO_4S$ (345.4): C, 62.59; H, 5.50; N, 4.06; Found: C, 62.38; H, 5.50; N, 4.10%.

3.2.15. Methyl (E)-3-[4-methoxy (phenylsulfonyl)anilino]-2-propenoate (**12e**)

Yellow oil, yield 0.55 g (80%). IR (KBr) (ν_{max}/cm^{-1}): 1716 (C=O), 1625 (C=C), 1357 and 1166 (N–SO_2). ^{1}H NMR: 3.65 (s, OCH_3), 3.8 (s, OCH_3), 4.66 (d, ^3J = 14, CH), 6.82 and 7.86 (dd, ^3J = 8, C_4H_6), 7.2–7.9 (m, C_6H_5), 8.39 (d, ^3J = 14, CH). ^{13}C NMR: 51.1 (OCH_3), 55.3 (OMe), 99.4 (CH), 114.9, 126.8, 127.5, 128.6, 130.0, 133.7 and 137.4 (11C, 2C_6H_5), 144.7 (CH), 160.3 (C) 167.3 (C=O). EI-MS: 347 (M^+, 10), 226 (5), 141 (40), 85 (35), 60 (25), 31 (50). Anal. Calcd for $C_{17}H_{17}NO_5S$ (347.4): C, 58.78; H, 4.93; N, 4.03; Found: C, 58.62; H, 4.84; N, 4.08%.

3.2.16. Ethyl (E)-3-[4-methoxy (phenylsulfonyl)anilino]-2-propenoate (**12f**)

Yellow oil, yield 0.59 g (83%). IR (KBr) (ν_{max}/cm^{-1}): 1704 (C=O), 1618 (C=C), 1359 and 1166 (N–SO_2). ^{1}H NMR: 1.23 (t, ^3J = 7.0, CH_3), 3.74 (s, OMe), 4.13 (q, ^3J = 7, CH_2), 4.7 (d, ^3J = 13, CH), 6.82 and 6.85 (dd, ^3J = 7 Hz, C_6H_4), 8.4 (d, ^3J = 13, CH). ^{13}C NMR: 14.0 (CH_3), 55.1 (OCH_3), 59.7 (OCH_2), 99.6 (CH), 114.7, 126.7, 127.4, 128.5, 130.4, 133.6 and 137.3 (11C, 2C_6H_5), 143.7 (CH), 160.1 (C–OMe), 166.8 (C=O). EI-MS:

361 (M^+, 7), 233 (37), 116 (52), 92 (100), 77 (44). Anal. Calcd for $C_{18}H_{19}NO_5S$ (361.4): C, 59.82; H, 5.30; N, 3.88; Found: C, 59.70; H, 5.37; N, 3.82%.

References

[1] A.B. Zaitsev, A.M. Vasil'tsov, E.Yu. Schmidt, A.I. Mikhaleva, L.V. Morozova, A.V. Afonin, I.A. Ushakov, B.A. Trofimov, Tetrahedron 58 (2002) 10043.

[2] K. Weissermel, H.J. Arfe, Industrial Organic Chemistry, 3rd ed., VCH, Weinheim, 1997, p. 358.

[3] K. Wilson, D.J. Adams, G. Rothenberg, J.H. Clark, J. Mol. Catal. A: Chem. 159 (2000) 309.

[4] L.D. Quin, A Guide to Organophosphorus Chemistry, Wiley–Interscience, New York, NY, 2000.

[5] B.M. Trost, G.R. Dake, J. Am. Chem. Soc. 119 (1997) 7595;
B.M. Trost, U. Kazmaier, J. Am. Chem. Soc. 114 (1992) 7933;
B.M. Trost, C. Li, J. Am. Chem. Soc. 116 (1994) 3167.

[6] S. Rafel, J.W. Leahy, J. Org. Chem. 62 (1997) 1521.

[7] I. Yavari, A. Ramazani, Synth. Commun. 27 (1997) 1449;
I. Yavari, H. Norouzi-Arasi, Phosphorus Sulfur Silicon 177 (2002) 87;
I. Yavari, S. Souri, M. Sirouspour, H. Djahaniani, F. Nasiri, Synthesis (2005) 1761.

[8] V. Nair, C. Rajesh, A.U. Vinod, S. Bindu, A.R. Sreekanth, J.S. Mathess, L. Balagopal, Acc. Chem. Res. 36 (2003) 899.

[9] C.D. Johnson, in: J. Zabicky (Ed.), The Chemistry of Amides, Wiley, New York, NY, 1970, pp. 187–245 (Chapter 3).

[10] N. Furukawa, H. Fujihara, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Sulphonic Acids, Esters and their Derivatives, Wiley, New York, NY, 1991, pp. 261–283 (Chapter 7).