Tetrahedron 64 (2008) 6196–6201

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Potassium permanganate/carboxylic acid/organic solvent: a powerful reagent for enone oxidation and aryl coupling reactions☆

Ayhan S. Demir*, Hamide Findik

Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

ARTICLE INFO

Article history:
Received 7 February 2008
Received in revised form 14 April 2008
Accepted 1 May 2008
Available online 3 May 2008

ABSTRACT

The α′-acetoxylation of enones and the α-acetoxylation of aromatic ketones were carried out with potassium permanganate and acetic acid, in which acetoxylation products were obtained in 74–96% yields. The same reaction was carried out with carboxylic acids other than acetic acid, which furnished corresponding acyloxy ketones with the same regioselectivity. For the first time, formyloxylation products were synthesized in a 61–85% yield by using formic acid. The potassium permanganate and acetic acid method was also used for aryl coupling reactions. The reaction of arylboronic acids and arylhydrazines in benzene with potassium permanganate and acetic acid in turn furnished biaryls in 85–96% yield. We have shown that potassium permanganate/carboxylic acid/organic solvent behaves as manganese(III) acetate.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Metal-promoted radical reactions have found widespread use in organic synthesis, in which one of the well-known examples of this application is the $Mn(OAc)_3$-mediated reaction.[2] Manganese(III) acetate dihydrate ($Mn(OAc)_3 \cdot 2H_2O$)-mediated free-radical reactions have emerged as important synthetic methods for a new bond formation as well as bond breaking. The application of $Mn(OAc)_3$ promoted free-radical reactions in numerous regio-, chemo-, and stereoselective carbon–carbon, carbon–heteroatom bond formations have been developed in both inter- and intramolecular reactions.[3]

Several sources of $Mn(OAc)_3$ are described in the literature.[4] The in situ preparation of $Mn(OAc)_3$ from $KMnO_4/Mn(OAc)_2$ is also described by Heiba and Linker.[5]

In our previous work, we showed the selective oxidation of enones leading to α′-acetoxy enones by $Mn(OAc)_3$ oxidation. In general, $Mn(OAc)_3$ oxidations are characterized by higher α′-regioselectivity, higher chemical yields, and milder reaction conditions, which also tolerate many sensitive functional groups. The use of $Mn(OAc)_3$ in combination with other carboxylic acids or manganese(II) carboxylates extends this methodology to the preparation of a variety of α′-acyloxy enones that are otherwise inaccessible in a one-step procedure.[6] The $Mn(OAc)_3$ oxidation was also applied to cyclic and non-cyclic aromatic ketones, in which the acyloxylation products were obtained in good to excellent yields. The oxidation worked with high selectivity and only α-oxidation products were obtained in high yields.[7] α-Acetoxy enones, as starting materials, opened an entry for the synthesis of their enantiomers by using enzymatic kinetic resolution, which are not readily available using other methods.[8]

We also developed a general method for the synthesis of biaryls starting from arylhydrazines/aromatic solvents and arylboronic acids/aromatic solvents in the presence of $Mn(OAc)_3$. We showed, for the first time, that $Mn(OAc)_3$ is a versatile reagent for the generation of aryl radicals from arylhydrazines and arylboronic acids.[9]

Although C–C and C–O bond formation reactions of a great variety of substrates have been reported so far by us and others as successful,[3] there are some problems associated with the use of $Mn(OAc)_3$. A brief list of them is as follows: (1) excess $Mn(OAc)_3$ (4–6 equiv) is generally used for acceptable yields and reaction times; (2) many contradictory results can be seen when the literature reports are closely inspected. These include the amount of $Mn(OAc)_3$ and irreproducible yields/reaction times.[10] In the present paper, we report our investigation of the nature of this reaction, and we found that the potassium permanganate/carboxylic acid system in an organic solvent is a powerful substitute for manganese(III) acetate. Here, we tried this method for acetoxylation and biaryl formation reactions.

2. Results and discussion

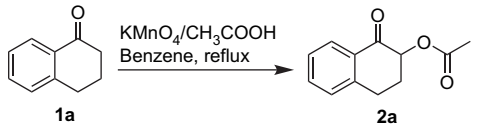
We selected 1-tetralone **1a** as a model substrate and investigated its reaction with $KMnO_4$/acetic acid in benzene. In an

☆ See Ref. 1.

* Corresponding author. Fax: +90 312 210 3200.
E-mail address: asdemir@metu.edu.tr (A.S. Demir).

0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.05.004

initial reaction, $KMnO_4$ was dissolved in acetic acid and benzene. This solution was refluxed under a Dean–Stark trap until the color of the solution turned brown. Then, 1-tetralone was added to this solution and reflux was continued. The reaction was monitored by TLC, and then filtered and neutralized with $NaHCO_3$. After work-up, 2-acetoxytetralone (**2a**) was isolated in a 64% yield (Scheme 1). The optimization of the reaction time and conditions furnished **2a** in a 89% yield. Several enones and aromatic ketones were converted into their acetoxy derivatives as shown in Table 1. The reactions work with the same regioselectivity. The yields are comparable to the $Mn(OAc)_3$-mediated direct oxidation of ketones and tolerate many sensitive functional groups. Most of the starting materials are commercially available and the ketones **1g–i,l** were synthesized according to the literature procedure.[11]



Scheme 1.

