Regioselective synthesis of functionalized 3,5-diketoesters and 2,4-diketosulfones by uncatalyzed condensation of 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadienes with α,β-unsaturated acid chlorides and sulfonyl chlorides†

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Received 16th June 2008, Accepted 26th June 2008
First published as an Advance Article on the web 25th July 2008
DOI: 10.1039/b810151e

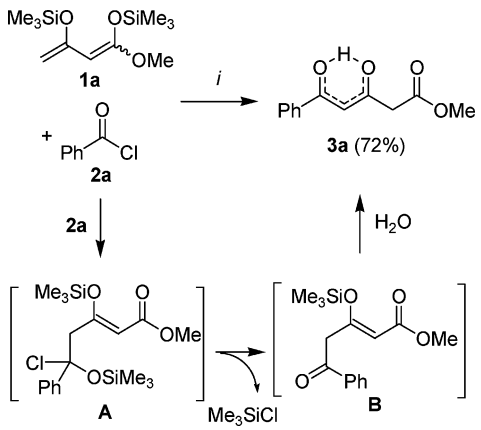
The reaction of 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadienes with α,β-unsaturated and functionalized acid chlorides afforded a variety of 3,5-diketoesters which are not readily available by other methods. The reaction of 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene with sulfonyl chlorides allows a direct synthesis of 2,4-diketosulfones.

Introduction

1,3,5-Tricarbonyl derivatives and their higher homologues are of considerable pharmacological relevance and occur in a variety of natural products (polyketides). In addition, they are versatile synthetic intermediates.[1] Important syntheses of polyketides rely on the condensation of 1,3-dicarbonyl dianions[2] with carboxylic acid derivatives.[3–5] However, there are several drawbacks, such as proton transfer and O-acylation. In addition, functionalized substrates, such as α,β-unsaturated esters, cannot be successfully used, due to various side-reactions (*e.g.* conjugate addition of the dianion onto the double bond of the substrate). In fact, the preparative scope is limited to substrates which tolerate the presence of strong nucleophiles and bases. The employment of *N*-acyl-2-methylaziridines[6] and Weinreb amides[7] allow some of these problems to be addressed.

Recently, we reported[8] the condensation of 1,3-bis(silyl enol ethers)[9] with acid chlorides. This strategy provides a convenient approach to several 1,3,5-tricarbonyl compounds under mild conditions. In our previous paper[8] we focussed on reactions of 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**1a**), readily available from methyl acetoacetate,[10] with various simple aromatic and aliphatic acid chlorides. For example, the reaction of **1a** with benzoyl chloride (**2a**) afforded 3,5-dioxoester **3a** in good yield (Scheme 1). Product **3a** mainly exists in its enol tautomeric form. The dashed line given in the structure of **3a** indicates that there is a fast equilibrium between two enolic forms. In fact, only one set of signals is observed by NMR. This type of fast equilibrium is also observed in case of acetylacetone.

It is of note that it proved to be important that the reaction was carried out in the *absence* of a Lewis acid. The formation of **3a** can be explained by attack of the terminal carbon atom of **1a** onto the acid chloride. This step might be catalyzed by the presence of a catalytic amount of HCl present in the acid chloride (formed by its hydrolysis). The reaction works equally well using commercially available (new bottle) or freshly distilled **2a**. The yields significantly dropped when relatively old material was employed. Due to the preparative utility of this reaction, we studied its scope in more detail and the results of our efforts are reported herein. The present study includes, for the first time, the variation of the 1-methoxy-1,3-bis(silyloxy)-1,3-butadiene and of the acid chloride (including unsaturated and functionalized derivatives and sulfonic acid chlorides). Note, the products reported herein are not available by direct reaction of 1,3-dicarbonyl dianions with carboxylic acid derivatives.



Scheme 1 Possible mechanism of the reaction of 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene **1a** with benzoyl chloride (**2a**).[8] *Conditions*: *i*: 1) CH_2Cl_2, −78 → 20 °C, 2) $NaHCO_3$, H_2O; keto : enol = 0 : 100.

