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TETRAHEDRON

Butenolide Annelation Using a Manganese(III) Oxidation. A Synthesis of 4-Arylfuran-2(5*H*)-ones[+]

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Abstract: A general procedure was developed for the annelation of a butenolide to an aromatic ketone that highlighted a manganese(III) oxidation of aromatic ketones. The oxidation of aromatic ketones with manganese(III) acetate in the presence of 2-bromoacetic acid or the Mn(II) salt of this carboxylic acid provided a regioselectively convenient synthesis of 2-(2-bromoacetoxy) ketones. An Arbuzov or Wittig reaction of 2-(2-bromoacetoxy) ketones followed by cyclisation furnished 4-arylfuran-2(5*H*)-ones in good yield.

INTRODUCTION

2(5*H*)-Furanones are widespread in a variety of biologically important natural products, and are used as versatile synthetic intermediates.[1-3] For their preparation the classic Reformatsky reaction and many other methods have been developed and reviewed.[4] Palladium(II)-or silicon-assisted methods have been published.[5] Kagabu *et al.*[6] described the preparation of furan-2(5*H*)-ones from β-aryl-or β-alkylcrotonic esters with selenium dioxide in acetic acid in the presence of a catalytic amount of perchloric acid. Sweeney *et al.*[7a] described the synthesis of furan-2(5*H*)-ones in 23-76% yields *via* palladium-catalyzed cross-coupling reactions of 3- and 4-tributylstannylfuran-2(5*H*)-ones. Recently, palladium mediated synthesis of 4,-5-disubstituted furan-2(5*H*)-ones from 3-ynoic acids and organic halides was reported by Rossi *et al.*[7b] The furan-2(5*H*)-ones are obtained in 15-76% yields.

In our previous work we developed a procedure for the acyloxylation of enones at the α-position using manganese(III) acetate in combination with either manganese(II) carboxylate or carboxylic acids.[8] Using manganese(III) oxidation we report in this work the simple and efficient synthesis of 4-arylfuran-2(5*H*)-ones starting from aromatic ketones.

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[+] *This work is dedicated to Professor Ayhan Ulubelen to mark her retirement from Istanbul University, Faculty of Pharmacy and for many achievements, both in research of natural products and teaching, during her career there.*

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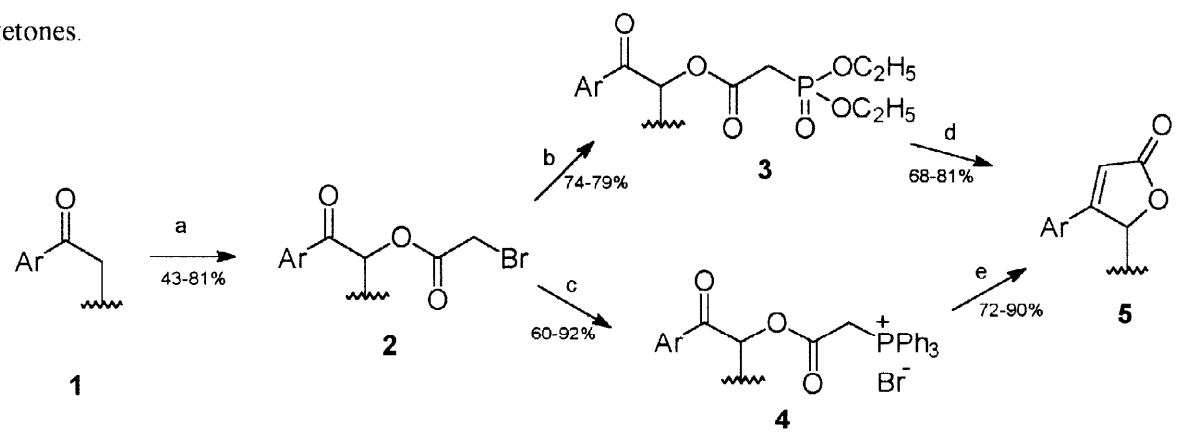
RESULTS AND DISCUSSIONS