This result prompted us to try an oxidation reaction with carboxylic acid other than acetic acid, wherein we found that this method can in fact be applied for the acyloxylation of enones and aromatic ketones in high yields as shown in Table 2 (Scheme 2). For the first time, formyloxylation was carried out with formic acid. In the literature, rather few works have been presented about the direct formyloxylation of ketones (Lee et al. reported that an initial treatment of ketones with thallium(III) triflate, formed in situ by the reaction of thallium(III) acetate with trifluoromethanesulfonic acid, in DMF at 60 °C followed by the addition of small amounts of H_2O provided the formyloxy ketones).[12]

Problems occurred when using some solid carboxylic acids, these reactions were carried out without benzene, wherein only acetic acid was used as a solvent and the corresponding acyloxy derivatives were synthesized in good yield. By using benzoic acid, the product was isolated along with an acetoxy derivative as a minor product. It was possible then to separate the product by column chromatography. No product formation was observed by using chloroacetic acid, even when we used cyclohexane and DMF as a solvent.

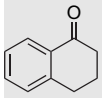
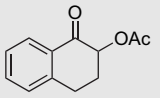
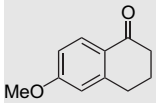
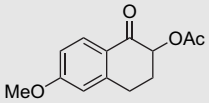
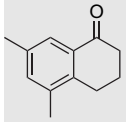
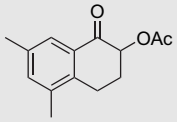
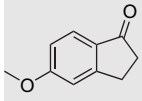
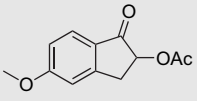
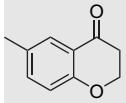
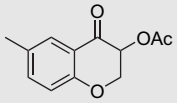
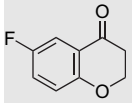
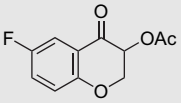
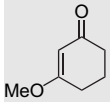
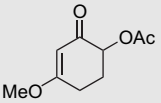
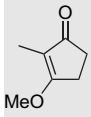
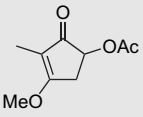
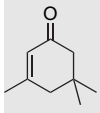
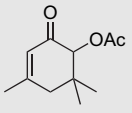
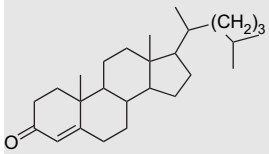
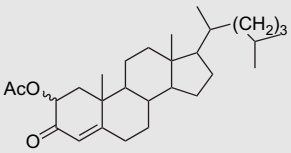
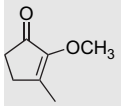
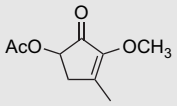
2.1. $KMnO_4$/AcOH mediated aryl coupling

Recently, we developed a general method for the synthesis of biaryls starting from arylhydrazines/aromatic solvents and arylboronic acids/aromatic solvents in the presence of $Mn(OAc)_3$. No isomerization of the formed radical was observed (Scheme 3a,b).[9]

Both the aryl coupling reactions, starting from arylhydrazines and arylboronic acids with benzene as a solvent, were carried out by using the $KMnO_4/CH_3COOH$ system. $KMnO_4$/acetic acid and benzene were refluxed under the Dean–Stark trap until the color of the solution turned brown. Then, arylboronic acid or arylhydrazine was added to this solution and reflux was continued. The reaction was controlled with TLC and the corresponding aryl coupling products were obtained in high yields with the same regioselectivity without isomerization. Arylboronic acids and arylhydrazines with the electron-withdrawing and electron-donating groups attached to the phenyl ring furnished comparable yields as shown in Tables 3 and 4 (Scheme 4).

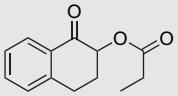
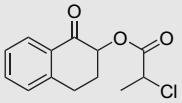
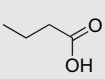
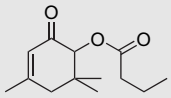
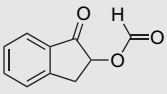
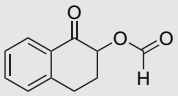
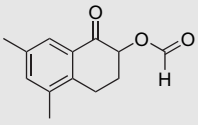
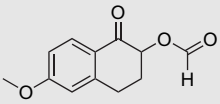
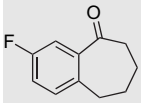
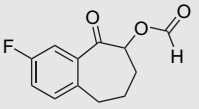
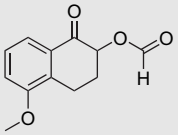
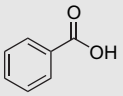
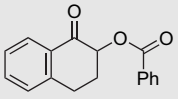
After all the reactions concluded, we found that the $KMnO_4/CH_3COOH$ system behaves as $Mn(OAc)_3$. Refluxing of $KMnO_4/CH_3COOH$ in organic solvent under the Dean–stark trap furnishes $Mn(OAc)_3$. In the case of the use of carboxylic acids other than