Results and discussion

Variation of the 1,3-bis(trimethylsilyloxy)-1,3-butadiene

The reaction of benzoyl chloride (**2a**) with 1-alkoxy-1,3-bis(silyloxy)-1,3-butadienes **1b** and **1c**, containing a substituent located at the central carbon atom, afforded the 3,5-dioxoesters

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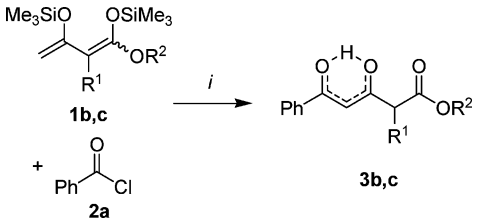
† Electronic supplementary information (ESI) available: Full experimental details. CCDC reference number 691729. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b810151e

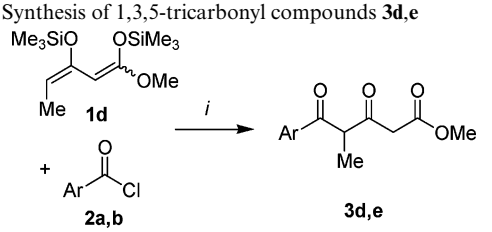
Table 1 Synthesis of 1,3,5-tricarbonyl compounds **3b**,**c**



3	R^1	R^2	Keto : enol	%[a]
b	Me	Et	87 : 13	43
c	Et	Me	67 : 33	50

[a] Yields of isolated products; the products contain benzoic acid which could not be separated (see Experimental section) *Conditions*: *i*: CH_2Cl_2, −78 → 20 °C, 2) $NaHCO_3$, H_2O.

Table 2 Synthesis of 1,3,5-tricarbonyl compounds **3d**,**e**



3	Ar	keto : enol	%[a]
d	Ph	100 : 0	32
e	4-$(NO_2)C_6H_4$	100 : 0	35

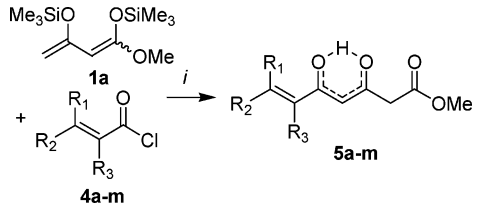
[a] Yields of isolated products; the products contain benzoic or 4-nitrobenzoic acid which could not be separated (see Experimental section) *Conditions*: *i*: 1) CH_2Cl_2, −78 → 20 °C, 2) $NaHCO_3$, H_2O.

3b and **3c**, respectively (Table 1). However, a considerable amount of benzoic acid could not be separated from the product. The presence of benzoic acid might be explained by the instability of the products which presumably undergo a retro-Claisen reaction during silica gel chromatography or during the reaction. In contrast to the unsubstituted diketoester **3a**, products **3b**,**c** mainly exist in their keto forms.

The reaction of benzoyl chlorides **2a**,**b** with 1-methoxy-1,3-bis(silyloxy)-1,3-butadiene **1d**, derived from methyl 3-oxopentanoate, afforded 1,3,5-tricarbonyl compounds **3d** and **3e**. The products again contained benzoic acid which could not be separated (Table 2). The ethyl ester analogue of **3d** has been previously reported.[6] Products **3d**,**e** exclusively reside in their keto form. This is not unexpected as the presence of a substituent located between the two carbonyl groups of 1,3-diketones usually results in a considerable increase of the amount of the keto tautomer.

The reaction of **2a** with 1-phenyl-1,3-bis(trimethylsilyloxy)-1,3-butadiene and 2,4-bis(trimethylsilyloxy)-1,3-pentadiene, derived from benzoylacetone and acetylacetone, respectively, proved to be unsuccessful (no conversion). This is a result of the lower reactivity of 1,3-diketone- compared to β-ketoester-derived 1,3-bis(silyl enol ethers). Due to these limitations, the variation of the 1,3-bis(silyloxy)-1,3-butadiene was not further studied. Taking into account the results of our previous study in this field,[8] the condensation of 1,3-bis(silyl enol ethers) with acid chlorides