In an initial study shown in Scheme 1, the oxidation of acetophenone **1a** with four equivalents of manganese(III) acetate in combination with six equivalents of manganese(II) bromoacetate, prepared according to the literature procedure,[9] or 12 equivalents of bromoacetic acid furnished the desired 2-(2-bromoacetoxy) ketone **2a** in 72-78% yields. Using chloroacetic acid instead of bromoacetic acid afforded chloroacetoxy derivative in 62-68 % yields. A small amount of α-acetoxylated ketone was also obtained in this reaction (5-7 % according to GLPC), but separation of the 2-acetoxy and 2-(2-bromoacetoxy) ketone **2a** was readily accomplished by column chromatography. Using the same reaction starting with different aromatic ketones the corresponding 2-(2-bromoacetoxy) derivatives **2a-g** are synthesized in good yields. In both cases, the acetylthiophene gave a low yield (43, 51%) of the product. The chloro- and bromoacetoxy ketones are mainly semisolids and show the typical singlet of X-CH_2 between δ 4.0- 4.5.

The highest yield for bromoacetoxylation of the ketones was obtained with 12 equivalents of bromoacetic acid or 6 equivalents of its Mn(II) salt. Using the free acid gives higher yield than the corresponding Mn(II) salt. Decreasing the bromoacetic acid component increases the yield of acetoxy ketones.

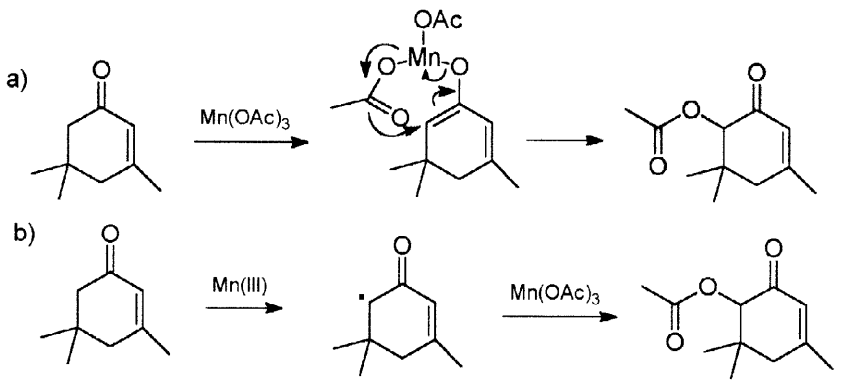


a) $Mn(OAc)_3$, $BrCH_2COOH$ or $(BrCH_2COO)_2Mn$, benzene, reflux. b) $P(OEt)_3$, reflux. c) PPh_3, benzene, reflux. d) LiBr, Et_3N, THF.[17] e) NaOH, or NEt_3, $CHCl_3$, RT.

Scheme 1

Williams and Hunter[10] suggested that the acetoxylation of enones with $Mn(OAc)_3$ works either via formation of a metal enolate with acetate transfer (Scheme 2a), analogous to the lead tetraacetate oxidation of enones proposed by Corey and Schaefer,[11] or via formation of an α-keto radical from the oxidation of an enol or enolate anion by Mn(III) followed by ligand transfer oxidation to obtain the product (Scheme 2b).[10,12] A similar mechanism was shown by Snider *et al.*[13] They found that kinetic enolization of the enone gives an Mn(III) enolate, which loses Mn(II) to give a α'-keto radical, which is oxidized by a second equivalent of $Mn(OAc)_3$ to give the α'-acetoxyenone (Scheme 2b).

We suggest that in the bromoacetoxylation of aromatic ketones the initial reaction between the manganese(III) acetate and bromoacetic acid or its manganese(II) salt leads to a mixed manganese(III) complex, which has both acetate and bromoacetoxy ligands. This mixed manganese(III) complex may interact with the ketone to form a metal enolate. The oxidation of an enolate by Mn(III)[12] produces an α-keto radical, which is trapped oxidatively with carboxylate to yield the product.



Scheme 2

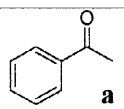
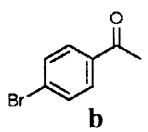
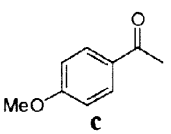
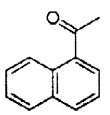
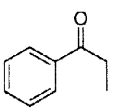
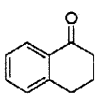
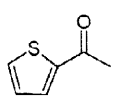
During this oxidation reaction the source of the manganese(III) acetate and the reaction time is very important for the yield of the products. The anhydrous manganese(III) acetate used in this oxidation was prepared from manganese(II) nitrate and acetic anhydride and dried using phosphorus pentoxide under vacuum prior to use.[8k,l] The reactions were monitored by TLC. Excess manganese(III) acetate and extended reflux caused the hydrolysis of the acyloxy ketones to hydroxy ketones.

