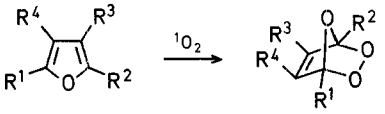
Photosensitized Oxidation of Furans; V[1]. An Efficient General Method for the Synthesis of 2-Aroylenol Esters

M. L. GRAZIANO, M. R. IESCE, B. CARLI, R. SCARPATI*

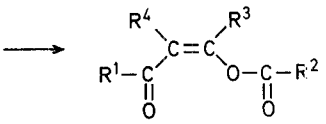
Istituto di Chimica Organica e Biologica dell'Università, Via Mezzocannone 16, I-80134 Napoli, Italy

2-Aroylenol esters **3** are interesting multifunctional compounds very susceptible to hydrolysis[2]. They are obtained by the reaction of β-diketones with acyl halides in pyridine[3] and, together with triacylmethanes, from reactions of metal chelates of β-diketones with acyl halides[4]. These procedures necessitate an inconvenient aqueous workup, therefore it was desirable to develop another synthetic method which, in addition, allows the preparation of 2-aroylenol esters containing an electron-withdrawing substituent at position 1; compounds which were never prepared, to our knowledge, by the aforementioned methods.

Recently, we reported that thermal conversion in carbon tetrachloride at 4 °C of the 1,4-diphenyl-2,3,7-trioxabicyclo[2.2.1]hept-5-enes **2a, 2d,** and **2g,** obtained in quantitative yields by photosensitized oxidation of the 2,5-diphenylfurans **1a, 1d, 1g,** leads to the parent furans (27–43%) and dibenzoylepoxides (32–34%) as major products, and enol esters (9–16%) and dibenzoylethylenes (3–20%) as minor products[1]. The conversion of *endo*-peroxides **2** into the parent furans and molecular oxygen, by comparison with similar retro-[4+2]-cycloadditions, can be considered both as a concerted fragmentation or as a decomposition via an initial diradical intermediate[5]. On the other hand, it has been suggested that furan *endo*-peroxides, like **2,** rearrange into enol esters **3** via dipolar intermediates[6]. As it is well known that a more polar environment enhances the rate of the reactions which involve such intermediates, an increase in solvent polarity should increase the yields in enol ester, the rearrangement overcoming the competing molecular oxygen elimination.



1 **2**



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Accordingly, the yields of the enol esters **3a, 3d, 3g** are remarkably improved when the conversion has been carried out in nitromethane. It is worthy of note that in nitromethane the yields in enol esters **3** are generally higher than expected on the basis of aforementioned remarks. It is evident that in this solvent the rearrangement partly prevails also over the forming of the epoxides. As shown in Table 1, the conversion of furans **1** into 2-aroyl enol esters **3** via *endo*-peroxides **2** has a wide range of applicability and the rearrangement occurs ste-

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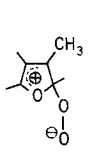
reospecifically in that only the *cis*-enol esters **3** are formed. Furthermore, the new synthetic method can be accomplished by thermal rearrangement without isolation of the *endo*-peroxide precursors.

When $R^1 = R^2$, the *endo*-peroxides **2b, 2c, 2d, 2e,** which have $R^3 \neq R^4$, could lead to two isomeric esters. [In carbon tetrachloride both enol esters **3d** and ethyl 2-benzoyl-3-benzoyloxyacrylate in approximately equal amounts were formed[1]. Under the above conditions, only a trace amount of the latter product was detected.] However, these peroxides **2** rearrange into **3b, 3c, 3d, 3e** independent of the electron-attracting or -donating character of the substituent.

In this connection, further investigation is needed to show whether a change in mechanism occurs, e.g. involving the cyclic zwitterion **4** with an electron-donating substituent and an acyclic zwitterion **5** with an electron-withdrawing substituent.



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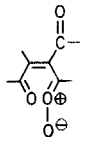

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We also examined the behaviour of **2h** and **2i** which have $R^1 \neq R^2$ and $R^3 \neq R^4$. Both give enol acetate **3h** and **3i** showing that a preferential oxygen-benzyl carbon breakdown is operating in these cases; however the yields in **3h** are very low as **2h** in preference polymerizes.

