Photosensitized Oxidation of Furans; Part 18:[1] A Simple Method for a One-Pot Synthesis of Functionalized Methyl *cis*-4-Oxoalk-2-enoates

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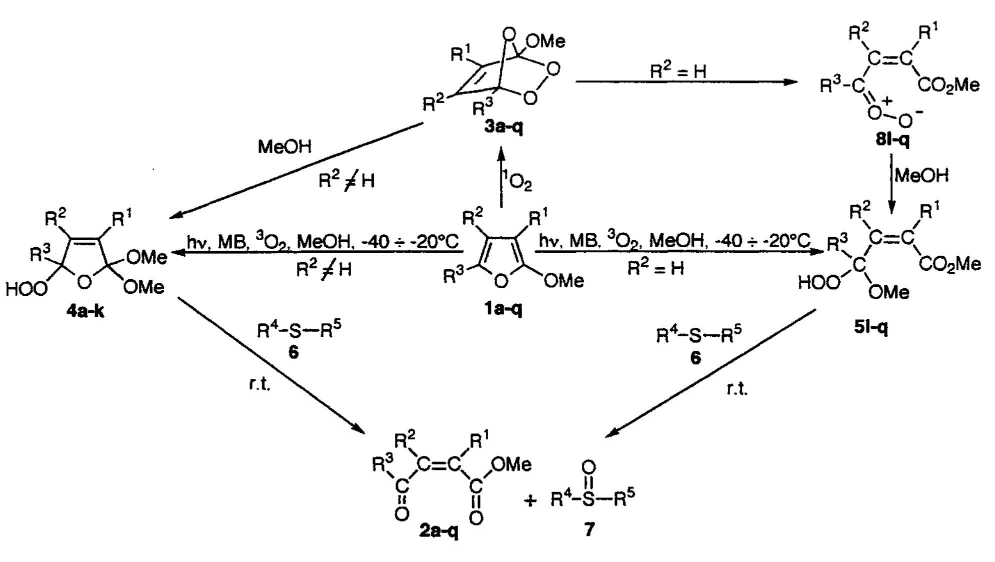
Functionalized methyl *cis*-4-oxoalk-2-enoates **2** are synthesized in a one-pot procedure by singlet oxygen oxygenation of the corresponding 2-methoxyfurans **1** in methanol and reduction of the resulting hydroperoxides **4** and **5** by the sulfides **6** which are selectively oxidized into the sulfoxides **7**. The synthetic method has a wide range of applicability and affords compounds **2** stereoselectively and in good yields; concomitantly the sulfoxides **7** are obtained in excellent yields.

Alkyl 4-oxoalk-2-enoates and corresponding acids are interesting multifunctional compounds which have been used as agrochemicals[2] or as drug[3-5] and agrochemical[5,6] intermediates. They have been obtained by various patent pathways,[4,5,7] such as the Friedel-Crafts acylation by maleic anhydride,[8] the Claisen–Schmidt condensation of glyoxylic acid[9] and also the Knoevenagel condensation of α-oxo aldehydes[10] or α-diketones.[11]

Long ago we obtained ethyl *cis*-4-oxoalk-2-enoates by air oxidation of 2-ethoxyfurans unsubstituted at C-3 and C-4, or methyl substituted at C-3.[12] A similar oxidation process was subsequently reported for 2-methoxyfurans methyl or phenyl substituted at C-4,[13] or at C-3 and C-4.[14] Recently we have observed that 2-methoxyfurans substituted at C-4 with alkyl or phenyl substituents un-



Entries	R¹	R²	R³
a	CO_2Me	Et	Et
b	CO_2Me	Me	Ph
c	CO_2Et	Ph	Ph
d	CO_2Me	Me	CH_2Ph
e	H	CO_2Me	Ph
f	H	COMe	Ph
g	H	CO_2Me	$4\text{-}BrC_6H_4$
h	H	CO_2Me	$4\text{-}MeC_6H_4$
i	H	CO_2Me	$3\text{-}MeOC_6H_4$
j	CO_2Me	CO_2Me	Ph
k	CO_2Me	CO_2Me	CH_2Ph
l	CO_2Me	H	Ph
m	COMe	H	Ph
n	CO_2Me	H	$4\text{-}BrC_6H_4$
o	CO_2Me	H	$4\text{-}MeOC_6H_4$
p	CO_2Me	H	$4\text{-}MeC_6H_4$
q	CO_2Me	H	$3\text{-}MeOC_6H_4$