Completion of the synthesis of the furanone involved an Arbuzov reaction of the 2-(2-bromoacetoxy) ketone **2a** with an excess of triethyl phosphite to afford the corresponding phosphonate **3a** as a viscous oil after purification by flash column chromatography in 78% yield. The cyclisation of **3a** using Horner-Wadsworth-Emmons modification of the Wittig reaction (HWE reaction) with LiBr and Et_3N in THF according the Rathke procedure[17] furnished 4-phenylfuran-2(5*H*)-one (**5a**) in 71% yield (Route A). The physical and spectral properties of **5a** are in agreement with values in the literature (mp 92-93 ^{0}C, lit. 92-93 ^{0}C[7]). Using the same reaction sequence, starting with different bromoacetoxy ketones, the 4-arylfuran-2(5*H*)-ones **5a-g** were synthesized in 68-81% yields as summarized in Table 1 (Scheme 1). The spectroscopic and physical properties of arylfuranones **5a-g** are identical in all respects with the reported values (Table 1).

Reactions of bromoacetoxy ketones with triphenylphosphine were carried out in a benzene solution to give triphenylphosphinoacetyl derivatives **4a-g** in yields from 60 to 92% (crude yields). The Wittig salts **4a-g** were not completely pure and, according to TLC and NMR, a variable quantity of butenolides **5a-g** were also formed. In the NMR spectra the signals of the CH_2P protons exhibit complex splitting in most cases. The Wittig salts were used for cyclization without further purification. Cyclization of

triphenylphosphinoacetyl derivatives **4a-g** to butenolides **5a-g** proceeded smoothly and yields of 72-90% were obtained, by stirring a chloroform solution of **4** with 0.5 M sodium hydroxide at room temperature for 10 minutes or by reaction of a chloroform solution of **4** with triethylamine (Route B). The Wittig salts were very easily cyclized to **5** in alkaline media. The NMR spectra of butenolides **5a-g** are in agreement with their structures.

Table: Synthesis of 4-arylfuran-2(5*H*)-ones starting from aromatic ketones

Ketones **1**	2-(2-Bromoacetoxy) ketones **2** Yield (%) Free acid	Mn(II) salt	Phosphonates **3** Yield(%)	4-Arylfuranones **5** Route A Yield(%)	Route B* Yield(%)	mp (^{0}C) (Lit.)
 **a**	78 **a**	72	78 **a**	71	81 **a**	89-91 (92.5)[6]
 **b**	73 **b**	70	76 **b**	78	72 **b**	160-162 (161-163)[5a]
 **c**	76 **c**	71	77 **c**	74	74 **c**	119-120 (121)[5a]
 **d**	81 **d**	73	74 **d**	72	68 **d**	99-101 (99)[6]
 **e**	76 **e**	68	77 **e**	73	70 **e**	61-63 (62.5-63.5)[14] (57-58)[15]
 **f**	77 **f**	73	79 **f**	81	72 **f**	114-116 (114-116)[15]
 **g**	51 **g**	43	79 **g**	68	43 **g**	91-93 (94-96)[7]

*The yields are based on **2a-g**

This work has demonstrated the novel application of manganese(III) oxidation for the synthesis of butenolides from aromatic ketones. The reactions provide a quick, easy and mild approach to furanone ring systems.

EXPERIMENTAL

All reagents were of commercial quality, and reagent quality solvents were used without further purification. IR spectra were determined on a Philips model PU9700 spectrometer. ^{1}H NMR spectra were determined on a Bruker AC 80 MHz FT, AC 200 MHz and Bruker DPX 400 MHz FT spectrometers. GC analyses were determined on a HP 5890 gas chromatograph.