Table 3 Synthesis of 6,7-unsaturated 3,5-dioxoesters **5a–m**



5	R^1	R^2	R^3	%[a]
a	H	Ph	H	71
b	H	Ph	Me	63
c	H	4-MeC_6H_4	H	17
d	H	4-$(MeO)C_6H_4$	H	37
e	H	3,4-$(MeO)_2C_6H_3$	H	35
f	H	3,4-(–OCH_2O–)C_6H_3	H	30
g	H	4-FC_6H_4	H	20
h	H	3-ClC_6H_4	H	14
i	H	4-$(O_2N)C_6H_4$	H	13
j	H	2-Furyl	H	30
k	H	2-Thienyl	H	30
l	Me	Me	H	71
m	H	CH_3CH=CH	H	47

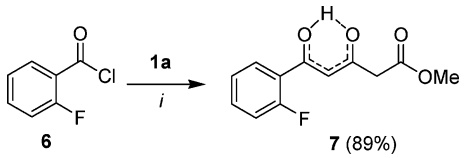
[a] Yields of isolated products; keto : enol = 0 : 100 for all products *Conditions*: *i*: 1) CH_2Cl_2, −78 → 20 °C, 2) $NaHCO_3$, H_2O.

seems to be restricted to β-ketoester-derived and unsubstituted 1,3-bis(silyl enol ethers), such as **1a**.

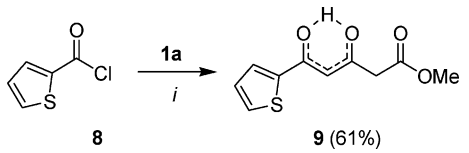
Variation of the acid chloride

The reaction of 1,3-bis(silyloxy)-1,3-butadiene **1a** with α,β-unsaturated acid chlorides **4a–m** afforded the 6,7-unsaturated 3,5-dioxoesters **5a–m** (Table 3). All products exclusively exist in their enol tautomeric form. Similar to compound **3a**, a rapid equilibrium between two enolic structures is present. Therefore, only one set of signals is observed by NMR. The best yields were obtained for phenyl- and methoxyphenyl-substituted acrylic acid chlorides. Good yields were obtained also for **5l** and **5m** which were prepared from 3-methylbutanoyl chloride and hexa-2,4-dienoic acid chloride, respectively. To our surprise, the yields of the products derived from aryl-substituted acrylic acid chlorides very much depend on the type of the aryl group. Whereas a good yield was obtained for products **5a**,**b** (containing a phenyl group), the yields dropped for electron-rich and (even more) for electron-poor aryl groups.

In contrast, we have reported earlier that equally good yields were obtained for the reaction of **1a** with electron-rich and electron-poor benzoyl chlorides. The yields dropped for sterically encumbered acid chlorides. The reaction of **1a** with 2-fluorobenzoyl chloride (**6**), carried out for reasons of comparison, gave the 5-(2-fluorophenyl)-3,5-dioxoester **7** in good yield (Scheme 2). The use of heterocyclic substrates has not been studied in our previous report. The reaction of **1a** with (thien-2-yl)carboxylic chloride (**8**), carried out again for reasons of comparison, afforded the 5-(thien-2-yl)-3,5-dioxoester **9** in good yield (Scheme 3). These results show that the reaction of 1,3-bis(silyloxy)-1,3-butadienes with α,β-unsaturated acid chlorides is much more prone to slight changes of the substitution pattern compared to the reaction with simple benzoyl chlorides. It is noteworthy, that relatively good yields were obtained for products



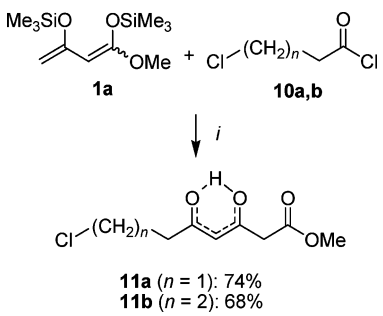
Scheme 2 Synthesis of 5-(2-fluorophenyl)-3,5-dioxoester **9** *Conditions*: *i*: 1) CH_2Cl_2, −78 → 20 °C, 2) $NaHCO_3$, H_2O; keto : enol = 0 : 100.



