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A novel one-pot synthesis of 3-carbomethoxy-4-arylfuran-2-(5*H*)-ones from ketones using [hydroxy(tosyloxy)iodo]benzene

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ABSTRACT

A novel one-pot procedure for the synthesis of 3-carbomethoxy-4-aryl furan-2-(5*H*)-ones is reported via α-tosyloxylation of enolisable ketones with [hydroxy(tosyloxy)iodo]benzene, followed by treatment with potassium monomethyl malonate and K_2CO_3.

Recently, there has been significant growth in the applications of hypervalent iodine reagents in organic synthesis.[1] [Hydroxy(tosyloxy)iodo]benzene (HTIB) commonly known as Kosser's reagent is the sole efficient reagent for inducing α-tosyloxylation of enolisable ketones.[2] The resulting α-tosyloxyketones are environmentally benign alternatives to the toxic and lachrymatory α-haloketones. Since it is generally not necessary to isolate the α-tosyloxyketone, they can be utilised in situ as strategic precursors for the one-pot synthesis of a wide range of heterocycles such as thiazoles, selenazoles, oxazoles, imidazoles, pyrazoles and benzofurans.[3]

The γ-butenolide structural subunit is present in a growing number of natural products and synthetic compounds with wide-ranging biological properties.[4] This biological importance of γ-butenolides has prompted the development of a plethora of methods for their synthesis.[5] The preparation of γ-lactones is achieved mainly by the halo- or seleno-lactonisation reactions of β,γ- and γ,δ-unsaturated carboxylic acids.[5a] The success of these reactions is due to the facile halo- and seleno-functionalisation of the carbon–carbon double bond followed by neighbouring group participation of the nucleophilic carboxyl group. As HTIB is known for the α-tosyloxylation of enolisable ketones[2] as well as for *vic*-ditosyloxylations of alkenes,[6] it can be used safely as an alternative to halogen or selenium reagents in the lactonisation reactions of appropriate carboxylic acids. The reactions of β,γ- and γ,δ-unsaturated carboxylic acids[7] and 5-oxocarboxylic acids[8] with HTIB are known for the efficient synthesis of γ-lactones. In spite of this excellent intramolecular strategy, precursors such as β,γ- and γ,δ-unsaturated carboxylic acids and 5-oxocarboxylic acids are poorly available commercially and therefore, special efforts are required for their preparation. Recently, Wirth and co-workers reported the efficient synthesis of γ-butenolides from β,γ-unsaturated carboxylic acids using $PhI(OCOCF_3)_2$ and a catalytic quantity of $(PhSe)_2$ under mild reaction conditions.[9] Furthermore, the free radical-based cyclisation of aliphatic carboxylic and benzoic acids using a hypervalent iodine(III) reagent and KBr to form γ-lactones was reported by Kita and co-workers[10] The above-discussed strategies for γ-lactone synthesis are based mainly upon intramolecular cyclisation of appropriate carboxylic acids.

A literature survey revealed that γ-lactones can be synthesised by the reaction between olefins and β-diketones or β-ketoesters,[11] or potassium monomethyl malonate[12] using a suitable single electron oxidant. The mono-potassium salt of dimethyl malonate is a readily accessible versatile building block possessing doubly nucleophilic character at the carbon and oxygen centres.[13] It has been used in combination with olefins in presence of $Mn(OAc)_3$ as a single electron oxidant to form γ-lactones in reasonably good yields.[12] However, the addition is not regioselective in the case of unsymmetrical olefins and therefore, side products are formed.[12b] In continuation of our interest in hypervalent iodine reagents,[14] herein we report a novel one-pot synthesis of 3-carbomethoxy-4-arylfuran-2-(5*H*)-ones from enolisable ketones and potassium monomethyl malonate using HTIB (Scheme 1).