6,7	R⁴	R⁵
a	Et	Et
b	Ph	Ph
c	Ph	Me
d	*t*-But	*t*-But

Scheme

dergo oxidation with triplet oxygen only very slowly when an electron-withdrawing group is linked at C-3, as in the case of furans **1a–d**.[1,15] In contrast, the absence of the alkyl or phenyl group and the presence of one or two electron-withdrawing groups at C-3 and/or C-4 make the furans stable to air oxidation, as observed for **1e–q**. Here we report a general method for the synthesis of the functionalized *cis* oxo esters **2** via the *endo*-peroxides **3** and the hydroperoxides **4** or **5**. At the same time, the procedure is a facile and a selective pathway for the oxidation of the sulfides **6** into the sulfoxides **7**[16] (Scheme).

Table 1. Methyl 4-Oxoalk-2-enoates **2** Prepared[a]

Product	Reaction Conditions[b] and Product Isolation[c]		Yield (%)[d]	mp (°C) (Lit.)	IR ($CHCl_3$) ν (cm^{-1})	^1H NMR ($CDCl_3$) δ, J (Hz)	^{13}C NMR ($CDCl_3$) δ
	Time (min)	Light petroleum/Et_2O					
2a	180	9 : 1	77	oil	1729 1638	1.09 (t, J = 7.3, Me) and 1.16 (t, J = 7.3, Me) (together 6H), 2.35 (q, J = 7.3, 2H, CH_2), 2.59 (q, J = 7.3, 2H, CH_2), 3.73 and 3.83 (2 × s, 6H, 2 × OMe)	7.2 (q, Me), 11.8 (q, Me), 25.5 (t, CH_2), 35.1 (t, CH_2), 52.5 and 52.6 (2 × q, 2 × OMe), 123.3 (s, C-2), 161.4 (s, C-3), 163.5 and 165.1 (2 × s, 2 × CO_2), 206.3 (s, CO)
2b[e]	60	9 : 1	75	87–88[f]	1729 1677 1648	2.18 (s, 3H, Me), 3.56 and 3.90 (2 × s, 6H, 2 × OMe), 7.40–8.00 (m, 5H, ArH)	19.1 (q, Me), 52.6 (q, 2 × OMe), 125.8 (s, C-2), 128.6, 128.9 and 133.8 (3 × d, CH of Ar), 134.0 (s, C-1 of Ar), 154.5 (s, C-3), 163.0 and 165.0 (2 × s, 2 × CO_2), 196.2 (s, CO)
2c	30	17 : 3	84	127–128[f]	1728 1676 1620	1.03 (t, J = 7.0, 3H, Me), 3.66 (s, 3H, OMe), 4.14 (q, J = 7.0, 2H, OCH_2), 7.30–7.80 (m, 10H, 2 × ArH)	13.5 (q, Me), 52.6 (q, OMe), 61.7 (t, OCH_2), 126.4 (s, C-2), 127.5, 128.8, 129.5, 130.0 and 133.6 (5 × d, CH of two Ar), 133.1 and 135.0 (2 × s, 2 × C-1 of two Ar), 154.9 (s, C-3), 163.2 and 165.0 (2 × s, 2 × CO_2), 193.8 (s, CO)
2d	30		83[g]		1750 1728 1642	1.89 (s, 3H, Me), 3.78 and 3.84 (2 × s, 6H, 2 × OMe), 3.95 (s, 2H, CH_2), 7.20–7.40 (m, 5H, ArH)	10.5 (q, Me), 48.0 (t, CH_2), 52.5 and 52.6 (2 × q, 2 × OMe), 124.6 (s, C-2), 127.2, 128.6 and 129.8 (3 × d, CH of Ar), 132.7 (s, C-1 of Ar), 156.2 (s, C-3), 163.5 and 164.9 (2 × s, 2 × CO_2), 203.4 (s, CO)
2e	15	17 : 3	98	83 (83.5[33])			
2f	15	4 : 1	76	oil[34]			
2g	15	4 : 1	98	71 (71–73[1])			
2h	15	17 : 3	92	77–79[f]	1727 1677	2.41 (s, 3H, Me), 3.62 and 3.77 (2 × s, 6H, 2 × OMe), 7.08 (s, 1H, CH), 7.27 and 7.60 (2d, J = 8.1, 4H, ArH)	21.7 (q, Me), 52.3 and 53 1 (2 × q, 2 × OMe), 128.8 and 129.5 (2 × d, CH of Ar), 130.2 (d, C-2), 133.2 (s, C-1 of Ar), 144.9 and 145.3 (2 × s, C-4 of Ar and C-3), 163.7 and 164.2 (2 × s, 2 × CO_2), 191.7 (s, CO)
2i	15	4 : 1	92	oil	1728 1682	3.64, 3.78 and 3.86 (3 × s, 9H, 3 × OMe), 7.00–7.50 (m, ArH) and 7.09 (s, CH) (together 5H)	52.3, 53.1 and 55.3 (3 × q, 3 × OMe), 112.2, 120.5, 121.6 and 129.7 (4 × d, CH of Ar), 130.3 (d, C-2), 136.8 (s, C-1 of Ar), 145.1 (s, C-3), 159.1 (s, C-3 of Ar), 163.4 and 164.0 (2 × s, 2 × CO_2), 191.7 (s, CO)
2j	15	4 : 1	92	66 (66–68[34])			
2k	720		90[h]	oil[1]			
2l	30	17 : 3	85	oil[20]			
2m	10		90[i]	oil[26]			
2n	30	17 : 3	80	121 (120–122[21])			
2o	30	17 : 3	88	oil[21]			
2p	15	9 : 1	89	86 (86–87[22])			
2q	30	9 : 1	94	oil	1737 1672 1625	3.83, 3.86 and 3.89 (3 × s, 9H, 3 × OMe), 7.10–7.60 (m, 4H, ArH), 7.86 (s, 1H, CH)	52.8, 53.2 and 55.5 (3 × q, 3 × OMe), 112.4, 121.2, 121.6 and 129.9 (4 × d, CH of Ar), 135.6 (d, C-3), 136.0 and 137.3 (2 × s, C-1 of Ar and C-2), 160.1 (s, C-3 of Ar), 163.2 and 165.0 (2 × s, 2 × CO_2), 188.6 (s, CO)

