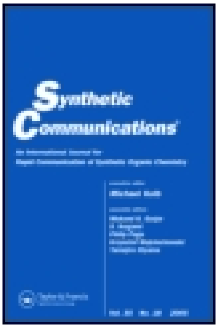

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A Novel Synthesis of β-Arylthio Propanoic Esters Promoted by Low-Valent Titanium

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A NOVEL SYNTHESIS OF β-ARYLTHIO PROPANOIC ESTERS PROMOTED BY LOW-VALENT TITANIUM

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ABSTRACT: Promoted by low-valent titanium, aryl sulfonyl chlorides react with α,β-unsaturated esters in THF to give β-arylthio propanoic esters in moderate to good yields.

In recent years an increasing interest in the reaction induced by low-valent titanium reagent is observed because of its exceedingly high ability in reductive coupling of carbonyl compounds[1]. A variety of other functional groups can also be reacted[2,3]. Recently, we have

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reported the low-valent titanium induced intermolecular reductive coupling reaction of carboxylic derivatives with aromatic ketones[4] and intramolecular reductive coupling reaction of 4,4-dicyano-1,3-diaryl-1-butanone[5]. However, few reaction promoted by low-valent titanium concerns the synthesis of sulfide containing compounds. We now describe the reaction of aryl sulfonyl chlorides with α,β-unsaturated esters by treatment with titanium tetrachloride and zinc in tetrahydrofuran at refluxing temperature.

When aryl sulfonyl chlorides and α,β-unsaturated esters were treated with $TiCl_4$-Zn in tetrahydrofuran at refluxing temperature, the reaction product β-arylthio propanoic esters was obtained.

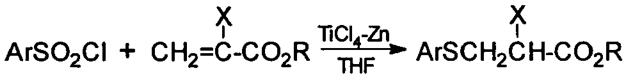
β-Arylthio propanoic esters could be prepared by reaction of thiophenol with α,β-unsaturated esters catalyzed by EtONa[6]. The method suffer from disadvantages, for example, strong base(EtONa) and heavy poisonous starting material(PhSH) were used. We here provide a simple and easy alternative method for the synthesis of β-arylthio propanoic esters in moderate to good yields.

EXPERIMENTAL

IR spectra were recorded on a FT IR-8101 spectrometer. ^1H NMR spectra were measured on a JEOL FX-90Q spectrometer using TMS as internal standard. Elemental analysis were determined using Perkin-Elmer 240C elemental analysis.

General procedure:

A dry 100 mL flask was charged with zinc dust(2.60g, 40 mmol), $TiCl_4$(2.2 mL, 20 mmol) and THF(20 mL). The mixture was



$$ArSO_2Cl + CH_2{=}\overset{X}{C}{-}CO_2R \xrightarrow[THF]{TiCl_4\text{-}Zn} ArSCH_2\overset{X}{C}H{-}CO_2R$$

Table: Reaction of aryl sulfonyl chlorides with α,β-unsaturated esters promoted by low-valent titanium

Entry	Ar	R	R'	Yield(%)
1	C_6H_5	H	CH_3	91
2	C_6H_5	H	CH_3CH_2	87
3	C_6H_5	H	n-Bu	80
4	C_6H_5	CH_3	CH_3	49
5	4-$CH_3C_6H_4$	H	CH_3	88
6	4-$CH_3C_6H_4$	H	CH_3CH_2	85
7	4-$CH_3C_6H_4$	H	n-Bu	83
8	4-$CH_3C_6H_4$	CH_3	CH_3	41

refluxed for 2h under argon atmosphere, then cooled to room temperature. A black slurry was formed. A solution of aryl sulfonyl chloride(10 mmol) and α,β-unsaturated ester(15 mmol) in the THF(20 mL) was dropped to the reaction mixture in 0.5h. After being stirred for 20h at 50 ℃, the mixture was cooled to room temperature and quenched with 10% HCl(50 mL) and extracted with $CHCl_3$(3 × 50 mL). The combined organic layer was washed with water(3 × 30 mL), dried(Na_2SO_4) and evaporated. The residue was purified by chromatography on silica gel(ethyl acetate: petroleum ether(60 ~ 90 ℃), 1:4) to give the product.

1[6]: Oil, ^1H NMR: 2.52-2.69(2H, t, J=7.3Hz, CH_2CO), 3.07-3.24(2H, t, J=7.3Hz, SCH_2), 3.65(3H, s, OCH_3), 7.15-7.37(5H, m, ArH); IR: 3030, 2950, 1740, 1580, 1480, 1440, 1405, 1250, 1175, 1020, 740, 690; Elemental analysis: found(%): C, 61.35; H, 6.09; Calcd. For $C_{10}H_{12}O_2S$: C, 61.20; H, 6.16.