Table 1
Oxidation of aromatic ketones and enones with $KMnO_4$/AcOH

Starting material **1**	Product[a] **2**	Yield (%)	Yield (%)[lit.]
 **a**	 **a**	89	88[10]
 **b**	 **b**	85	97[10]
 **c**	 **c**	96	—
 **d**	 **d**	81	—
 **e**	 **e**	83	—
 **f**	 **f**	74	—
 **g**	 **g**	97	87[11]
 **h**	 **h**	75	88[8c]
 **i**	 **i**	86	99[10]
 **j**	 **j**	84[b]	98[10]
 **k**	 **k**	88	88[8f]

[a] All the spectral data of the known compounds were identical with the values in the literature.
[b] Mixture of isomers.

Table 2
Oxidation of aromatic ketones and enones with $KMnO_4$/RCOOH

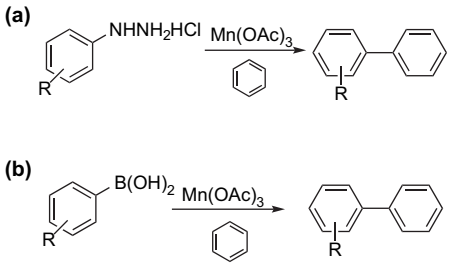
Starting material **1**	Carboxylic acid	Product[a] **3**	Yield (%)	Yield (%)[lit.]
a		 **a**	87	—
a		 **b**	91	67[13]
i		 **c**	82	—
 **m**		 **d**	80	98[12]
a		 **e**	85	—
c		 **f**	75	—
b		 **g**	76	—
 **n**		 **h**	61	—
d		 **i**	70	—
a		 **j**	65[b]	89[14]

[a] All the spectral data of the known compounds were identical with the values in the literature.
[b] The crude product contains 20% acetoxy ketone, which was separated by column chromatography.

acetic acid, the corresponding Mn(III) acyloxy derivative should be formed in order to obtain acyloxy ketones after the oxidation reaction.[23]

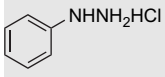
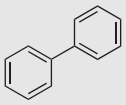
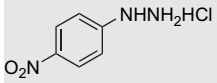
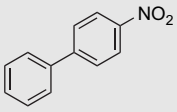
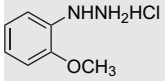
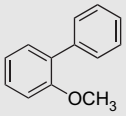
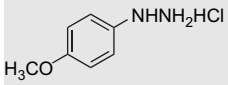
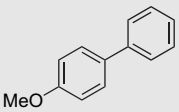
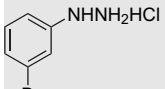
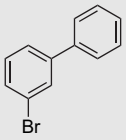
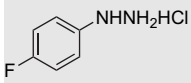
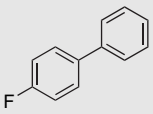
For the close inspection of the species for oxidation, after the reflux of the $KMnO_4$/RCOOH in benzene, the brown mixture was evaporated to dryness and cyclic voltammetric studies were then carried out and compared with the commercially available Mn(III) acetate. As a result, both reacted the same in cyclic voltammetry.

Scheme 2.



Scheme 3.

Table 3
Synthesis of biaryls from arylhydrazines

Arylhydrazine **4**	Biaryl[a] **6**	Yield (%)	Yield (%)[lit.]
 **a**	 **a**	95	75[15]
 **b**	 **b**	95	93[15]
 **c**	 **c**	95	75[9a]
 **d**	 **d**	90	83[9a]
 **e**	 **e**	90	73[9a]
 **f**	 **f**	85	92[16]

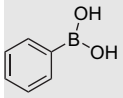
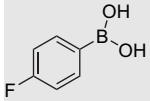
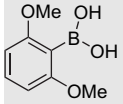
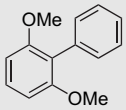
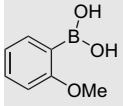
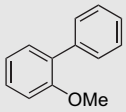
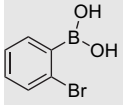
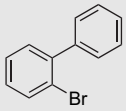
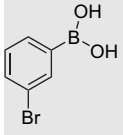
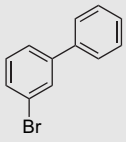
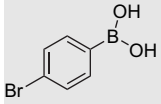
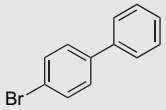
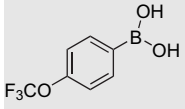
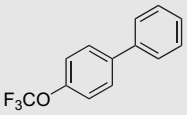
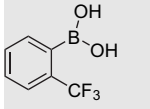
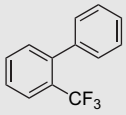
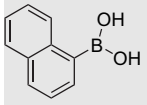
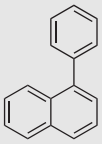
[a] All the spectral data of the known compounds were identical with the values in the literature.