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[a] Satisfactory microanalyses were obtained (C ±0.25, H ±0.15) except for **2d** which is unchromatographable.

[b] One-pot procedure: Et_2S reduction of the solutions obtained by MB sensitized photo-oxygenation in MeOH of the furans **1**.

[c] Column chromatography on silica gel (light petroleum/Et_2O) except for **2d**, **2k**,[1] **2m**.[26]

[d] Yield of isolated **2** (compatible with product stability, cf. [g,h,i]) based on the furans **1**.

[e] Compound previously obtained, but physical and spectroscopic data were not reported.[32]

[f] Recrystallization solvent: hexane/Et_2O.

[g] Obtained with a purity of 85% (^1H NMR) (see Experimental).

[h] Obtained with a purity of 90% (^1H NMR) (see Experimental).

[i] Obtained with a purity of 75% (^1H NMR) (see Experimental).

Recently, we obtained in almost quantitative yields the 5-hydroperoxy-2,2-dimethoxy-2,5-dihydrofurans **4** in a one-pot synthesis by reaction of some 2-methoxyfurans **1** with singlet oxygen and methanol addition to the formed *endo*-peroxides **3**.[1] We also reported that the 2-methoxyfurans unsubstituted at C-4, under the same conditions, lead only to the methyl 4-hydroperoxy-4-methoxy-2-methoxycarbonylbut-2-enoates **5**,[1] as methanol adducts of the carbonyl oxides **8** arising from the cleavage of the peroxides **3** with unsubstituted C-5[17] (Scheme).