General procedure for 2-(2-Bromoacetoxy) ketones: A mixture of manganese(III) acetate (2.12 g, 10mmol) and bromoacetic acid (3.24 g, 30 mmol) or its manganese(II) salt (4.90 g, 15 mmol) in benzene (40 mL) was refluxed for 1 h using a Dean-Stark trap. The mixture was cooled, and ketone (2.5 mmol) was added. The mixture was refluxed for 6-12 h, depending on the quality of the manganese(III) acetate, and checked by TLC. The mixture was cooled to 25^{0}C, diluted with EtOAc, washed with 1M aqueous HCl, saturated aqueous $NaHCO_3$ and brine, and dried over anhydrous $MgSO_4$. The crude product was chromatographed on preparative thin-layer chromatography silica-gel F-254 plates or by flash column chromatography (EtOAc/hexane 1:3).

General procedure for the preparation of 2-(2-triphenylphosphinoacetoxy) ketones: A suspension of bromoacetoxy ketone (10 mmol) and triphenylphosphine (3.14 g, 12 mmol) in benzene (30 ml) was refluxed for 4-6 h. After cooling, the precipitate was separated, washed with benzene and used for further experiments without recrystallization.

General procedures for the preparation of butenolide from triphenylphosphinoacetoxy ketones: A solution of the bromide (5 mmol) in chloroform (50 ml) was stirred with 0.5 M sodium hydroxide (20 ml) for 30 min. The chloroform layer was separated, washed with water, and dried over anhydrous sodium sulfate. The crude product was purified by column chromatography, or by treating the solution of the bromide (5 mmol) in chloroform (50 ml), with 10 mmol of triethylamine in benzene. The reaction mixture was stirred for 2 h. Triethylamine hydrobromide was filtered of and the residue obtained from the filtrate was purified by column chromatography.

General procedure for Arbuzov reaction: A mixture of 2-(2-bromoacetoxy) ketone (2.5 mmol) and triethyl phosphite (1.3 g, 8 mmol) was refluxed under argon for 2 h. The reaction was monitored by TLC on silica-gel (EtOAc-hexane 1:1). During this time, additional triethyl phosphite (1.3 g, 8 mmol) was added at 1h intervals. The excess triethyl phosphite was removed by distillation under vacuum, and the residue was chromatographed on preparative thin-layer chromatography silica-gel F-254 plates (EtOAc/hexane 1:1) to afford the phosphonate.

General procedure for annulation (HWE rection): A solution of phosphonate (2 mmol) in dry THF (80 ml) was cooled to 0^{0}C under nitrogen and treated with LiBr (521 mg, 6 mmol) , followed by Et_3N (2.78 ml, 20 mmol). After stirring at 0^{0}C for 15 min, the reaction mixture was allowed to stir at room temperature for 4h. The solution was then filtered through a plug of SiO_2, washing with ethyl acetate. The filtrate was

concentrated, and the residue was chromatographed on preparative thin-layer chromatography silica-gel F-254 plates (EtOAc/hexane 1:5) to give the furanone.

2-(2-Bromoacetoxy)-1-phenylethanone (2a): Yellow solid; mp 84-85^{0}C; IR (KBr) 1740, 1720, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.02 (s, 2H, CH_2Br), 5.52 (s, 2H, CH_2), 7.41- 7.62 (m, 5H, ArH); Anal. Calcd for $C_{10}H_9BrO_3$ (257.08): C, 46.72; H, 3.53. Found: C, 46.48; H, 3.65.

2-(2-Bromoacetoxy)-1-(4-bromophenyl) ethanone (2b): Yellow semisolid; IR (KBr): 1750, 1715, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.98 (s, 2H, CH_2Br), 5.43 (s, 2H, CH_2), 7.38 (d, 2H, J=9Hz, ArH), 7.62 (d, 2H, J=9Hz, ArH); Anal. Calcd for $C_{10}H_8Br_2O_3$ (335.95): C, 35.75; H, 2.40. Found: C, 35.56; H, 2.48.

2-(2-Bromoacetoxy)-1-(4-methoxyphenyl)ethanone (2c): Yellow semisolid; IR (KBr): 1760, 1720, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.88 (s, 3H, OCH_3), 4.02 (s, 2H, CH_2Br), 5.28 (s, 2H, CH_2), 6.98 (d, 2H, J=9.1 Hz, ArH), 7.45 (d, 2H, J=9.1 Hz, ArH). Anal. Calcd for $C_{11}H_{11}BrO_4$ (287.11): C, 46.02; H, 3.86. Found: C, 46.38; H, 4.21.