The formation of Mn(III) species can be explained via the following equation:

$$4H^+(aq) + MnO_4^- \rightarrow Mn^{3+}(aq) + O_2(g) + 2H_2O(l) (\Delta\Sigma^0 = +0.28\,V)$$

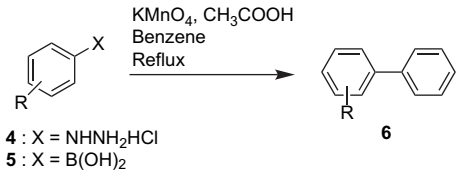
More work concerning the nature of oxidants is currently under investigation.

Table 4
Synthesis of biaryls from arylboronic acids

Arylboronic acid **5**	Biaryl[a] **6**	Yield (%)	Yield (%)[lit.]
 **a**	**a**	96	75[16]
 **b**	**f**	86	92[17]
 **c**	 **g**	90	89[18]
 **d**	 **h**	90	89[18]
 **e**	 **i**	90	95[19]
 **f**	 **e**	90	90[20]
 **g**	 **f**	88	92[21]
 **h**	 **g**	95	—
 **h**	 **h**	89	98[22]
 **i**	 **i**	87	94[16]

[a] All the spectral data of the known compounds were identical with the values in the literature.

In summary, the oxidation reactions of enones and aromatic ketones were carried out with potassium permanganate/carboxylic acid in an organic solvent and acyloxy enones were obtained in high yields. The potassium permanganate/carboxylic acid system in an organic solvent was applied to aryl coupling reactions with arylboronic acids and arylhydrazines, in which biaryl products were obtained in high yields. This method enables one to obtain Mn(III) acyloxy derivatives in situ. The reactions are simple, selective, and cheap compared to other methods. The results showed that the potassium permanganate/carboxylic acid system is a powerful substitute for manganese(III) acetate.



Scheme 4.

3. Experimental section

3.1. General

^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance DPX 400 spectrometers at 300 MHz. All of the resonances are referenced to the residual solvent signals. Elemental analyses: Leco CHNS 932 Analyzer. IR spectra were obtained on Bruker IFS 66/s. Column chromatography was conducted on silica gel 60 (40–63 μm). TLC was carried out on aluminum sheets pre-coated with silica gel 60F_{254} (Merck), in which the spots were visualized with UV light (λ=254 nm).

3.2. General procedure for α-acyloxylation of enones

A solution of 3 mmol of $KMnO_4$ in 100 mL benzene–carboxylic acid (10:1) was stirred under reflux (Dean–Stark apparatus) until the purple color of $KMnO_4$ turned brown (15–30 min.). To this solution, 1 mmol of enone was added and reflux was continued. The reaction was monitored by TLC. After all the starting material was consumed, the reaction mixture was diluted with ether and neutralized with $NaHCO_3$. The resulting organic phase was dried over $MgSO_4$ and concentrated under vacuum. If necessary, the crude products were purified by column chromatography using EtOAc–hexane as an eluent.

3.3. General procedure for the coupling of arylhydrazines or arylboronic acids

A solution of 3 mmol of $KMnO_4$ in 100 mL benzene–AcOH (10:1) was stirred under reflux (Dean–Stark apparatus) until the purple color of $KMnO_4$ turned brown (15–30 min.). To this solution 1 mmol of aryl hydrazine or arylboronic acid was added and reflux was continued. The reaction was monitored by TLC. After all the starting material was consumed, the reaction mixture was diluted with ether and neutralized with $NaHCO_3$. The resulting organic phase was dried over $MgSO_4$ and concentrated under vacuum. If necessary, the crude products were purified by column chromatography using EtOAc–hexane as an eluent. In most cases, the direct filtering of the reaction mixture through a pad of silica provided pure products.

*3.3.1. 1,2,3,4-Tetrahydro-5,7-dimethyl-1-oxonaphthalen-2-yl acetate (**2c**)*

Yield 222 mg, 96%, yellow solid (mp 101–103 °C). IR ($CHCl_3$) ν_{max}: 763, 1608, 1693, 3447 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.09–2.20 (1H, m, C*H*), 2.15 (3H, s, CH_3), 2.21 (3H, s, CH_3), 2.27 (3H, s, CH_3), 2.20–2.45 (1H, m, CH_2), 2.80–3.00 (m, 2H, CH_2), 5.39 (1H, dd, J=5.0, 13.7 Hz, C*H*), 7.09 (1H, s, C*H*), 7.60 (1H, s, C*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 169.9, 138.2, 136.3, 136.2, 135.9, 131.7,

125.8, 74.2, 28.4, 25.0, 20.9, 19.3. Anal. Calcd for $C_{14}H_{16}O_3$ (232.28): C, 72.39; H, 6.94. Found: C, 72.61; H, 6.64.