2: Oil, ^{1}H NMR: 1.15-1.31(3H, t, J=7.1Hz, CH_3), 2.51-2.67(2H, t, J=7.1Hz, CH_2CO), 3.07-3.24(2H, t, J=7.1Hz, SCH_2), 4.00-4.24(2H, q, J=7.1Hz, OCH_2), 7.18-7.36(5H, m, ArH); IR: 3030, 2980, 2950, 1740, 1580, 1480, 1440, 1370, 1180, 1025, 740, 690; Elemental analysis: found(%): C, 62.98; H, 6.41; Calcd. For $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71.

3: Oil, ^{1}H NMR: 0.93-1.00(3H, t, J=6.4Hz, CH_3), 1.24-1.65(4H, m, CH_2CH_2), 2.51-2.68(2H, t, J=7.1Hz, CH_2CO), 3.08-3.25(2H, t, J=7.1Hz, SCH_2), 4.01-4.15(2H, t, J=6.4Hz, OCH_2), 7.16-7.40(5H, m, ArH); IR: 3030, 2980, 2960, 1740, 1580, 1480, 1440, 1350, 1240, 1175, 740, 690; Elemental analysis: found(%): C, 65.64; H, 7.78; Calcd. For $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61.

4: Oil, ^{1}H NMR: 1.48-1.59(3H, d, J=6.3Hz, CH_3), 2.43-2.78(1H, m, CHCO), 3.23-3.34(2H, d, J=10.3Hz, SCH_2), 3.51(3H, s, OCH_3), 7.19-7.38(5H, m, ArH); IR: 3030, 2950, 1740, 1580, 1480, 1460, 1440, 1370, 740, 690; Elemental analysis: found(%): C, 62.75; H, 6.53; Calcd. For $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71.

5: Oil, ^{1}H NMR: 2.30(3H, s, $ArCH_3$), 2.48-2.65(2H, t, J=7.2Hz, CH_2CO), 3.01-3.45(2H, t, J=7.2Hz, SCH_2), 3.64(3H, s, OCH_3), 7.03-7.12(2H, d, J=8.2Hz, ArH), 7.23-7.32(2H, d, J=8.2Hz, ArH); IR: 3030, 2950, 1740, 1490, 1430, 1360, 1240, 1175, 810; Elemental analysis: found(%): C, 63.15; H, 6.49; Calcd. For $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71.

6: Oil, ^{1}H NMR: 1.16-1.32(3H, t, J=7.1Hz, CH_3), 2.32(3H, s, $ArCH_3$), 2.50-2.66(2H, t, J=7.6Hz, CH_2CO), 3.03-3.19(2H, t, J=7.6Hz, SCH_2), 4.01-4.25(2H, q, J=7.1Hz, OCH_2), 7.05-7.14(2H, d, J=8.1Hz, ArH), 7.25-7.34(2H, d, J=8.1Hz, ArH); IR: 3030, 2960, 1740, 1490, 1375, 1340, 1240, 1180, 810; Elemental analysis: found(%): C, 64.47; H, 6.87; Calcd. For $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19.

7: Oil, ^1H NMR: 0.84-1.00(3H, t, J=6.3Hz, CH_3), 1.26-2.16(4H, m, CH_2CH_2), 2.31(3H, s, $ArCH_3$), 2.48-2.66(2H, t, J=7.0Hz, CH_2CO), 3.02-3.19(2H, t, J=7.0Hz, SCH_2), 4.00-4.14(2H, t, J=6.3Hz, OCH_2), 7.04-7.13(2H, d, J=8.1Hz, ArH), 7.24-7.33(2H, d, J=8.1Hz, ArH); IR: 3030, 2950, 1740, 1490, 1460, 1430, 1350, 1240, 1175, 810; Elemental analysis: found(%): C, 66.90; H, 7.65; Calcd. For $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99.

8: Oil, ^1H NMR: 1.46(3H, d, J=7.1Hz, CH_3), 2.30(3H, s, $ArCH_3$), 2.40-3.02(1H, m, CHCO), 3.18-3.29(2H, d, J=10.3Hz, SCH_2), 3.52(3H, s, OCH_3), 7.02-7.11(2H, J=8.1Hz, ArH), 7.26-7.35(2H, d, J=8.1Hz, ArH); IR: 3030, 2950, 1740, 1490, 1370, 1270, 1205, 1100, 810; Elemental analysis: found(%): C, 64.46; H, 7.32; Calcd. For $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19.

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References

1. McMurry, J. E., *Chem. Rev.*, **1989**, *89*, 1513
2. Dams, R., Malinowski, M., Westdrop, I. and Geise, H. J., *J. Org. Chem.*, **1981**, *46*, 2407
3. Mangeney, P., Tejero, T., Alexakis, A., Grosjean, F. and Normant, J., *Synthesis*, **1988**, 255

4. Shi, D. Q., Chen, J. X., Chai, W. Y., Chen, W. X. and Kao, J. Y., *Tetrahedron Lett.*, **1993**, *34*, 2963
5. Shi, D. Q., Lu, Z. S., Mu, L. L. and Dai, G. Y., *Synth. Commun.*, in press.
6. Charles, D. H., Leon, L. G., *J. Am. Chem. Soc.*, **1947**, *69*(9): 2328

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