Scheme 3 Synthesis of 5-(thien-2-yl)-3,5-dioxoester **9** *Conditions*: *i*: 1) CH_2Cl_2, −78 → 20 °C, 2) $NaHCO_3$, H_2O; keto : enol = 0 : 100.

5l and **5m** containing a methyl and a (prop-1-en-1-yl) group, respectively.

Some years ago, we reported the synthesis of 3(2*H*)furanones based on reactions of 1,3-bis(silyl enol ethers) with chloroacetyl chloride.[11] The reaction of 1,3-bis(silyloxy)-1,3-butadiene **1a** with 3-chloropropanoyl chloride (**10a**) and 4-chlorobutanoyl chloride (**10b**) proceeded with very good chemoselectivity and afforded the ω-chloro-3,5-dioxoesters **11a** and **11b**, respectively, in very good yields (Scheme 4). It is of note that the reaction of the dianion of methyl acetoacetate with **10a** and **10b** and their corresponding ester derivatives failed. Compounds **7**, **9**, and **11a**,**b** exclusively exist in their enol tautomeric form.

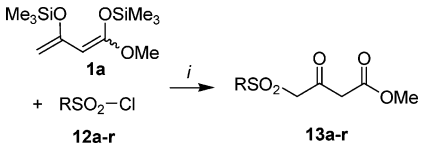


Scheme 4 Synthesis of **11a**,**b** *Conditions*: *i*: 1) CH_2Cl_2, −78 → 20 °C, 2) $NaHCO_3$, H_2O; keto : enol = 0 : 100 for both products.

The reaction of enolates with sulfonyl chlorides was previously reported to result in chlorination rather than formation of β-ketosulfones.[12,13] β-Ketosulfones are available by reaction of enolates with disulfides and subsequent oxidation of the sulfide moiety.[14] Kamigata *et al.* reported the synthesis of β-ketosulfones by $Ru(PPh_3)_2Cl_2$-catalyzed reaction of silyl enol ethers with sulfonyl chlorides.[15] However, the scope of this method is limited to acetophenone-derived silyl enol ethers. Other reactions of silyl enol ethers with sulfonyl chlorides have, to the best of our knowledge, not been reported to date.

Our starting point was the reaction of the dianion of methyl acetoacetate with tosyl chloride which resulted in the formation of complex mixtures under various conditions. In contrast, the reaction of 1,3-bis(silyloxy)-1,3-butadiene **1a** with sulfonyl chlorides proved to be, in principle, possible. However, the yields strongly depended on the type of substrate employed. The best

Table 4 Synthesis of 3-oxo-sulfonylesters **13a–p**



13	R	keto : enol	% (**13**)[a]
a	Ph	60 : 40	61
b	4-MeC_6H_4	78 : 22	87
c	4-$iPrC_6H_4$	60 : 40	99
d	4-$tBuC_6H_4$	67 : 33	38
e	4-PhC_6H_4	60 : 40	17
f	4-$(MeO)C_6H_4$	33 : 67	89
g	3,4-$(MeO)_2C_6H_3$	60 : 40	78
h	2-Naph	75 : 25	33
j	4-ClC_6H_4	60 : 40	61
k	4-FC_6H_4	55 : 45	20
l	2,5-$Cl_2C_6H_3$	60 : 40	6
m	4-Cl-3-FC_6H_3	50 : 50	14
n	4-BrC_6H_4	55 : 45	6
o	4-$(MeCO)C_6H_4$	55 : 45	12
p	Me	100 : 0	10
q	*n*Bu	100 : 0	20
r	*n*Oct	100 : 0	15

[a] Yields of isolated products *Conditions*: *i*: 1) CH_2Cl_2, −78 → 20 °C, 2) $NaHCO_3$, H_2O.