Both the dihydrofurans **4** and the hemiperacetals **5** in apolar solvents when reacted with diethyl sulfide **6a** yielded the *cis* oxo esters **2**.[18] The reduction could also be carried out in methanol solution. Therefore, diethyl sulfide **6a** was added to the methanol solutions of **4a–k** and of **5l–q**, obtained by methylene-blue-sensitized photo-oxygenation in anhydrous methanol of the furans **1a–k** and **1l–q**, respectively. In this way the oxo esters **2a–q** were obtained and, after removal of the excess diethyl sulfide **6a** and methanol, were isolated by silica gel chromatography (except **2d**, **2k** and **2m**, see later) in the yields reported in Table 1. It is necessary to remove methanol as soon as the reduction is complete because the oxo esters **2** may give methanol adducts. Owing to the high reactivity of the oxo esters **2d**, **2k** and **2m** towards methanol, it is more convenient to perform the reduction in carbon tetrachloride; moreover, in order to avoid the transformation which the aforementioned oxo esters **2d**, **2k** and **2m** undergo on contact with the chromatographic adsorbents, the separation from the photosensitizer and diethyl sulfoxide **7a** was performed by treatment with water (see Experimental). In this way compounds **2d**, **2k** and **2m** were obtained in high yields although not in a pure state (Table 1).

In the chromatographic separation, after elution of the oxo ester **2**, the diethyl sulfoxide **7a** was eluted with a more polar solvent and isolated in very good yields. Variously substituted sulfides can be used as reducing agents. Representative experiments were carried out using the furans **1e** (via the dihydrofuran **4e**) and **1l** (via the hemiperacetal **5l**) and the sulfides **6**. In order to obtain sulfoxides free from sulfones it is necessary to remove oxygen from the reaction mixture before adding the sulfide **6**. In this way singlet oxygen oxidation of the sulfides **6** into sulfones[19] is prevented. In Table 2, the reaction conditions and the yields of the sulfoxides **7** isolated by silica gel chromatography are reported.

This one-pot synthetic method for the functionalized oxo esters **2** is very convenient owing to its stereoselectivity and simplicity as well as for its general use and high yields. Concomitantly, it allows the selective oxidation of sulfides into sulfoxides which can be isolated in excellent yields. It is evident that in order to obtain the 2,3-unsubstituted and C-2 and/or C-3 alkyl or phenyl substituted alkyl 4-oxoalk-2-enoates the triplet oxygen oxidation of the related 2-alkoxyfurans[12-14] remains the more convenient pathway.

Table 2. Sulfoxides **7** Prepared[a]

Product	Method A		Method B		bp (°C)/Torr or mp (°C) (Lit.)
	Reaction time (min)	Yield (%)[b]	Reaction time (min)	Yield (%)[b]	
7a	15	98	30	84	40–42/0.3 (42–43/0.7)[35]
7b	1440	93	4320	80	69–71 (69–72)[35]
7c	30	98	150	83	27–29 (28–30)[35]
7d	30	92	90	84	60–62 (63.5–65)[36]

[a] One-pot procedures: sulfide **6** oxidation by the solutions obtained by MB sensitized photo-oxygenation in MeOH of the furan **1e** (Method A) and of the furan **1l** (Method B).

[b] Yield of isolated pure **7** based on the furans **1**.

Melting points were determined using a Gallenkamp melting-point apparatus and are uncorrected. The IR spectra were obtained on a Perkin-Elmer 1760X-FT spectrophotometer. The NMR spectra were recorded with a Varian XL-200 or a Bruker AC-270 spectrometer using TMS as internal standard. C and H microanalyses were obtained using a Carlo Erba EA 1108-Elemental Analyzer. Compounds **1h,i,q**, **4h,i** and **5p,q** gave C, H analysis ± 0.4%. MeOH used in photo-oxygenation reactions was anhydrous. Silica gel (0.063–0.2 mm Macherey-Nagel) and light petroleum (bp 40–60 °C) were used for column chromatography. TLC was performed on silica gel layers (Whatman PK6F). Methyl propiolate, diethyl sulfide, diphenyl sulfide, methyl phenyl sulfide, *tert*-butyl sulfide, methylene blue (MB) were used as purchased from Aldrich Chemical Co.

The furans **1a–d,g,k**,[1] **1e,f,j,l,m**,[20] **1n,o**[21] and **1p**[22] were prepared according to the literature procedures.