2-(2-Bromoacetoxy)-1-(1-naphthyl) ethanone (2d): Yellow solid; mp 112-114^{0}C; IR (KBr); 1760, 1725, 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.01 (s, 2H, CH_2Br), 5.18 (s, 2H, CH_2), 7.28-8.10 and 8.41-8.68 (m, 7H, ArH). Anal. Calcd for ($C_{14}H_{11}BrO_3$ (307.14): C, 54.75; H, 3.61. Found: C, 54.62; H, 3.64.

2-(2-Bromoacetoxy)-1-phenylpropanone (2e): Yellow semisolid; IR(KBr): 1760, 1720, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.41 (d, 3H, J=6.8 Hz, CH_3), 4.12 (s, 2H, CH_2), 5.22 (q, 1H, J= 6.8 Hz, CH), 7.42-7.63 (m, 5H, ArH); Anal. Calcd for $C_{11}H_{11}BrO_3$ (271.11): C, 48.73; H, 4.09. Found: C, 48.61; H, 4.17.

2-(2-Bromoacetoxy)tetralone (2f): Yellow semisolid; IR (KBr): 1765, 1680, 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.15- 2.48 (m, 2H, CH_2), 3.01- 3.22 (m, 2H, C-3 CH_2), 4.08 (s, 2H, CH_2), 5.38 (m, 1H, CH), 6.65- 6.96 and 7.08- 7.61 (m, 4H, ArH); Anal. Calcd for $C_{12}H_{11}BrO_3$ (283.12): C, 50.91; H, 3.92. Found C, 50.71, H, 4.22.

2-(2-Bromoacetoxy)-1-(2-thienyl)ethanone (2g): Yellow oil; IR (neat): 1760, 1720, 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.11 (s, 2H, CH_2Br), 5.20 (s, 2H, CH_2), 7.13, 7.32, 7.56 (m, 3H, thienyl C-4H, C-3H, C-5H). Anal. Calcd for $C_8H_7BrO_3S$ (263.11): C, 36.52; H, 2.68. Found: C, 36.13; H, 2.82.

2-(2-Diethoxyphosphoryl)acetoxy-1-phenylethanone (3a): Yellow oil; IR (neat): 1740, 1635, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.26-1.38 (m, 6H, 2 CH_3), 3.16 (d, 2H, J=22 Hz, CH_2P), 3.92- 4.23 (m, 4H, 2 CH_2), 5.28 (s, 2H, CH_2), 7.38- 7.61 (m, 5H, ArH). HRMS Calcd for $C_{14}H_{19}O_6P$: 314.0919; Found: 314.0916.

2-(2-Diethoxyphosphoryl)acetoxy-1-(4-bromophenyl)ethanone (3b): Yellow oil; IR(neat): 1755, 1630, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.25- 1.36 (m, 6H, 2 CH_3), 3.12 (d, 2H, J=22 Hz, CH_2P), 3.90- 4.12 (m, 4H, 2 CH_2), 5.36 (s, 2H, CH_2), 7.36 (m, 2H, ArH), 7.61 (m, 2H, ArH). Anal. Calcd for $C_{14}H_{18}BrO_6P$ (393.17): C, 42.77; H, 4.61. Found: C, 43.12; H, 4.85.

2-(2-Diethoxyphosphoryl)acetoxy-1-(4-methoxyphenyl)ethanone (3c) : Yellow oil; IR (neat): 1740, 1630, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.24-1.36 (m, 6H, 2 CH_3), 3.12 (d, 2H, J=21 Hz, CH_2P), 3.86 (s, 3H,

OCH_3), 3.92- 4.21 (m, 4H, 2 CH_2), 5.26 (s, 2H, CH_2), 6.96 and 7.45 (2d, 4H, ArH); Anal. Calcd for $C_{15}H_{21}O_7P$ (344.3): C, 52.33; H, 6.15. Found: C, 52.65; H, 6.43.