The success of this reaction is due to the facile in situ formation of α-tosyloxyketones **2** followed by efficient trapping with potassium monomethyl malonate to form methyl 2-oxo-2-arylethyl malonate **3**, which finally undergoes base (K_2CO_3) catalysed

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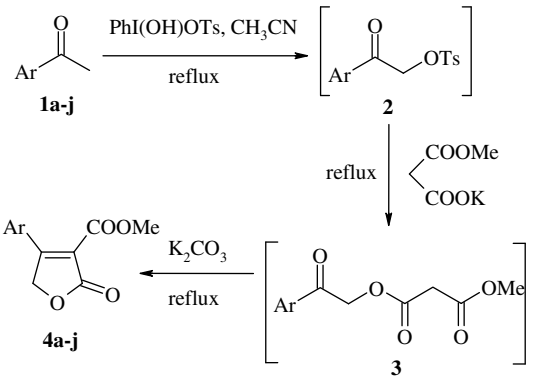
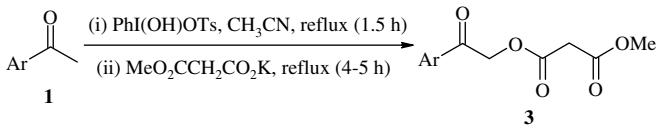


Scheme 1.

cyclisation to form γ-butenolides **4**. Intermediates **2** and **3** are not isolated during the reaction.

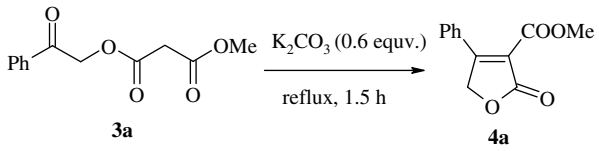
The reaction conditions were optimised by considering the model reaction of acetophenone and potassium monomethyl malonate using HTIB as oxidant. A mixture of acetophenone (0.360 g, 3 mmol) and HTIB (1.293 g, 3.3 mmol) was refluxed in CH_3CN for 1.5 h with TLC monitoring of the reaction. After the successful formation of α-tosyloxyacetophenone **2**, potassium monomethyl malonate (0.468 g, 3 mmol) was added and the reaction mixture was refluxed (5 h) until complete consumption of **2** had occurred. Finally, K_2CO_3 (0.248 g, 1.8 mmol) was added and the reaction mixture was refluxed for 1.5 h to afford methyl 2,5-dihydro-2-oxo-4-phenylfuran-3-carboxylate **4a** in 72% yield.[15] Simultaneous addition of potassium monomethyl malonate and K_2CO_3 to the in situ formed α-tosyloxyacetophenone resulted in the formation of several side products. This is due to competition between O-alkylation and C-alkylation reactions of α-tosyloxyacetophenone with potassium monomethyl malonate. Alternative bases such as Et_3N and piperidine were found to be inferior to K_2CO_3. The optimised reaction conditions required 0.6 equiv of K_2CO_3 with respect to 1 equiv of ketone to provide satisfactory yields of the product. The insolubility of potassium monomethyl malonate in CH_3CN affects the yields of methyl 2-oxo-2-arylethyl malonates **3a–g**. However, a slight excess of potassium monomethyl malonate (1.2 equiv w.r.t. ketone) improved the yield of the open-chain malonate **3**. The key intermediate, methyl 2-oxo-2-arylethyl malonate **3**, was isolated in a few cases (Table 1) and characterised by IR, NMR and mass spectral analysis.[16] The ^{1}H NMR spectra of **3a–g** exhibited three sharp signals readily recognised as arising from two methylenes (δ 3.59 and δ 5.34) and –COOMe (δ 3.78) protons.