*3.3.2. 2,3-Dihydro-5-methoxy-1-oxo-1H-inden-2-yl acetate (**2d**)*

Yield 178 mg, 81%, yellow oil. IR (neat) ν_{max}: 762, 1060, 1245, 1615, 1710 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 2.11 (3H, s, CH_3), 2.89 (1H, dd, J_1=4.3 Hz, J_2=17.1 Hz, CH_2), 3.53 (1H, dd, J_1=8.1 Hz, J_2=17.1 Hz, CH_2), 3.83 (3H, s, CH_3), 5.30 (dd, J_1=4.7 Hz, J_2=7.7 Hz, C*H*), 6.78 (1H, s, C*H*), 6.85 (1H, d, J=7.0 Hz, C*H*), 7.65 (1H, d, J=7.6 Hz, C*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.6, 55.5, 73.9, 109.7, 116.0, 124.8, 126.9, 127.8, 128.2, 153.2, 166.1, 170.0, 198.0. Anal. Calcd for $C_{12}H_{12}O_4$ (220.22): C, 65.45; H, 5.49. Found: C, 65.61; H, 5.64.

*3.3.3. 3,4-Dihydro-6-methyl-4-oxo-2H-chromen-3-yl acetate (**2e**)*

Yield 182 mg, 83%, yellow oil. IR (neat) ν_{max}: 762, 1060, 1609, 1693, 3443 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 2.12 (3H, s, CH_3), 2.25 (3H, s, COCH_3), 4.27 (1H, t, J=11.3 Hz, CH_2), 4.43 (1H, dd, J_1=5.4 Hz, J_2=11.0 Hz, CH_2), 5.52 (1H, dd, J_1=5.4 Hz, J_2=11.4 Hz, C*H*), 6.79 (1H, d, J=8.5 Hz, C*H*), 7.24 (1H, d, J=11.7 Hz, C*H*), 7.58 (1H, s, C*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 20.5, 68.3, 69.4, 117.5, 119.6, 127.2, 131.3, 137.2, 159.4, 169.0, 187.5. Anal. Calcd for $C_{12}H_{12}O_4$ (220.22): C, 65.45; H, 5.49. Found: C, 65.34; H, 5.67.

*3.3.4. 6-Fluoro-3,4-dihydro-4-oxo-2H-chromen-3-yl acetate (**2f**)*

Yield 166 mg, 74%, yellow semisolid. IR ($CHCl_3$) ν_{max}: 762, 845, 1254, 1612, 1701, 3443 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 2.15 (3H, s, CH_3), 4.32 (1H, dd, J_1=5.4 Hz, J_2=11.3 Hz, CH_2), 4.48 (1H, dd, J_1=5.5 Hz, J_2=11.1 Hz, CH_2), 5.56 (1H, dd, J_1=5.5 Hz, J_2=11.4 Hz, C*H*), 6.91 (1H, dd, J_1=4.1 Hz, J_2=9.1 Hz, C*H*), 7.17–7.23 (1H, m, CH_3), 7.47 (1H, dd, J_1=5.5 Hz, J_2=11.1 Hz, C*H*, C*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 68.9, 69.6, 113.0 (d, $^2J_{CF}$=23.4 Hz), 119.8 (d, $^3J_{CF}$=7.2 Hz), 120.8 (d, $^3J_{CF}$=6.6 Hz), 124.2 (d, $^2J_{CF}$=24.6 Hz), 157.8, 158.0 (d, $^3J_{CF}$=241.9 Hz), 169.3, 187.1. Anal. Calcd for $C_{11}H_9FO_4$ (224.19): C, 58.93; H, 4.05. Found: C, 59.14; H, 4.27.

*3.3.5. 1,2,3,4-Tetrahydro-1-oxonaphthalen-2-yl propionate (**3a**)*

Yield 190 mg, 87%, brown viscous oil. IR ($CHCl_3$) ν_{max}: 762, 1060, 1615, 1710 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.17 (3H, t, J=7.5 Hz, CH_3), 2.22 (1H, ddd, J_1=4.7 Hz, J_2=12.7 Hz, J_3=25.6 Hz, CH_3), 2.29–2.53 (3H, m, CH_2, CH_2), 2.93–3.22 (2H, m, CH_2), 5.45 (1H, dd, J_1=5.2 Hz, J_2=13.2 Hz, C*H*), 7.18 (1H, t, J=4.8 Hz, C*H*), 7.25 (1H, t, J=7.5 Hz, C*H*), 7.41 (1H, t, J=7.0 Hz, C*H*), 7.95 (1H, d, J=7.8 Hz, C*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.8, 9.2, 27.4, 28.0, 29.2, 74.2, 126.9, 127.9, 128.5, 131.5, 133.7, 142.9, 173.3, 192.4. Anal. Calcd for $C_{13}H_{14}O_3$ (218.25): C, 71.54; H, 6.47. Found: C, 71.31; H, 6.29.