Methyl 2-Methoxy-5-(4-tolyl)furan-4-carboxylate (1h):

This compound was obtained, in addition to the furan **1p**,[22] according to the procedure reported for **1e** and **1l**[20] by heating a mixture of 5-methoxy-4-methyl-2-(4-tolyl)oxazole (1.40 g, 6.9 mmol) and methyl propiolate (1.16 g, 13.8 mmol) at 90 °C. The reaction mixture was chromatographed on silica gel. Elution with light petroleum/Et$_2$O (19:1, 9:1) gave successively the furans **1h** and **1p**.[22] Yield of **1h**: 0.540 g (32%), mp 80–82 °C (hexane/Et$_2$O).

^{1}H NMR (CDCl$_3$): $\delta = 2.36$ (s, 3 H, Me), 3.80 and 3.90 (2 s, 6 H, 2 × OMe), 5.58 (s, 1 H, CH), 7.19 and 7.81 (2 d, $J = 8.1$ Hz, 4 H, ArH).

Methyl 2-Methoxy-5-(3-methoxyphenyl)furan-4-carboxylate (1i) and Methyl 2-Methoxy-5-(3-methoxyphenyl)furan-3-carboxylate (1q):

These compounds were prepared as for **1e** and **1l**[20] by heating a mixture of 5-methoxy-2-(3-methoxyphenyl)-4-methyloxazole (see below) (1.40 g, 6.4 mmol) and methyl propiolate (1.10 g, 13 mmol) at 90 °C. The reaction mixture was chromatographed on silica gel. Elution with light petroleum/Et$_2$O (19:1, 9:1) gave successively the furans **1i** and **1q** as oils.

Yield of **1i**: 0.450 g (27%).

^{1}H NMR (CDCl$_3$): $\delta = 3.82$, 3.85 and 3.91 (3 s, 9 H, 3 × OMe), 5.61 (s, 1 H, CH), 6.85–7.60 (m, 4 H, ArH).

Yield of **1q**: 0.700 g (42%).

^{1}H NMR (CDCl$_3$): $\delta = 3.83$, 3.84 and 4.20 (3 s, 9 H, 3 × OMe), 6.86 (s, CH) and 6.70–7.40 (m, ArH) (together 5 H).

5-Methoxy-2-(3-methoxyphenyl)-4-methyloxazole was prepared according to the literature procedure for similar oxazoles.[23] Yield: 98% of an oil after silica gel chromatography eluting with light petroleum/Et$_2$O (4:1). Elemental analysis: C, H ± 0.3%.

^{1}H NMR (CDCl$_3$): $\delta = 2.13$ (s, 3 H, Me), 3.87 and 3.99 (2 s, 6 H, 2 × OMe), 6.90–7.60 (m, 4 H, ArH).

Methyl 4-Oxoalk-2-enoates 2; General Procedure:

A solution of the furan **1** (0.5 mmol) in dry MeOH at the concentration and temperature reported below (**1h,i,p,q**) or previously (**1a–g,j,k**,[1] **l,m**,[20] **n,o**[21]) for the synthesis of **4** or **5** was irradiated with a halogen superhot lamp (Osram 650 W) in the presence of

MB (4×10^{-3} mmol) while dry oxygen was bubbled through the solution. The progress of each reaction was checked by periodically monitoring (^{1}H NMR) the disappearance of furan **1**.

When the reaction was complete, the solution was degassed at r.t. by bubbling with N_2.[24] For entries **a–c,e–j,l,n–q**, Et_2S **(6a)** (0.090 g, 1 mmol) was added to each solution. As soon as each reduction was complete (Table 1, ^{1}H NMR), MeOH and unchanged Et_2S were removed under reduced pressure and the residue was chromatographed on silica gel. Elution with light petroleum/Et_2O, as reported in Table 1, gave the oxo esters **2a–c**, **e–j**, **l**, **n–q** with the yields reported in Table 1. For entries **d**, **k** and **m**, when the photo-oxygenation was complete (^{1}H NMR), MeOH was removed at r.t. under reduced pressure. The residue was dissolved in CCl_4[25] (10 mL) and the resulting mixture treated with Et_2S as reported above. When the reaction was complete (Table 1, ^{1}H NMR), the mixture was rapidly washed with H_2O (3 × 6 mL) in order to remove Et_2SO and MB. Each organic layer was dried ($MgSO_4$) and the solvent and unchanged Et_2S were removed under reduced pressure. The yields reported in Table 1 were determined from the crude reaction mixtures by ^{1}H NMR. All attempts to purify **2d,k** and **m** by chromatographic methods failed since **2d** and **2k**[1] decompose and **2m** partly isomerizes into the *trans* isomer[26] on contact with the adsorbents.