Table 1
Formation of methyl 2-oxo-2-arylethyl malonates from substituted acetophenones and the potassium monomethyl malonate using HTIB in CH_3CN



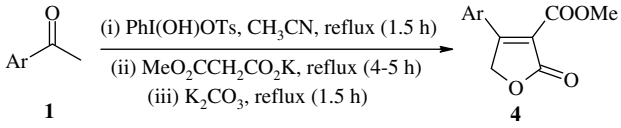
Entry	Ar **1**	Product	Yield[a] (%)
a	C_6H_5–	**3a**	87
b	4-$MeOC_6H_4$–	**3b**	84
c	2-$MeOC_6H_4$–	**3c**	77
d	4-ClC_6H_4–	**3d**	83
e	2-ClC_6H_4–	**3e**	81
f	4-Br–C_6H_4–	**3f**	80
g	4-O_2N–C_6H_4–	**3g**	74

[a] Isolated yield.



Scheme 2.

Table 2
Synthesis of 3,4-disubstituted furan-2-(5*H*)-ones from various acetophenones



Entry	Ar **1**	Product	Reaction time (h)	Yield[a] (%)
a	C_6H_5–	**4a**	11	72
b	4-$MeOC_6H_4$–	**4b**	12	76
c	2-$MeOC_6H_4$–	**4c**	14	69
d	2,4-$(MeO)_2C_6H_3$–	**4d**	13	68
e	4-MeC_6H_4–	**4e**	10	67
f	4-BrC_6H_4–	**4f**	13	66
g	2-BrC_6H_4–	**4g**	14	64
h	4-ClC_6H_4–	**4h**	11	69
i	2,4-$Cl_2C_6H_3$–	**4i**	13	71
j	4-$O_2NC_6H_4$–	**4j**	12	63

[a] Isolated yield.

To check the validity of the above-mentioned strategy for γ-butenolide synthesis (Scheme 1), we carried out the reaction of isolated methyl 2-oxo-2-phenylethyl malonate **3a** (1 mmol) with K_2CO_3 (0.6 mmol) in acetonitrile at reflux (1.5 h). We obtained methyl 2,5-dihydro-2-oxo-4-phenylfuran-3-carboxylate **4a** in 69% yield (Scheme 2). Comparing the ^{1}H NMR spectral data of **3a** with cyclisation product **4a** showed that the signal corresponding to the methylene protons flanked by the two ester groups around δ 3.58 had disappeared in the case of **4a**.

After establishing optimum reaction conditions, we carried out the synthesis of 3-carbomethoxy-4-arylfuran-2-(5*H*)-ones by treating variously substituted acetophenones with potassium monomethyl malonate using HTIB and the results are summarised in Table 2. The corresponding 3,4-disubstituted furan-2-(5*H*)-ones were obtained in good to excellent yields. To the best of our knowledge, this is the first report on the synthesis of 2-furan-(5*H*)-ones possessing an aryl group at C-4 position using potassium monomethyl malonate and substituted acetophenones.

In conclusion, we have developed a novel one-pot synthesis of 3-carbomethoxy-4-arylfuran-2-(5*H*)-ones via α-tosyloxylation of ketones with HTIB followed by treatment with potassium monomethyl malonate and K_2CO_3. Extension of this method to the preparation of other heterocyclic compounds of biological significance is underway in this laboratory.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.05.012.