*3.3.6. 4,6,6-Trimethyl-2-oxocyclohex-3-enyl butyrate (**3c**)*

Yield 184 mg, 82%, yellow oil. IR (neat) ν_{max}: 1609, 1665, 1713, 3010 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.91–0.97 (9H, m, CH_3), 1.02 (3H, s, CH_3), 1.66 (2H, sextet, J=7.3 Hz, CH_2CH$_3$), 1.88 (3H, s, CH_3), 2.07–2.12 (1H, m, C*H*), 2.30–2.50 (3H, m, CH_2, CH_2), 5.12 (1H, s, C*H*), 5.81 (1H, s, C*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 18.5, 20.0, 24.2, 27.3, 36.0, 37.6, 46.1, 80.0, 124.9, 158.0, 172.5, 192.4. Anal. Calcd for $C_{13}H_{20}O_3$ (224.3): C, 69.61; H, 8.99. Found: C, 69.42; H, 8.77.

*3.3.7. 1,2,3,4-Tetrahydro-1-oxonaphthalen-2-yl formate (**3e**)*

Yield 165 mg, 85%, yellow oil. IR (neat) ν_{max}: 740, 1612, 1690, 2933, 3435 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 2.26 (1H, ddd, J_1=4.8 Hz, J_2=12.8 Hz, J_3=17.5 Hz, CH_2), 2.34–2.39 (1H, m, CH_2), 3.03 (1H, dt, J_1=4.5 Hz, J_2=17.0 Hz, CH_2), 3.12–3.20 (1H, m, CH_2), 5.54 (1H, dd, J_1=5.1 Hz, J_2=13.3 Hz, C*H*), 7.18 (1H, d, J=8.0 Hz, C*H*), 7.27 (1H, t, J=7.7 Hz, C*H*), 7.43 (1H, t, J=7.5 Hz, C*H*), 7.96 (1H, d, J=7.9 Hz, C*H*), 8.16 (1H, s, C*H*O); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 29.1, 73.9, 127.0, 128.1, 128.5, 131.5, 133.9, 42.7, 159.4, 191.3. Anal. Calcd for $C_{11}H_{10}O_3$ (190.2): C, 69.46; H, 5.30. Found: C, 69.33; H, 5.48.

*3.3.8. 1,2,3,4-Tetrahydro-5,7-dimethyl-1-oxonaphthalen-2-yl formate (**3f**)*

Yield 164 mg, 75%, brown oil. IR (neat) ν_{max}: 762, 1609, 1693, 2927, 3443 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 2.14–2.24 (1H, m, CH_2), 2.21 (3H, s, CH_3), 2.27 (3H, s, CH_3), 2.35–2.40 (1H, m, CH_2), 2.82–2.90 (1H, m, CH_2), 2.95–3.02 (1H, m), 5.51 (1H, dd, J_1=5.0 Hz, J_2=13.6 Hz, C*H*), 7.12 (1H, s, C*H*), 7.62 (1H, s, C*H*), 8.16 (1H, s, C*H*O); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 20.3, 24.3, 27.8, 73.2, 125.5, 131.1, 135.5, 135.8, 137.5, 159.0, 191.3. Anal. Calcd for $C_{13}H_{14}O_3$ (218.25): C, 71.54; H, 6.47. Found: C, 71.68; H, 6.55.

*3.3.9. 1,2,3,4-Tetrahydro-6-methoxy-1-oxonaphthalen-2-yl formate (**3g**)*

Yield 167 mg, 76%, yellow oil. IR (neat) ν_{max}: 1250, 1615, 1703, 2930, 3430 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 2.23 (1H, ddd, J_1=4.6 Hz, J_2=12.6 Hz, J_3=17.3 Hz, CH_2), 2.31–2.37 (1H, m, CH_2), 2.99 (1H, dt, J_1=3.6 Hz, J_2=16.9 Hz, CH_2), 3.07–3.15 (1H, m, CH_2), 3.79 (3H, s, OCH_3), 5.50 (1H, dd, J_1=5.4 Hz, J_2=12.9 Hz, C*H*), 6.56 (1H, s, C*H*), 6.77 (1H, dd, J_1=2.1 Hz, J_2=8.8 Hz, C*H*), 7.93 (1H, d, J=8.8 Hz, C*H*), 8.16 (1H, s, C*H*O); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.1, 29.1, 55.3, 73.6, 112.5, 113.6, 125.0, 130.5, 145.2, 159.6, 164.0, 190.0. Anal. Calcd for $C_{12}H_{14}O_4$ (220.22): C, 65.45; H, 5.49. Found: C, 65.66; H, 5.27.