2-(2-Diethoxyphosphoryl)acetoxy-1-(1-naphthyl)ethanone (3d): Yellow oil; IR (neat) 1760, 1710, 1610 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.23-1.35 (m, 6H, 2 CH_3), 3.12 (d, 2H, J=22 Hz, CH_2P), 3.92- 4.22 (m, 4H, 2 CH_2), 5.21 (s, 2H, CH_2), 7.26- 8.12 and 8.40-8.66 (m, 7H, ArH); Anal. Calcd for $C_{18}H_{21}O_6P$ (364.33): C, 59.34; H, 5.81. Found: C, 58.98; H, 5.58.

2-(2-Diethoxyphosphoryl)acetoxy-1-phenylpropanone (3e): Yellow oil; IR (neat): 1760, 1720, 1610 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.22- 1.35 (m, 6H, 2 CH_3), 1.42 (d, 3H, J=7 Hz, CH_3), 3.10 (d, 2H, J=22 Hz, CH_2P), 3.91- 4.16 (m, 4H, 2 CH_2), 5.23 (m, 1H, CH), 7.41- 7.62 (m, 5H, ArH); Anal. Calcd for $C_{15}H_{21}O_6P$ (328.30): C, 54.88; H, 6.45. Found: C, 55.12; H, 6.71.

2-(2-Diethoxyphosphoryl)acetoxytetralone (3f): Yellow oil; IR (neat): 1770, 1680, 1610 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.22- 1.35 (m, 6H, 2 CH_3), 2.18-2.46 (m, 2H, CH_2), 3.0- 3.24 (m, 4H, C-3 CH_2, CH_2P), 3.89- 4.14 (m, 4H, 2 CH_2), 5.41 (m, 1H, CH), 6.68-6.98 and 7.60- 7.71 (m, 4H, ArH). Anal. Calcd for $C_{16}H_{21}PO_6$ (340.31): C, 56.47; H, 6.22. Found: C, 56.12; H, 6.41.

2-(2-Diethoxyphosphoryl)acetoxy-1-(2-thienyl)ethanone (3g): Yellow oil; IR (neat): 1750, 1710, 1600 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.23- 1.33 (m, 6H, 2 CH_3), 3.12 (d, 2H, J=22 Hz, CH_2P), 3.90- 4.12 (m, 4H, 2 CH_2), 5.21 (s, 2H, CH_2), 7.13 (m, 1H, CH), 7.35 (m, 1H, CH), 7.56 (m, 1H, CH); Anal. Calcd for $C_{12}H_{17}O_6PS$ (320.30): C, 45.0; H, 5.35. Found: C, 45.41; H, 5.16.

4-(2-Thienyl)furan-2(*5H*)-one (5g); Yellow solid; mp 91-93 °C; IR(KBr) 1780, 1750, 1620 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.21 (d, J= 1.7 Hz, 2H, CH_2), 6.15 (t, J=1.7 Hz, 1H, C-3 H), 7.17 (dd, J=3.7 and 5.2 Hz, 1H, thienyl C-4 H), 7.28 (m, 1H, thienyl C-3 H), 7.58 (dd, J= 5.2 and 1.1 Hz, 1H, thienyl C-5 H); Anal. Calcd for $C_8H_6OS_2$ (166.19): C, 57.82; H, 3.64. Found: C, 57.52; H, 3.48.

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REFERENCES

1. (a) Bourguignon, J.-J.;Schoenfelder, A.; Schmitt, M.; Wermuth, C.-G.; Hechler, V.; Charlier, B.; Maitre, M. *J. Med. Chem.* **1988**, *31*, 893. (b) Figadere, B. *Acc. Chem. Res.* **1995**, *28*, 359. (c) Gamarad, P,; Sauriol, F.; Benhamou, N.; Belanger, R. R.; Paulitz, T. C. *J. Antibiot.* **1997**, *50*, 742. (d) Gibson, C. L.; Handa, S. *Tetrahedron: Asymmetry* **1996**, *7*, 1281. (e) Freer, A. A.; Kirby, G. W.; Rao, G. V.; Cain, R. B. *J. Chem. Soc. Perkin Trans I* **1996**, 2111.
2. Brownbridge, P.; Egert, E.; Hunt, P. G.; Kennard, O.; Warren, S. J. *J. Chem. Soc. Perkin Trans.* 1, **1981**, 2751.
3. Falsone, G.; Wingen, H. P. *Arch. Pharm.* (Weiheim) **1986**, *317*, 80.