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13. Reaction of dimethyl malonate with 1 equiv of KOH in MeOH at room temperature with stirring readily affords monopotassium methyl malonate.
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15. *Experimental procedure:* To a solution of ketone (3 mmol) in MeCN (15 mL) was added [hydroxyl(tosyloxy)iodo]benzene (3.3 mmol) and the mixture was refluxed for 1.5 h. After successful formation of the α-tosyloxyketone (as monitored by TLC), potassium monomethyl malonate (3.6 mmol) was added and the reaction mixture was refluxed for 4–5 h until complete consumption of the α-tosyloxyketone had taken place. Then the reaction mixture was cooled to room temperature and K_2CO_3 (1.8 mmol) was added and the reaction mixture was refluxed for another 1.5 h. After completion of the reaction, it was diluted with water and extracted with $CHCl_3$ (15 mL × 2). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a crude product, which was purified by silica gel column chromatography using petroleum ether and ethyl acetate as eluent to afford the pure product.
16. Spectral data of selected products:*Methyl 2-oxo-2-phenylethyl malonate* (**3a**): IR (KBr): ν = 3024, 2983, 2939, 1759, 1736, 1701, 1597, 1450, 1371, 1336, 1228, 1149, 1031, 973, 759, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.59 (s, 2H, CH_2), 3.78 (s, 3H, $COOCH_3$), 5.41 (s, 2H, OCH_2), 7.51 (t, J = 7.48 Hz, 2H, ArH), 7.61 (t, J = 7.48 Hz, 1H, ArH), 7.90 (d, 2H, J = 7.12 Hz, ArH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 41.08, 52.77, 70.64, 119.14, 127.86, 129.15, 132.21, 162.75, 165.22, 169.55. LCMS (M+1): m/z = 237.
Methyl 2-oxo-2-(4-methoxyphenyl)ethyl malonate (**3b**): IR (KBr): ν = 2981, 2953, 2845, 1749, 1712, 1693, 1600, 1506, 1431, 1284, 1161, 1022, 844, 779 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.58 (s, 2H, CH_2), 3.78 (s, 3H, $COOCH_3$), 3.88 (s, 3H, OCH_3), 5.36 (s, 2H, CH_2), 6.96 (d, 2H, J = 8.96 Hz, ArH), 7.89 (d, 2H, J = 8.96 Hz, ArH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 41.02, 52.64, 55.60, 66.57, 114.17, 127.08, 130.16, 164.22, 166.08, 189.80. LCMS (M+1): m/z = 267.
Methyl 2-oxo-2-(2-methoxyphenyl)ethyl malonate (**3c**): ^1H NMR (400 MHz, $CDCl_3$): δ = 3.57 (s, 2H, CH_2), 3.78 (s, 3H, $COOCH_3$), 3.95 (s, 3H, OCH_3), 5.31 (s, 2H), 6.99 (d, 1H, J = 8.52 Hz, ArH), 7.05 (t, 1H, J = 8 Hz, ArH), 7.52–7.55 (m, 1H, ArH), 7.94 (d, 1H, J = 7.95 Hz, ArH). LCMS (M+1): m/z = 267.
Methyl 2-oxo-2-(4-chlorophenyl)ethyl malonate (**3d**): ^1H NMR (400 MHz, $CDCl_3$): δ = 3.59 (s, 2H, CH_2), 3.78 (s, 3H, $COOCH_3$), 5.37 (s, 2H, CH_2), 7.48 (d, 2H, J = 8.6 Hz, ArH), 7.85 (d, 2H, J = 8.6 Hz, ArH). LCMS (M+1): 271.
Methyl 2-oxo-2-(2-chlorophenyl)ethyl malonate (**3e**): IR (KBr): ν = 3026, 2956, 2928, 1759, 1741, 1589, 1431, 1338, 1217, 1149, 971, 785 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.54 (s, 2H, CH_2), 3.76 (s, 3H, $COOCH_3$), 5.29 (s, 2H), 7.37 (m, 1H, ArH), 7.45 (m, 2H, ArH), 7.64 (m, 1H, ArH). ^{13}C NMR (400 MHz, $CDCl_3$):δ = 40.82, 52.69, 69.00, 127.23, 130.17, 130.68, 131.70, 133.06, 135.49, 165.91, 166.53, 194.33. LCMS (M+1): m/z = 271.