2,5-Dihydrofurans 4; General Procedure:

The previously unreported dihydrofurans **4h,i** were obtained by MB sensitized photo-oxygenation of the furans **1h,i** (0.5 mmol) in MeOH (25 mL) at −40 °C. When the reaction was complete (2 h for **1h** and 3 h for **1i**, ^{1}H NMR), MeOH was removed on a rotary evaporator at r.t. and the crude mixtures were chromatographed on a short column of silica gel (5 g). Elution with light petroleum/Et_2O (4:1) gave the dihydrofurans **4h** and **4i** as oils.

Yield of **4h**: 0.140 g (90 %).

IR ($CHCl_3$): $\nu = 3520, 3210, 1723, 1673\ cm^{-1}$.

^{1}H NMR ($CDCl_3$): $\delta = 2.35$ (s, 3H, Me), 3.49 and 3.53 (2 s, 6H, 2 × OMe), 3.75 (s, 3H, CO_2Me), 6.94 (s, 1H, CH), 7.17 and 7.51 (2 d, $J = 8.3$ Hz, 4H, ArH), 8.93 (br s, 1H, OOH).

Yield of **4i**: 0.155 g (95 %).

IR ($CHCl_3$): $\nu = 3536, 3422, 1719, 1674\ cm^{-1}$.

^{1}H NMR ($CDCl_3$): $\delta = 3.49$ and 3.51 (2 s, 6H, 2 × OMe), 3.75 and 3.80 (2 s, 6H, CO_2Me and ArO*Me*), 6.93 (s, CH) and 6.80–7.30 (m, ArH) (together 5H), 8.92 (br s, 1H, OOH).

4-Aryl-4-hydroperoxy-4-methoxy-2-methoxycarbonylbut-2-enoates 5; General Procedure:

The previously unreported hemiperacetals **5p** and **5q** were quantitatively obtained by MB sensitized photo-oxygenation in MeOH (50 mL) of the furan **1p** (1 mmol) at −20 °C and of the furan **1q** (0.5 mmol) at −40 °C, respectively. After completion of the reaction (2 h, ^{1}H NMR) and removal of MeOH at r.t. under reduced pressure, the residue was taken up in dry Et_2O and the suspension filtered to remove MB. Evaporation of the filtrate gave pure **5p** and **5q**, as oils. All attempts to separate compounds **5p** and **5q** from MB chromatographically failed since **5** partly polymerize and partly hydrolyse on contact with the adsorbent.

Yield of **5p**: 0.304 g (98 %).

IR ($CHCl_3$): $\nu = 3511, 3350, 1734, 1660\ cm^{-1}$.

^{1}H NMR ($CDCl_3$): $\delta = 2.35$ (s, 3H, Me), 3.24 (s, 3H, OMe), 3.76 and 3.88 (2 s, 6H, 2 × CO_2Me), 6.95 (s, 1H, CH), 7.05–7.40 (m, 4H, ArH), 8.77 (br s, 1H, OOH).

Yield of **5q**: 0.155 g (95 %).

IR ($CHCl_3$): $\nu = 3510, 3350, 1734, 1660\ cm^{-1}$.

^{1}H NMR ($CDCl_3$): $\delta = 3.26$ (s, 3H, OMe), 3.76, 3.82 and 3.88 (3 s, 9H, 2 × CO_2Me and ArO*Me*), 6.80–7.30 (m, ArH) and 6.94 (s, CH) (together 5H), 8.67 (br s, 1H, OOH).