4. (a) Rao, Y. S. *Chem. Rev.* **1976**, 70. (b) Knight, D. W. *Contemp. Org. Synth.*, **1994**, *1*, 287.
5. (a) Ciattini, P. G.; Ortar, G. *Synthesis* **1986**, 70. (b) Kita, Y.; Sekihachi, J.; Hayashi, Y.; Da, Y.; Yamamoto, M.; Akai, S. *J. Org. Chem.* **1990**, *55*, 1109.
6. Kagabu, S.; Shimizu, Y.; Ito, C.; Moriya, K. *Synthesis* **1992**, 830.
7. (a) Hollingworth, G.; Perkins, G.; Sweeney, J. *J. Chem. Soc. Perkin Trans.*1, **1996**, 1913. (b) Rossi, R.; Bellina, F.; Biagetti, M.; Mannina, L. *Tetrahedron Lett.* **1998**, *39*, 7599.
8. (a) Demir, A.S; Saatçioglu, A. *Synthetic Commun.* **1993**, 23(5), 571. (b) Demir, A.S.; Jeganathan, A. *Synthesis*,**1992**, 235. (c) Demir, A.S.; Çamkerten, N.; Akgün, H.; Tanyeli, C.; Mahasneh, A.S.; Watt, D.S. *Synthetic Commun.* **1990**, 20(15), 2279. (d) Demir, A.S.; Sayraç, T.; Watt, D.S. *Synthesis* **1990**, 1119. (e) Demir, A. S.; Akgün, H.; Tanyeli, C.; Watt D.S. *Synthesis* **1991**, 719. (f) Demir, A.S.; Tanyeli, C.; Akgün, H.; Çaliskan, Z.; Özgül, E.; *Bull. Chem. Soc. Fr.* **1995**, *132*, 423. (g) Demir, A.S.; Tanyeli , C.; Gülbeyaz, V.; Akgün H. *Turkish J. Chemistry* **1996** , *20*, 244. (h) Tanyeli, C.; Çaliskan, Z.; Demir A. S. *Synthetic Commun.* **1997** , 27(19), 3471. (i) Chretien, A.; Varga, G. *Bull. Soc. Chim. Fr.* **1936**, *3*, 2385. (j) Demir, A. S.; Hamamci, H.; Tanyeli, C.; Akhmedov, I. M.; Doganel, F. *Tetrahedron: Asymmetry* **1998**, *9*, 1673. (k) Bauer, G. *"Handbuch der Praeparativen Anorganischen Chemie"*, Stuttgart, **1962**, p. 1283. (l) Nikishin, G. I.; Vinogradov, M. G.; Verenchikov, S. P. *Izv. Akad. Nauk SSSR Ser. Khim.* **1969**, 1835; Bull. Acad. Sci. USSR Div. Chem. Sci. 1969, 1698.
9. a) Espersen, W. G.; Martin, R. B. *J. Phys. Chem.* **1976**, *80*, 161. b) Demir, A. S.; Jeganathan, A.; Watt, D. S. *J. Org. Chem.* **1989**, *54*, 4020; and references cited therein.
10. Williams, G. J.; Hunter, N. R. *Can. J. Chem.* **1976**, *54*, 3830.
11. Corey, E. J.; Schaefer, J. P. *J. Am. Chem Soc.* **1960**, *82*, 918.
12. Arndt, D. *Manganese Compounds as Oxidizing Agents in Organic Chemistry;* Open Court Publishing Co.: La Salle, IL, 1981;Chapter 1.
13. (a) Snider, B. B.; Han, L.; Xie, C. *J. Org. Chem.* **1997**, *62*, 6978. (b) Snider, B. B. *Chem. Rev.* **1996**, *96*, 339. (c) Snider, B. B.; Kiselhof, E. Y.; *Tetrahedron Lett.* **1996**, *52*, 6073.
14. Guenter, H. J.; Gruenbaum, E.; Jaeger, V. *Liebigs Ann. Chem.* **1984**, 15.
15. Okazaki, R.; Negishi, Y.; Inamoto, N. *J. Org. Chem.* **1984**, *49*, 3819.
16. Chatterjee, A.; Banerjee, D.; Mallik, R. *Tetrahedron*, **1977**, *33*, 85.
17. Rathke, M. W.; Nowak, M. *J. Org. Chem.* **1985**, *50*, 2624.