*3.3.10. 2-Fluoro-6,7,8,9-tetrahydro-9-oxo-5H-benzo[7]annulen-8-yl formate (**3h**)*

Yield 135 mg, 61%, colorless oil. IR (neat) ν_{max}: 762, 1605, 1692, 2926, 3440 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.73–1.84 (1H, m, CH_2), 2.00–2.23 (3H, m, CH_2, CH_2), 2.92–2.95 (1H, m, CH$_2$), 5.44 (1H, dd, J_1=6.9 Hz, J_2=12.6 Hz, C*H*), 7.04 (1H, td, J_1=2.7 Hz, J_2=10.7 Hz, C*H*), 7.11–7.16 (1H, m, C*H*), 7.38 (1H, dd, J_1=2.8 Hz, J_2=8.9 Hz, C*H*), 8.02 (1H, s, C*H*O); ^{13}C NMR ($CDCl_3$) δ 23.1, 28.6, 33.0, 76.9, 96.3, 116.2 (d, J=27.8 Hz, C*F*), 119.3 (d, J=21.3 Hz, C*F*), 132.1 (d, J=7.2 Hz, C*F*), 137.5 (d, J=3.4 Hz, C*F*), 138.3 (d, J=6.4 Hz, C*F*), 159.8, 160.3, 163.6, 197.2. Anal. Calcd for $C_{12}H_{11}FO_3$ (222.21): C, 64.86; H, 4.99. Found: C, 64.73; H, 4.81.

*3.3.11. 1,2,3,4-Tetrahydro-5-methoxy-1-oxonaphthalen-2-yl formate (**3i**)*

Yield 154 mg, 70%, brown oil. IR (neat) ν_{max}: 762, 1264, 1609, 1693, 2927, 3443 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 2.18 (1H, ddd, J_1=5.0 Hz, J_2=12.8 Hz, J_3=17.8 Hz, CH_2), 2.34–2.40 (1H, m, CH_2), 2.74–2.83 (1H, m, CH_2), 3.20 (1H, ddd, J_1=2.7 Hz, J_2=4.6 Hz, J_3=18.0 Hz, CH$_2$), 3.81 (3H, s, CH$_3$), 5.53 (1H, dd, J_1=5.0 Hz, J_2=13.6 Hz, C*H*), 6.95 (1H, d, J=8.0 Hz, C*H*), 7.22 (1H, t, J=8.0 Hz, C*H*), 7.55 (1H, d, J=7.9 Hz, C*H*), 8.17 (1H, s, C*H*O); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 28.2, 55.5, 114.5, 119.5, 127.6, 131.8, 132.6, 156.6, 159.5, 191.6. Anal. Calcd for $C_{12}H_{12}O_4$ (220.22): C, 65.45; H, 5.49. Found: C, 65.54; H, 5.71.

*3.3.12. 4-(Trifluoromethoxy)-1,1′-biphenyl (**6g**)*

Yield 226 mg, 95%, white solid (mp 56–58 °C). IR ($CHCl_3$) ν_{max}: 762, 832, 1245, 1625 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (2H, d, J=8.7 Hz, C*H*), 7.26 (1H, t, J=7.4 Hz, C*H*), 7.34 (2H, d, J=7.4 Hz, C*H*, C*H*), 7.44 (2H, t, J=7.4 Hz, C*H*, C*H*), 7.49 (2H, t, J=8.6 Hz, C*H*, C*H*); ^{13}C NMR (100 MHz $CDCl_3$) δ 121.2, 127.1, 127.6, 128.4, 128.8, 139.9, 140.1, 148.7. Anal. Calcd for $C_{13}H_9F_3$ (238.21): C, 65.55; H, 3.81. Found: C, 65.34; H, 3.77.

Acknowledgements

The authors would like to thank Prof. H. Isci and Prof. A. Cihaner for fruitful discussions. The financial support from the Scientific and Technical Research Council of Turkey (TUBITAK), the Turkish Academy of Sciences (TÜBA), the Turkish State Planning Organization, and the Middle East Technical University is gratefully acknowledged.