Sulfoxides 7; General Procedure:

The reactions were carried out using the furans **1e** and **1l** according to the general method used when Et_2S **(6a)** was the reducing agent.[27] When the reaction was complete (^{1}H NMR, Table 2), MeOH and the sulfide (when volatile) were removed under reduced pressure. The residue analyzed by TLC and/or ^{1}H NMR, showed only the presence of **2**, **6** (when unvolatile) and **7**. Chromatography on silica gel (15 g), eluting with light petroleum/Et_2O (19:1, 17:3) and Et_2O gave successively the unreacted sulfide **6** (when unvolatile) the product **2** and the sulfoxide **7** [the sulfoxides **7a** and **7b** were recovered eluting with Et_2O/MeOH (19:1) and light petroleum/Et_2O (4:1), respectively]. The yield of the sulfoxide **7** for each entry is reported in Table 2. Purity was checked by TLC and/or ^{1}H NMR. Compounds **7a**,[28] **7b**,[29] and **7c**[30] exhibit spectroscopic data in good agreement with the literature. A control experiment performed as reported in literature[31] gave di(*tert*-butyl) sulfoxide **(7d)** (mp 60–62 °C; $\delta_H = 1.34$) which exhibits physical and spectroscopic data in agreement with **7d** obtained by Methods A and B (Table 2).

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(1) For Part 17 see: Iesce, M.R.; Cermola, F.; Graziano, M.L.; Scarpati, R. *Synthesis* **1994**, 944.

(2) For example see:
Nippon Synthetic Chemical Industry Jpn. Kokai 5838202, 1983; *Chem. Abstr.* **1983**, *99*, 1818d.
Nippon Synthetic Chemical Industry Jpn. Kokai 81127302, 1981; *Chem. Abstr.* **1982**, *96*, 2180q.

(3) Yamada, K.; Ino, K.; Takahashi, S.; Ohashi, T.; Watanabe, K. Eur. Pat. Appl. EP 239062, 1987; *Chem. Abstr.* **1988**, *109*, 110904z.

(4) Chosakon, Y.; Yamamoto, N. Jpn. Kokai 63104940, 1988; *Chem. Abstr.* **1988**, *109*, 230551d.

(5) Ikeda, T.; Hirano, H.; Aoki, K. Jpn. Kokai 63130564, 1988; *Chem. Abstr.* **1989**, *110*, 7866k.

(6) Schoenbeck, R.; Kloimstein, E.; Woerther, R.; Reich-Rohrwig, P. Austrian 330195, 1976; *Chem. Abstr.* **1976**, *85*, 143128p.
Schoenbeck, R.; Kloimstein, E.; Woerther, R.; Reich-Rohrwig, P. Ger. Offen. 2435244, 1976; *Chem. Abstr.* **1976**, *84*, 150649s.
Pyridazin-3-ones are well known herbicides: Crowley, P.J. In *Comprehensive Heterocyclic Chemistry*, Vol. 1, Part 1; Katritzky, A.R.; Rees, C.W., Eds.; Pergamon: Oxford, 1984; p 185.

(7) Takahashi, S.; Ueda, Y.; Yanagida, Y.; Namito, Y.; Ohashi, T.; Watanabe, K. Eur. Pat. Appl. EP 204286, 1986; *Chem. Abstr.* **1987**, *106*, 84179h.

(8) Peto, A.G. In *Friedel–Crafts and Related Reactions*, Vol. 3, Part 1; Olah, G.A., Ed.; Interscience: New York, 1964; p 535.

(9) Sustmann, R.; Korth, H.G. In *Houben-Weyl*: Band E5/1; Falbe, J., Ed.; Thieme: Stuttgart, 1985; p 417.

(10) Jones, G. *Organic Reactions* **1967**, *15*, 204.

(11) Tietze, L.F.; Beifuss, U. In *Comprehensive Organic Synthesis*, Vol. 2; Trost, B.M.; Fleming, I., Eds.; Pergamon: Oxford, 1991; p 341.

(12) Scarpati, R.; Graziano, M.L.; Nicolaus, R. *Gazz. Chim. It.* **1967**, *97*, 1317.

(13) Pincock, J.A.; Moutsokapas, A.A. *Can. J. Chem.* **1977**, *55*, 979.

