Supporting Information
for DOI: 10.1055/s-0032-1317343
© Georg Thieme Verlag KG Stuttgart · New York 2012
Supporting Information

Woollins Reagent: A Chemoselective Reducing agent for 1,4-enediones and 1,4-ynediones to Saturated 1,4-Diones

Madhumita Mandal, Sourav Chatterjee and Parasuraman Jaisankar*

Department of Chemistry, CSIR-Indian Institute of Chemical Biology, 4, Raja S.C. Mullick Road, Calcutta-700032, India
Fax: +91-33-24735197; E-mail: jaisankar@iicb.res.in

Table of Contents

General Information.............................................................S2
Experimental Section..........................................................S2
Characterization data of 2e and 3a...........................................S2
1H and 13C NMR spectra of compounds 2a, 2e, 5b, 6b and 3a ..........S3
References..............................................................................S10
**General Information:** Woollins reagent was procured from Sigma Aldrich and used as such. NMR spectra were obtained using a Bruker DRX 600 (or Bruker AMX 300) MHz NMR spectrometer with TMS as the internal standard. All chemical shifts are reported in ppm. Analytical thin-layer chromatography (TLC) was carried out on Merck 20 × 20 cm silica gel 60-F254 plates. Column chromatography was done with silica gel 60-120 mesh or with neutral alumina. All starting materials were synthesized according to literature procedure and characterized. All final compounds were characterized by $^1$H, $^{13}$C, and MS analysis. All synthesized reported compounds analytical data are consistent to those reported in the literature. EI-MS were recorded on a GCMS-Shimadzu-QP5050A and ESI-MS spectra on a Waters® Micromass® Q-TOF Micro™ spectrometer. Elemental analyses were performed by Perkin-Elmer CHN/O analyzer model 2400, series II.

**Experimental Section:**

**General experimental procedure for 1,4-enediones:** *Trans*-1, 2-dibenzoyl ethylene (1a, 236 mg, 1 mmol) was dissolved in dry methanol (5 ml) and to this solution Woollins reagent (266 mg, 0.5 mmol) was added. The reaction mixture was then stirred at room temperature for 1.5 h, the progress of the reaction being monitored by TLC using chloroform-petroleum ether (1:1). After completion of the reaction, the solid formed was filtered through a short pad of celite and the filtrate evaporated under reduced pressure to yield a yellow residue. This was purified by column chromatography over neutral alumina using petroleum-ether with increasing proportion of chloroform. Petroleum-ether: chloroform (95:5) eluent gave the solid alkane dione 2a (159 mg, 67%). The same experimental procedure was followed for the chemoselective reduction of 1,4-diaryl alkenes 1b-e, unsymmetrical alkenone 5a and *trans*-1,2-diacetyl ethylene 5b.

**General experimental procedure for 1,4-ynediones:** To a solution of 1, 2-dibenzoyl acetylene (4a, 234 mg, 1 mmol) in dry methanol (5 ml) was added Woollins reagent (532 mg, 1 mmol) portion wise. The reaction mixture was stirred at room temperature for 1.5 h, the progress of the reaction being monitored by TLC using chloroform-petroleum ether (1:1). After completion of the reaction, the solid formed was filtered through a short pad of celite and the filtrate was evaporated under reduced pressure to yield a yellow residue. This was purified by column chromatography over neutral alumina using petroleum-ether with increasing proportion of chloroform. Petroleum-ether: chloroform (95:5) as eluent gave a solid identified as 1,2-dibenzoyl ethane (2a) (145 mg, 61%).

**Charaterization data:**

1,4-Bis-(3-chloro-4-methyl-phenyl)-butane-1,4-dione (2e):
White solid, mp 113-115°C; $^1$H NMR (300 MHz, CDCl$_3$), δ 7.89 (s, 2H), 7.79 (d, $J = 7.5$ Hz, 2H), 7.44 (d, $J =8.1$ Hz, 2H), 3.41 (s, 4H), 2.44 (s, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 197.7, 139.7, 136.5,135.0, 130.5, 129.3, 126.8, 32.5, 20.1. ESI-MS m/z: 357.10 [M+Na$^+$]. Anal. Calcd for C$_{18}$H$_{16}$Cl$_2$O$_2$: C, 64.49; H, 4.81. Found : C, 64.40; H, 4.79.

2,5-Diphenyl furan (3a): $^1$H NMR (300 MHz, CDCl$_3$), δ 7.75 (d, $J = 7.2$ Hz, 4H), 7.39 (m, 4H), 7.28 (m, 2H), 6.74 (s, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 153.3, 130.8, 128.7, 127.3,123.7, 107.2. GCMS m/z: 220 (M$^+$, 100), 191 (15), 165 (10), 115 (30), 105 (20).

---

S2
$\text{1H NMR spectrum of (E)-hex-3-ene-2,5-dione (5b) in CDCl}_3, 300\text{MHz}$

$\text{13C NMR spectrum of (E)-hex-3-ene-2,5-dione (5b) in CDCl}_3, 75\text{ MHz}$
$^1$H NMR spectrum of hexane-2,5-dione (6b) in CDCl$_3$, 300MHz

$^{13}$C NMR spectrum of hexane-2,5-dione (6b) in CDCl$_3$, 75 MHz
1H NMR spectra of 1,2-dibenzoyl ethane (2a) in CDCl₃, 300 MHz

1H NMR spectra of deuteriated 1,2-dibenzoyl ethane (2a) in CDCl₃, 300 MHz
$^1$H NMR spectrum of 1,4-Bis-(3-chloro-4-methyl-phenyl)-butane-1,4-dione (2e) in CDCl$_3$, 300 MHz

$^{13}$C NMR spectrum of 1,4-Bis-(3-chloro-4-methyl-phenyl)-butane-1,4-dione (2e) in CDCl$_3$, 75 MHz

$^{13}$C NMR spectrum of 1,4-Bis-(3-chloro-4-methyl-phenyl)-butane-1,4-dione (2e) in CDCl$_3$, 75 MHz
$^1$H NMR spectrum of 2,5-diphenyl furan (3a) in CDCl$_3$, 300MHz

$^{13}$C NMR spectrum of 2,5-diphenyl furan (3a) in CDCl$_3$, 75 MHz
$^1$H NMR spectrum of cis-1,2-dibenzoyl ethylene

$^{13}$C NMR spectrum of cis-1,2-dibenzoyl ethylene
'H NMR of crude reaction product from 1,2-dibenzoyl acetylene (after 10 min reaction)
References:


(2) For spectral data of cis-1,2-dibenzoyl ethylene, see: Rappai, J. P.; Synth. Commun. 2007, 37, 569.