References and notes

1. First presented at 232nd ACS National Meeting, San Francisco, CA, United States, September 10–14, 2006 (ORGN-275).
2. de Klein, W. J. *Organic Syntheses by Oxidation with Metal Compounds*; Mijs, W. J., de Jonge, C. R. H. I., Eds.; Plenum: New York, NY, 1986.
3. (a) Demir, A. S.; Emrullahoglu, M. *Curr. Org. Synth.* **2007**, *4*, 321; (b) Melikyan, G. G. *Synthesis* **1993**, 833; (c) Snider, B. B. *Chem. Rev.* **1996**, *96*, 339; (d) Melikyan, G. G. *Aldrichimica Acta* **1998**, 50.
4. (a) Heiba, E. I.; Dessau, R. M.; Koehl, W. J., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 5905; (b) Bush, J. B., Jr.; Finkbeiner, H. *J. Am. Chem. Soc.* **1968**, *90*, 5903; (c) Heiba, E. I.; Dessau, R. M. *J. Org. Chem.* **1974**, *39*, 3456.
5. (a) Heiba, E. I.; Dessau, R. M.; Rodewald, P. G. *J. Am. Chem. Soc.* **1974**, *96*, 7977; (b) Linker, T. *J. Organomet. Chem.* **2002**, *661*, 159.
6. (a) Demir, A. S.; Jeganathan, A. *Synthesis* **1992**, 235; (b) Demir, A. S.; Gross, R. S.; Dunlap, N. K.; Hashemi, A. B.; Watt, D. S. *Tetrahedron Lett.* **1986**, *27*, 5567; (c) Dunlap, N. K.; Sabol, M. R.; Watt, D. S. *Tetrahedron Lett.* **1984**, *25*, 5839.
7. (a) Demir, A. S.; Saatcioglu, A. *Synth. Commun.* **1993**, *23*, 571; (b) Demir, A. S.; Gercek, Z.; Reis, O.; Duygu, A. N.; Arikan, E. *Tetrahedron* **1999**, *55*, 2441; (c) Demir, A. S.; Camkerten, N.; Akgun, H.; Tanyeli, C.; Mahasneh, A. S.; Watt, D. S. *Synth. Commun.* **1990**, *20*, 2279; (d) Floresca, R.; Kurihara, M.; Watt, D. S.; Demir, A. S. *J. Org. Chem.* **1993**, *58*, 2196.
8. (a) Demir, A. S.; Hamamci, H.; Doganel, F.; Camkerten, N.; Aksoy-Cam, H. *Turk. J. Chem.* **2000**, *24*, 141; (b) Demir, A. S.; Aybey, A.; Sesenoglu, O.; Polat, F. *Tetrahedron: Asymmetry* **2003**, *14*, 1489; (c) Demir, A. S.; Findik, H.; Kose, E. *Tetrahedron: Asymmetry* **2004**, *15*, 777; (d) Gercek, Z.; Karakaya, D.; Demir, A. S. *Tetrahedron: Asymmetry* **2005**, *16*, 1743; (e) Demir, A. S.; Senocak, D. *Tetrahedron: Asymmetry* **2004**, *15*, 2641; (f) Demir, A. S.; Caliskan, Z.; Aydin, A. E.; Bicer, I. *Tetrahedron: Asymmetry* **2006**, *17*, 786.
9. (a) Demir, A. S.; Reis, O.; Ozgul-Karaaslan, E. *J. Chem. Soc., Perkin Trans. 1* **2001**, 3042; (b) Demir, A. S.; Reis, O.; Emrullahoglu, M. *J. Org. Chem.* **2003**, *68*, 578; (c) Demir, A. S.; Reis, O.; Emrullahoglu, M. *Tetrahedron* **2002**, *58*, 8055.
10. Demir, A. S.; Reis, O.; Igdir, A. C. *Tetrahedron* **2004**, *60*, 3427.
11. Demir, A. S.; Sesenoglu, O. *Org. Lett.* **2002**, *4*, 2021.
12. Lee, J. C.; Jin, Y. S.; Choi, J.-H. *Chem. Commun.* **2001**, 956.
13. Demir, A. S.; Gercek, Z.; Duygu, N.; Igdir, A. C.; Reis, O. *Can. J. Chem.* **1999**, *77*, 1336.
14. Zhu, Y.; Shu, L.; Tu, Y.; Shi, Y. *J. Org. Chem.* **2001**, *66*, 1818.
15. Kostas, I. D.; Coutsolelos, A. G.; Charalambidis, G.; Skondra, A. *Tetrahedron Lett.* **2007**, *48*, 6688.
16. Maegawa, T.; Kitamura, Y.; Sako, S.; Udzu, T.; Sakura, A.; Tanaka, A.; Kobayashi, Y.; Endo, K.; Bora, U.; Kurita, T.; Kozaki, A.; Monguchi, Y.; Sajiki, H. *Chem.—Eur. J.* **2007**, *13*, 5937.
17. Namboodiri, V. V.; Varma, R. S. *Org. Lett.* **2002**, *4*, 3161.
18. Song, C.; Ma, Y.; Chai, Q.; Ma, C.; Jiang, W.; Andrus, M. B. *Tetrahedron* **2005**, *61*, 7438.
19. Yasuike, S.; Qin, W.; Sugawara, Y.; Kurita, J. *Tetrahedron Lett.* **2007**, *48*, 721.
20. Espino, G.; Kurbangalieva, A.; Brown, J. M. *Chem. Commun.* **2007**, 1742.
21. Taylor, R. H.; Felpin, F.-X. *Org. Lett.* **2007**, *9*, 2911.
22. Ren, Y.; Yu, G.-A.; Guan, J.; Liu, S. H. *Appl. Organomet. Chem.* **2007**, *21*, 1.
23. In an earlier work (Ref. 10), by the reinvestigation of the synthetic and mechanistic aspects of Mn(III) acetate-mediated oxidation of enones, an improved procedure that was based on the use of acetic acid as a co-solvent was presented. Excellent results were obtained for a variety of structurally diverse and synthetically important enones under optimized conditions, in which we showed that 1.25 equiv $Mn(OAc)_3$ can be used compared to the previously used 4–6 equiv. Because $Mn(OAc)_3$ is one-electron oxidant, we experienced difficulties in explaining the low equivalencies. After the result with the $KmnO_4/CH_3COOH$ system, we suggested that our self-made extra dried $Mn(OAc)_3$, synthesized from $KmnO_4/Mn(OAc)_2$, can contain some $KMnO_4$, which could give in situ $Mn(OAc)_3$. More work concerning the nature of oxidants is currently under investigation.