# Furan-3(2*H*)-ones by Tandem Photo-oxidation–Intramolecular Michael Addition

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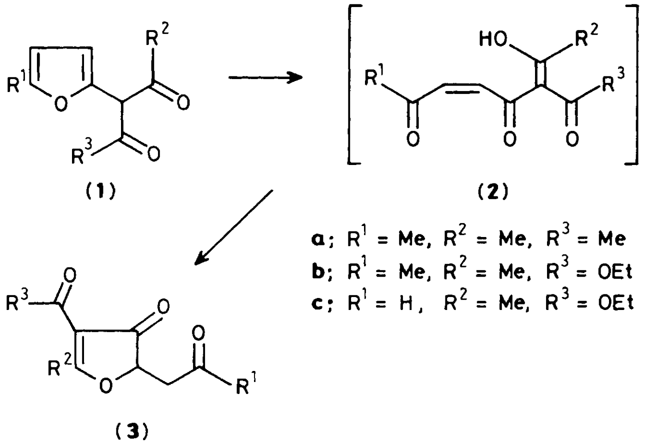
Photo-sensitized oxygenation of the furyl diketones (**1**) affords furan-3(2*H*)-ones (**3**) in satisfactory yields, presumably *via* the intermediate open-chain enetriones (**2**).

Increasing interest in the reactivity of singlet-excited molecular oxygen ($^1O_2$) has resulted in the elucidation of many mechanistic aspects of the photo-oxidation of furan, in particular with regard to the formation of endoperoxides, their rearrangement reactions, and their conversion into hydroperoxides.[1] Furthermore, the photo-oxidation of suitable furan derivatives has been widely exploited for the preparation of polyfunctional synthons, key intermediates in the synthesis of natural products.[2]

In the course of investigations on the reactivity of furans bearing additional functional groups, sensitive to oxidation, we have found that the 2-(2-furyl) 1,3-dicarbonyl compounds



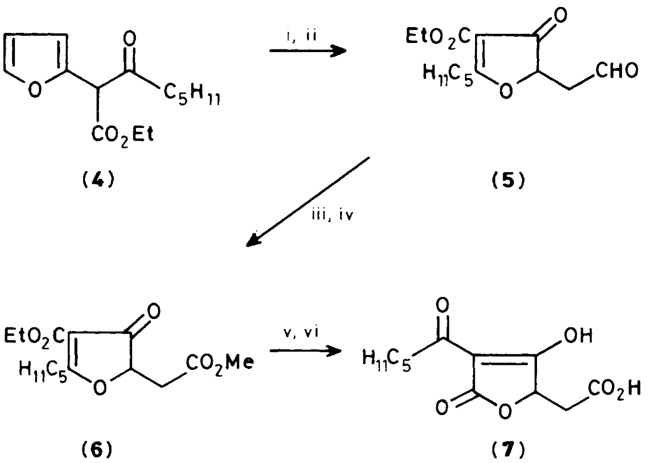
a; $R^1$ = Me, $R^2$ = Me, $R^3$ = Me
b; $R^1$ = Me, $R^2$ = Me, $R^3$ = OEt
c; $R^1$ = H, $R^2$ = Me, $R^3$ = OEt

**Scheme 1**

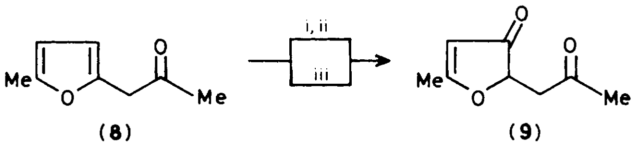
(1) can be converted directly into the functionalized furan-3(2*H*)-ones (3) by the action of singlet oxygen.

Photo-irradiation of the furans (**1**) (5 mmol) in $CH_2Cl_2$, in the presence of a catalytic amount of tetraphenylporphyrin (TPP), with a 300 W lamp at −78 °C for 1 h, followed by treatment with dimethyl sulphide (15 mmol), according to Gollnick's procedure,[1] led, after the usual work-up, to the crude furanones (**3**). Purification by column chromatography on silica gel afforded pure (**3a**) (79%), (**3b**) (71%), or (**3c**) (51%).†

The only moderate yield of isolated (**3c**) (g.l.c. yield 80%) must be attributed to significant decomposition in the course of purification.



**Scheme 2.** *Reagents and conditions*: i, $^1O_2$, TPP, −78 °C, 1 h; ii, $Me_2S$, −78 °C, 1 h (85%); iii, Jones' reagent (2.5 equiv.), $Me_2CO$, 0 °C, 30 min (94%); iv, AcOEt, $CH_2N_2$, 0 °C, 10 min (100%); v, THF, aq. 0.8 M-NaOH (5 equiv.), room temp., 16 h; vi, 4 M-HCl (ref. 4) (36%).



**Scheme 3.** *Reagents and conditions*: i, $^1O_2$, TPP, $CH_2Cl_2$, −40 °C, 1 h; ii, silica gel, room temp., 16 h (60%); iii, $^1O_2$, TPP, $CH_2Cl_2$, silica gel, room temp., 1 h (97%).

The conversion (**1**) → (**3**) (Scheme 1) can be reasonably explained on the basis of chemoselective attack of $^1O_2$ on the furan nucleus, leading, after reduction with $Me_2S$, to the open-chain intermediate (**2**), conversion of which into the final products (**3**) takes place through internal Michael addition of the enolic OH to the activated C=C bond of the enedicarbonyl moiety.