yields were again obtained when the reactions were carried out in the absence of Lewis acid. The reaction of **1a** with phenylsulfonyl chloride (**12a**) and its alkyl-substituted derivatives **12b–d** afforded the 3-oxo-4-sulfonylesters **13a–d** in good to excellent yield (Table 4). In contrast, the yield of biphenyl derivative **13e** was rather low. The condensation of **1a** with methoxy-substituted phenylsulfonyl chlorides **12f**,**g** gave products **13f**,**g** in very good yields. 3-Oxo-4-sulfonylester **13h** was prepared in moderate yield from 2-naphthylsulfonyl chloride. The reactions of **1a** with 1-naphthylsulfonyl chloride (**12i**) failed, presumably due to steric reasons. The reaction of **1a** with halogen-substituted phenylsulfonyl chlorides gave the 3-oxo-4-sulfonylester **13j–n**. Except from 4-chlorophenyl-derivative **13j** (61%), the yields were rather low. The great difference between the yields of 4-chlorophenyl and 4-bromophenyl derivatives **13j** and **13n** is surprising. The results are reproducible but cannot convincingly be explained at present. The individual quality of the sulfonyl chlorides may have a considerable influence on the reactions. The reaction of **1a** with (4-acetylphenyl)sulfonyl chloride gave **13o**, albeit, in low yield. The arylsulfones **13a–o** exist as mixtures of keto-enol-tautomers. The condensation of **1a** with alkylsulfonyl chlorides **12p–r** afforded products **13p–r** in low yields. These products exclusively exist in their keto form.

The structures of all products were confirmed by spectroscopic methods. The structure of **13j** was independently confirmed by X-ray crystal structure analysis (Fig. 1).†

Conclusions

In conclusion, we have reported the synthesis of 3-oxo-5-hydroxy-hepta-4,6-dienoates by reaction of 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene with α,β-unsaturated acid chlorides. The reaction of 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene with sulfonyl chlorides provides a convenient

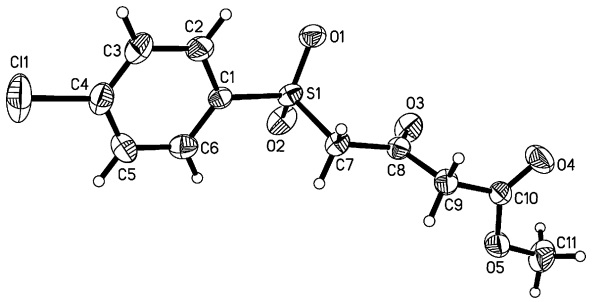


Fig. 1 Ortep plot of **13j** (50% probability level).

approach to 4-arylsulfonyl-3-ketobutanoates. It is worth noting that the products reported herein are not available by direct reaction of 1,3-dicarbonyl dianions with carboxylic acid derivatives.

Experimental section

General comments

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^{1}H and ^{13}C NMR spectra the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, H_2O) or electrospray ionization (ESI). For preparative scale chromatography, silica gel (60–200 mesh) was used. Melting points are uncorrected.

General procedure for the synthesis of 3,5-dioxoalkanoates 3, 5, 7, 9, and 11

To a CH_2Cl_2 solution of **1** (2.0 equiv.) was slowly added the acid chloride (1.0 equiv.) at −78 °C. The reaction mixture was slowly warmed to 20 °C during 6 h and the solution was stirred at 20 °C for further 6–8 h. To the solution was added a saturated aqueous solution of $NaHCO_3$ (20 mL). The organic and the aqueous layer were separated and the latter was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo.* The residue was purified by column chromatography (silica gel, *n*-heptane–EtOAc) to give the respective products.

Methyl 5-hydroxy-7-phenyl-3-oxohepta-4,6-dienoate (5a)