(14) Wulff, W.D.; Gilbertson, S.R.; Springer, J.P. *J. Am. Chem. Soc.* **1986**, *108*, 520.

(15) As previously reported for other 2-alkoxyfurans,[14] contact with silica gel accelerates the air oxidation of the furans **1a–d** so that the isolation of the latter was carried out by silica gel chromatography under N_2.[1] However, in order to obtain the corresponding alkenoates in good yields, this oxidative pathway is not convenient, being accompanied by side reactions.

(16) Sulfoxides are receiving considerable interest as intermediates in organic synthesis and recent studies have been devoted to increasing the range of such compounds or improving their methods of preparation: Siedlecka, R.; Skarzewski, J. *Synthesis* **1994**, *401*, and references therein.

(17) Graziano, M. L.; Iesce, M. R.; Cermola, F.; Giordano, F.; Scarpati, R. *J. Chem. Soc., Chem. Commun.* **1989**, 1608.
Iesce, M. R.; Graziano, M. L.; Cermola, F.; Cimminiello, G.; Scarpati, R. *Gazz. Chim. It.* **1990**, *120*, 629.

(18) The *cis* oxo ester **2k** was previously obtained by Et_2S reduction of the *endo*-peroxide **3k**[1]. However the latter procedure is not convenient owing to the previously reported[1] difficult handling of the unstable peroxides **3**.

(19) Ando, W.; Takata, T. In *Singlet O_2*, Vol. 3, Part 2; Frimer, A. A., Ed.; CRC Boca Raton: Florida, 1985, p 1.

(20) Graziano, M. L.; Iesce, M. R.; Cimminiello, G.; Scarpati, R. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1699.

(21) Iesce, M. R.; Cermola, F.; Graziano, M. L.; Scarpati, R. *J. Chem. Soc., Perkin Trans. 1* **1994**, 147.

(22) Iesce, M. R.; Cermola, F.; Giordano, F.; Scarpati, R.; Graziano, M. L. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3295.

(23) Gotthardt, H.; Huisgen, R.; Bayer, H. O. *J. Am. Chem. Soc.* **1970**, *92*, 4340.

(24) This is unnecessary when the concomitant obtention of the sulfoxides **7** is not required.

(25) Although the very small amount of MB present in the oxygenation mixture is unsoluble in CCl_4, the latter is preferred to $CHCl_3$, since the trace amount of HCl frequently present in this solvent catalyzes the hydrolysis of compounds **4**[1] and **5**[20].

(26) Graziano, M. L.; Iesce, M. R.; Scarpati, R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1955; *cf.* Ref. 20.

(27) When the concomitant obtention of the oxo esters **2** is required, the reaction with the scarcely reactive sulfide **6b** must be performed in CCl_4 in order to avoid the formation of MeOH adducts of **2**.

(28) Dyer, J. C.; Slayton, A. E., Jr. *Magn. Res. Chem.* **1991**, *29*, 286.

(29) *The Aldrich Library of NMR Spectra*: Vol. 10, Pouchert, C. J.; Campbell, J. R., Eds.; Aldrich Chemical Company: Milwaukee, 1974.

(30) Traynelis, V. J.; Yoshikawa, Y.; Tarka, S. M.; Livingston, J. R., Jr. *J. Org. Chem.* **1973**, *38*, 3986.

(31) Drabowicz, J.; Lyzwa, P.; Popielarczyk, M.; Mikolajczyk, M. *Synthesis* **1990**, 937.

(32) Graziano, M. L.; Iesce, M. R.; Cermola, F.; Giordano, F.; Scarpati, R. *J. Chem. Soc., Chem. Commun.* **1991**, 1061.

(33) Winterfeldt, E.; Dillinger, H. J. *Chem. Ber.* **1966**, *99*, 1558.

(34) Graziano, M. L.; Iesce, M. R.; Cimminiello, G.; Scarpati, R. *J. Chem. Soc., Perkin Trans. 1* **1989**, 241.

(35) Drabowicz, J.; Midura, W.; Mikolajczyk, M. *Synthesis* **1979**, 39.

(36) Barnard, D.; Bateman, L.; Cain, M. E.; Colclough, T.; Cunneen, J. I. *J. Chem. Soc.* **1961**, 5339.