At present, the aforementioned method seems to be limited for the synthesis of 2-aroylenol esters; in fact 1,4-dimethyl derivatives of **2** rearrange into diepoxides or polymeric material[1,8] also in dipolar aprotic solvents.

cis-2-Aroylenol Esters 3a–3h; General Procedure:
A 2% solution of the furan **1** (1 mmol) and methylene blue (8×10^{-3} mmol) in dry nitromethane is irradiated with a halogen-superphot lamp (Osram 650 W). During the irradiation, dry oxygen is bubbled through the solution which is cooled at −15 °C. Periodically, samples are syringed into a ^{1}H-N.M.R. tube and monitored for furan **1** disappearance and *endo*-peroxide **2** appearance. After completion of singlet oxygenation, the solution is warmed to the temperature recorded in Table 1 and kept until complete disappearance of **2** (^{1}H-N.M.R.). Removal of the nitromethane in vacuo gives the crude **3a–3h,** which are purified by column chromatography over silica gel using light petroleum/ether (4:1 v/v) as eluent. Enol ester **3g** needs successive cleaning according to the procedure previously described[1].

Methyl *cis*-2-Acetoxy-4-oxo-4-phenylbutenoate (3i):
The *endo*-peroxide **2i** owing to the high hydrolytic reactivity, is prepared as previously described[9] and dissolved in dry nitromethane (2% solution). The solution is worked-up as reported in the general procedure.

2,3,7-Trioxabicyclo[2.2.1]hept-5-enes 2:
The previously unreported compounds **2,** except for **2b** which in nitromethane is very unstable, after completion of singlet oxidation and removal of the nitromethane at −15 °C in vacuo can be isolated in quantitative yields according to the procedure used for **2i**[9]. *Endo*-peroxide **2b** can be prepared according to the procedure used for **2a**[1]. Spectral data are summarized in Table 2.

Table 1. *cis*-2-Aroylenol Esters **3a–i** ($R^1 = C_6H_5$)

Product No.	R^2	R^3	R^4	Irradiation time at −15 °C	Conversion temp. and time	Yield [%][a]	m.p. [°C]	Molecular formula[b] or Lit. m.p.	^{1}H-N.M.R. ($CDCl_3$/TMS)[c] δ [ppm]	I.R. ($CHCl_3$)[d] ν [cm^{-1}]
3a	C_6H_5	H	H	200 min	18–22 °C/ 30 min	70	oil	oil[1]	—	—
3b	C_6H_5	CH_3	H	240 min[e]	−15 °C	90	oil	oil[3a]	—	1745, 1694, 1682, 1678
3c	C_6H_5	$COOCH_3$	H	90 min	4 °C/40 h	72	72–74[c]	$C_{18}H_{14}O_5$ (310.3)	3.86 (s, 3H); 7.54, 7.4–8.2 (s+m, 11H)	1740, 1681, 1628
3d	C_6H_5	$COOC_2H_5$	H	90 min	4 °C/40 h	70	oil	oil[1]	—	—
3e	C_6H_5	CO—CH_3	H	150 min	18–22 °C/ 2 h	54	oil	$C_{18}H_{14}O_4$ (294.3)	2.42 (s, 3H); 7.40, 7.35–8.2 (s+m, 11H)	1742, 1708, 1668, 1620
3f	C_6H_5	CH_3	$COOC_2H_5$	120 min	18–22 °C/ 48 h	76	oil	$C_{20}H_{18}O_5$ (338.3)	1.10 (t, 3H, J=7 Hz); 2.62 (s, 3H); 4.14 (q, 2H, J=7 Hz); 7.3–8.05 (m, 10H)	1738, 1720, 1678, 1603
3g	C_6H_5	$COOCH_3$	$COOCH_3$	60 min	18–22 °C/ 48 h	30	oil	oil[1]	—	—
3h	CH_3	H	$COOC_2H_5$	150 min	18–22 °C/ 10 d	15	oil	$C_{14}H_{14}O_5$ (262.3)	1.20 (t, 3H, J=7 Hz); 2.06 (s, 3H); 4.21 (q, 2H, J=7 Hz); 7.35–8.05 (m, 5H); 8.56 (s, 1H)	1790, 1720, 1680, 1655
3i	CH_3	$COOCH_3$	H	—	4 °C/30 h	63	oil	oil[7]	—	—