Starting with **4a** (0.96 g, 5.76 mmol) and **1a** (3.00 g, 11.52 mmol), dissolved in CH_2Cl_2 (10 ml), **5a** was isolated as an orange oil (1.01 g, 71%). ^{1}H NMR (300 MHz, $CDCl_3$, keto : enol = 0 : 100): $\delta = 3.46$ (s, 2H, CH_2), 3.75 (s, 3H, CH_3), 5.76 (s, 1H, CH), 6.58 (d, $^{3}J = 15.9$ Hz, 1H, C*H*=CH), 7.37–7.54 (m, 5H, Ph), 7.63 (d, $^{3}J = 15.9$ Hz, 1H, C*H*=CH), 14.84 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 47.1$ (CH_2), 52.8 (CH_3), 101.1 (CH), 122.4 (*C*H=CH), 128.4, 129.3, 130.5 (Ph), 135.2 (C), 150.0 (*C*H=CH), 168.3, 177.1, 192.9 (CO). IR (neat, cm^{-1}): $\nu = 3061$ (m), 3027 (m), 2953 (m), 1742 (s), 1636 (s), 1584 (s, br), 1496 (m), 1437 (s), 1328 (s), 1261 (s), 1203 (m), 1129 (s), 1073 (m), 1017 (m), 973 (m), 945 (m), 931 (m), 867 (m), 770 (m). MS (CI, isobutane) m/z (%) = 247 ([M + 1]$^+$, 100). Anal. calcd. for $C_{14}H_{14}O_4$ (246.26): C, 68.28; H, 5.73. Found: C, 68.20; H, 5.39%.

Methyl 3,5-dioxo-5-(thiazol-2-yl)pentanoate (9)

Starting with **8** (0.84 g, 5.76 mmol), CH_2Cl_2 (10 ml) and 1,3-bis(silyl enol ether) **1a** (3.00 g, 11.52 mmol), **9** was isolated as a brownish oil (0.80 g, 61%). ^{1}H-NMR (300 MHz, $CDCl_3$, keto : enol = 0 : 100): $\delta = 3.43$ (s, 2H, CH_2), 3.77 (s, 3H, CH_3), 6.15 (s, 1H, CH), 7.14 (dd, $^{3}J = 5.0$ Hz, $^{3}J = 3.8$ Hz, 1H, CH), 7.63 (dd, $^{3}J = 5.0$ Hz, $^{4}J = 1.2$ Hz, 1H, CH), 7.72 (dd, $^{3}J = 3.8$ Hz, $^{4}J = 1.2$ Hz, 1H, CH), 15.49 (s, 1H, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 44.0$ (CH_2), 52.8 (CH_3), 97.3, 128.7, 131.2, 133.3 (CH), 141.0 (C), 168.4, 181.4, 182.8 (CO). IR (neat, cm^{-1}): $\nu = 3106$ (m), 3001 (w), 2953 (m), 2845 (w), 1742 (s), 1618 (s, br), 1519 (s), 1436 (s), 1412 (s), 1353 (m), 1272 (s, br), 1156 (m), 1084 (m), 1067 (m), 1015 (m), 948 (m), 861 (m), 789 (m), 727 (m). MS (EI, 70 eV) $m/z = 226$ (M$^+$, 13.9), 194 (19.5), 166 (24.3), 153 (40.4), 111 (100), 69 (40.6). HRMS (EI, 70 eV): calcd. for $C_{10}H_{10}O_4S$ (M$^+$) 226.0294, found 226.0298.

Methyl 7-chloro-5-hydroxy-3-oxohept-4-enoate (11a)

Starting with **10a** (0.55 ml, 5.76 mmol) dissolved in CH_2Cl_2 (10 ml) and **1a** (3.00 g, 11.52 mmol), **11a** was isolated as a yellow oil (0.88 g, 74%). ^{1}H-NMR (300 MHz, $CDCl_3$, keto : enol = 0 : 100): $\delta = 2.80$ (t, $^{3}J = 6.6$ Hz, 2H, CH_2), 3.38 (s, 2H, CH_2), 3.75 (s, 3H, CH_3), 3.76–3.78 (m, 2H, CH_2), 5.68 (s, 1H, CH), 14.93 (s, 1H, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 39.4$, 41.1, 44.8 (CH_2), 52.8 (CH_3), 101.2 (CH), 168.1, 186.4, 189.8 (CO). IR (neat, cm^{-1}): $\nu = 3002$ (m), 2956 (s), 2848 (m), 1742 (s), 1617 (s, br), 1437 (s), 1407 (m), 1331 (s), 1263 (s), 1157 (s), 1015 (m), 922 (m), 785 (m, br). MS (EI, 70 eV) $m/z = 206$ (M$^+$, 8.2), 174 (17.9), 146 (10.4), 143 (73.6), 139 (13.1), 135 (13.8), 133 (41.1), 116 (16.9), 111 (20.3), 101 (67.0), 97 (26.3), 93 (14.4), 91 (43.0), 84 (16.2), 69 (100). HRMS (EI, 70 eV): calcd. for $C_8H_{11}O_4Cl$ (M$^+$) 206.0340, found 206.0342.