Methyl 2-oxo-2-(4-bromophenyl)ethyl malonate (**3f**): IR (KBr): ν = 3022, 2995, 1753, 1730, 1701, 1585, 1432, 1346, 1203, 1159, 1068, 981, 821 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.58 (s, 2H, CH_2), 3.78 (s, 3H, $COOCH_3$), 5.33 (s, 2H, OCH_2), 7.64 (d, 2H, J = 8.64 Hz, ArH), 7.76 (d, 2H, J = 8.64 Hz, ArH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 40.88, 52.69, 66.59, 129.29, 132.30, 132.45, 132.71, 165.95, 166.58, 190.53. LCMS (M+1):m/z = 316.
Methyl 2,5-dihydro-2-oxo-4-phenylfuran-3-carboxylate (**4a**): IR (KBr): ν = 3024, 2970, 2937, 1751, 1732, 1637, 1442, 1372, 1340, 1242, 1069, 1039, 768, 696 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.89 (s, 3H, $COOCH_3$), 5.18 (s, 2H, OCH_2), 7.46–7.55 (m, 5H, ArH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 52.79, 70.66, 119.10, 127.87, 129.15, 132.24, 162.77, 165.31, 169.60. LCMS (M+1): m/z = 219.
Methyl 2,5-dihydro-4-(4-methoxyphenyl)-2-oxofuran-3-carboxylate (**4b**): IR (KBr): ν = 3018, 2953, 2927, 1739, 1605, 1515, 1435, 1215, 1179, 1030, 753, 667 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.87 (s, 3H, OMe), 3.91 (s, 3H, OMe), 5.16 (s, 2H, OCH_2), 6.98 (d, 2H, J = 8.92 Hz, ArH), 7.56 (d, 2H, J = 8.88 Hz, ArH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 52.72, 55.56, 70.38, 114.57, 116.49, 121.35, 130.08, 162.91, 163.34, 164.51, 170.08. LCMS (M+1): m/z = 249.
Methyl 2,5-dihydro-4-(2-methoxyphenyl)-2-oxofuran-3-carboxylate (**4c**): IR (KBr): ν = 3076, 2951, 2838, 1731, 1599, 1536, 1462, 1434, 1248, 1165, 1022, 802, 754 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.81 (s, 3H, OMe), 3.84 (s, 3H, OMe), 5.18 (s, 2H, OCH_2), 6.99 (d, 1H, J = 11.2 Hz, ArH), 7.04 (t, 1H, J = 8.8 Hz, ArH), 7.31 (d, 1H, J = 8.0 Hz, ArH), 7.47 (t, 1H, J = 7.6 Hz, ArH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 52.43, 55.45, 71.45, 111.51, 118.67, 120.44, 120.93, 129.29, 133.20, 156.93, 162.76, 163.93, 169.85. LCMS (M+1):m/z = 249.
Methyl 2,5-dihydro-2-oxo-4-p-tolylfuran-3-carboxylate (**4e**): IR (KBr): ν = 3032, 2960, 2926, 2870, 1750, 1716, 1631, 1609, 1433, 1344, 1249, 1132, 819, 787, 713 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H, $ArCH_3$), 3.78 (s, 3H, $COOCH_3$), 5.39 (s, 2H, OCH_2), 7.28 (d, 2H, J = 8.96 Hz, ArH), 7.81 (d, 2H, J = 8 Hz, ArH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 21.64, 52.73, 70.54, 118.09, 126.24, 127.89, 129.85, 143.23, 163.01, 165.11, 169.79. LCMS (M+1): m/z = 233.
Methyl 2,5-dihydro-4-(4-bromophenyl)-2-oxofuran-3-carboxylate (**4f**): ^1H NMR (400 MHz, $CDCl_3$): δ = 3.90 (s, 3H, OMe), 5.15 (s, 2H, OCH_2), 7.43 (d, 2H, J = 8.68 Hz, ArH), 7.63 (d, 2H, J = 8.68 Hz, ArH). LCMS (M+1): m/z = 297.
Methyl 2,5-dihydro-4-(4-chlorophenyl)-2-oxofuran-3-carboxylate (**4h**): IR (KBr): ν = 2982, 2847, 1747, 1723, 1617, 1488, 1376, 1341, 1299, 1252, 832, 764 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 3H, OMe), 5.17 (s, 2H, OCH_2), 7.53 (d, 2H, J = 11.2 Hz, ArH), 7.48 (d, 2H, J = 11.2 Hz, ArH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 52.93, 70.49, 119.51, 127.57, 129.32, 129.53, 138.60, 162.52, 164.20, 169.24. LCMS (M+1): m/z = 253.