As shown in Scheme 2, the present procedure has been exploited for a convenient synthesis of (±)-viridicatic acid (**7**), a metabolite of *Penicillium viridicaticum*;[3] the key intermediate (**6**) can be obtained in 80% yield from the furan (**4**).

The same photochemical behaviour is shown by the furfuryl ketone (**8**) (Scheme 3), which is converted into the corresponding furan-3(2*H*)-one (**9**) through a modified procedure involving use of silica gel to decompose the product of $^1O_2$ oxidation.

A much more satisfactory yield of (**9**) (97%) is obtained by photo-oxidation of (**8**) directly in the presence of silica gel.

Further investigations on the mechanism of these conversions are in progress.

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† *Spectral data* for (**3a**): i.r. $\nu_{max}$ ($CCl_4$) 1735, 1715, 1685, and 1565 $cm^{-1}$; $^1H$ n.m.r. δ ($CDCl_3$) 4.90 (dd, 1H, $J_1$ 4, $J_2$ 8 Hz), 3.20 (dd, 1H, $J_1$ 4, $J_2$ 17 Hz), 2.80 (dd, 1H, $J_1$ 8, $J_2$ 17 Hz), 2.56 (s, 3H), 2.40 (s, 3H), and 2.20 (s, 3H); *m/z* ($M^+$) 196. For (**3b**): i.r. $\nu_{max}$ ($CCl_4$) 1750—1700 br. and 1605 $cm^{-1}$; $^1H$ n.m.r. δ ($CDCl_3$) 4.80 (dd, 1H, $J_1$ 4, $J_2$ 8 Hz), 4.19 (q, 2H, *J* 7 Hz), 3.18 (dd, 1H, $J_1$ 4, $J_2$ 18 Hz), 2.75 (dd, 1H, $J_1$ 8, $J_2$ 18 Hz), 2.53 (s, 3H), 2.17 (s, 3H), and 1.30 (t, 3H, *J* 7 Hz); *m/z* ($M^+$) 226. For (**3c**): i.r. $\nu_{max}$ ($CHCl_3$) 1740, 1715, and 1596 $cm^{-1}$; $^1H$ n.m.r. δ ($CDCl_3$) 9.7 (m, 1H), 4.97 (dd, 1H, $J_1$ 4, $J_2$ 8 Hz), 4.28 (q, 2H, *J* 7 Hz), 3.17 (dd, 1H, $J_1$ 4, $J_2$ 18, Hz), 2.80 (dd, 1H, $J_1$ 8, $J_2$ 18 Hz), 2.58 (s, 3H), and 1.32 (t, 3H, *J* 7 Hz); *m/z* ($M^+$) 212. For (**5**): i.r. $\nu_{max}$ ($CDCl_3$) 1740, 1720, and 1594 $cm^{-1}$; $^1H$ n.m.r. δ ($CDCl_3$) 9.8 (m, 1H), 4.95 (dd, 1H, $J_1$ 3.5, $J_2$ 8.5 Hz), 4.30 (q, 2H, *J* 7 Hz), 3.15 (dd, 1H, $J_1$ 3.5, $J_2$ 18 Hz), 2.97 (t, 2H, *J* 8 Hz), 2.83 (dd, 1H, $J_1$ 8.5, $J_2$ 18 Hz), 1.33 (t, 3H, *J* 7 Hz), and 1.8—0.8 (m, 9H); *m/z* ($M^+$) 268. For (**6**): i.r. $\nu_{max}$ ($CCl_4$) 1758, 1730, and 1598 $cm^{-1}$; $^1H$ n.m.r. δ ($CDCl_3$) 4.87 (dd, 1H, $J_1$ 4, $J_2$ 8 Hz), 4.27 (q, 2H, *J* 7 Hz), 3.72 (s, 3H), 3.07 (partially visible dd, 1H, $J_1$ 4, $J_2$ 18 Hz), 2.9 (m, 2H), 2.62 (partially visible dd, 1H, $J_1$ 8, $J_2$ 18 Hz), 1.32 (t, 3H, *J* 7 Hz), and 1.9—0.7 (m, 9H); *m/z* ($M^+$) 298. For (**7**): m.p., 162—164 °C (lit.,[4] 158—160 °C); i.r. $\nu_{max}$ ($CHCl_3$) 3600—2300br., 1730, 1700, and 1605 $cm^{-1}$; $^1H$ n.m.r. δ [($(CD_3)_2CO$]) 7.0—6.0 (br., 2H, disappears after shaking with $D_2O$), 5.1—4.8 (m, 1H), 3.1—2.9 (m, 4H), 2.1—1.0 (m, 6H), and 0.87 (m, 3H); *m/z* ($M^+$) 256. For (**9**): i.r. $\nu_{max}$ ($CHCl_3$) 1730, 1700, and 1605 $cm^{-1}$; n.m.r. δ ($CCl_4$) 5.33 (s, 1H), 4.72 (dd, 1H, $J_1$ 4, $J_2$ 8 Hz), 2.97 (dd, 1H, $J_1$ 8, $J_2$ 18 Hz), 2.55 (dd, 1H, $J_1$ 4, $J_2$ 18 Hz), and 2.15 (s, 6H); *m/z* ($M^+$) 154.

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