General procedure for the synthesis β,δ-diketosulfones 13a–r

To a CH_2Cl_2 solution (10 mL) of 1,3-bis(silyl enol ether) **1a** (11.5 mmol) was added sulfonyl chloride **12a–r** (5.8 mmol) at −78 °C under argon atmosphere. The temperature of the reaction mixture was allowed to rise to 20 °C during 14 h and, subsequently, a saturated aqueous solution of $NaHCO_3$ (20 mL) was added. The organic layer was separated and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, *n*-heptane : EtOAc = 10 : 1).

Methyl 3-oxo-4-(phenylsulfonyl)butanoate (13a)

Starting with **12a** (1.02 g, 5.8 mmol) and **1a** (3.00 g, 11.5 mmol), dissolved in CH_2Cl_2 (10 mL), **13a** was isolated as a yellow solid (0.90 g, 61%), mp 62–64 °C. ^{1}H-NMR (300 MHz, $CDCl_3$, keto : enol = 60:40): enol: $\delta = 3.74$ (s, 3H, OCH_3), 3.94 (s, 2H, CH_2), 5.19 (s, 1H, CH), 7.54–7.61 (m, 2H, Ar), 7.66–7.73 (m, 1H, Ar), 7.88–7.94 (m, 2H, Ar), 11.76 (s, 1H, OH); keto: $\delta = 3.75$ (s, 3H, OCH_3), 3.78, 4.37 (s, 2H, CH_2), 7.54–7.61 (m, 2H, Ar), 7.66–7.73 (m, 1H, Ar), 7.88–7.94 (m, 2H, Ar). ^{13}C-NMR (75 MHz, $CDCl_3$): enol: $\delta = 52.0$ (OCH_3), 62.1 (CH_2), 95.5 (CH), 128.6, 129.8, 134.9, 138.7 (Ar), 164.4, 172.4 (CO); keto: $\delta = 49.6$ (CH_2), 53.0 (OCH_3), 67.1 (CH_2), 128.6, 129.6, 134.6, 138.8 (Ar), 167.2, 191.3 (CO). IR

(KBr, cm^{-1}): ν = 3439 (w), 3103 (s), 3068 (s), 2959 (s), 2911 (s), 2854 (s), 1747 (m), 1724 (m), 1587 (s), 1481 (s), 1446 (m), 1439 (s), 1409 (s), 1373 (s), 1339 (m), 1323 (m), 1264 (s), 1205 (m), 1154 (m), 1127 (s), 1090 (s), 1072 (s), 1057 (s), 1024 (s), 948 (s), 869 (s), 796 (s), 748 (s), 720 (s), 688 (s), 652 (s), 607 (s), 541 (s), 528 (s), 461 (s). MS (EI, 70 eV): m/z (%) = 256 (M^+, 2), 225 (19), 224 (11), 192 (31), 183 (25), 174 (9), 160 (18), 141 (87), 135 (17), 125 (17), 118 (13), 115 (39), 101 (45), 94 (12), 91 (19), 78 (20), 77 (100), 74 (14), 69 (16), 59 (13), 51 (37), 43 (14). HRMS (EI, 70 eV): calcd for $C_{11}H_{12}O_5S$ (M^+) 256.0400, found: 256.0396. Anal. calcd. for $C_{11}H_{12}O_5S$ (256.27): C 51.55, H 4.72, S 12.51; found: C 51.70, H 4.58, S 12.40%.

Acknowledgements

Financial support from the State of Mecklenburg-Vorpommern is gratefully acknowledged.

Notes and references

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