[a] Yield of pure, isolated product.
[b] Satisfactory microanalyses obtained: C ±0.25, H ±0.12.
[c] Perkin-Elmer R 12 A spectrometer.
[d] Perkin-Elmer 399 spectrophotometer.
[e] **2b** cannot be detected due to its instability in nitromethane at −15 °C; when the photooxidation of **1b** is complete only **3b** is detectable by ^{1}H-N.M.R. in the reaction mixture.

Table 2. 2,3,7-Trioxabicyclo[2.2.1]hept-5-enes **2** ($R^1 = C_6H_5$)

Product[a]	m.p. [°C]	Molecular formula[b]	^{1}H-N.M.R. ($CDCl_3$/TMS)[c] δ [ppm]	I.R. ($CHCl_3$)[d] ν [cm^{-1}]
2b	oil	—	1.28 (s, 3H); 5.77 (s, 1H); 7.2–7.7 (m, 10H)[e]	—
2c	oil	$C_{18}H_{14}O_5$ (310.3)	3.65 (s, 3H); 7.58, 7.35–7.85 (s+m, 11H)	1732, 1615
2e	68° (dec.)	$C_{18}H_{14}O_4$ (294.3)	2.21 (s, 3H); 7.39, 7.35–7.75 (s+m, 11H)	1690, 1605
2f	oil	$C_{20}H_{18}O_5$ (338.3)	1.00 (t, 3H, J=7 Hz); 2.10 (s, 3H); 3.93, 3.97 (2q, 2H, J=7 Hz); 7.4–7.85 (m, 10H)	1715, 1655
2h	oil	$C_{14}H_{14}O_5$ (262.3)	1.05 (t, 3H, J=7 Hz); 1.88 (s, 3H); 4.05 (q, 2H, J=7 Hz); 7.07 (s, 1H); 7.25–7.75 (m, 5H)	1720, 1620

[a] For R^2, R^3, R^4, see Table 1.
[b] Satisfactory microanalyses obtained: $O_{act} \pm 0.30$.
[c] Perkin-Elmer R 12 A spectrometer.
[d] Perkin-Elmer 399 spectrophotometer.
[e] In CCl_4 solution.

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[1] For Part IV see: M. L. Graziano, M. R. Iesce, R. Scarpati, *J. Chem. Soc. Perkin Trans. 1*, in press.
[2] H. D. Murdoch, D. C. Nonhebel, *J. Chem. Soc.* **1962,** 2153.
[3] (a) J. Larkin, M. G. Murray, D. C. Nonhebel, A. D. Mitchell, *J. Chem. Soc. Perkin Trans. 1* **1976,** 380.
(b) T. Rull, G. Le Strat, *Bull. Soc. Chim. Fr.* **1975,** 1375.
(c) H. O. House, *Modern Synthetic Reactions*, 2nd Edn., W. A. Benjamin, Inc., Menlo Park, 1972, p. 763.
[4] Inter alia: H. D. Murdoch, D. C. Nonhebel, *J. Chem. Soc.* **1968,** 2298.
M. G. Murray, D. C. Nonhebel, *J. Chem. Soc.* **1970,** 1172.
[5] N. J. Turro, M. F. Chrow, J. Rigaudy, *J. Am. Chem. Soc.* **103,** 7218 (1981).
M. Balci, *Chem. Rev.* **81,** 91 (1981).
[6] W. Adam, A. Rodriguez, *J. Am. Chem. Soc.* **102,** 404 (1980).
[7] M. L. Graziano, R. Scarpati, *J. Chem. Soc. Perkin Trans. 1* **1981,** 1811.
[8] M. L. Graziano, M. R. Iesce, R. Scarpati, *J. Chem. Soc. Chem. Commun.* **1981,** 720.
[9] M. L. Graziano, M. R. Iesce, R. Scarpati, *J. Chem. Soc. Perkin Trans. 1* **1980,** 1955.

0039-7881/82/0932-0738 $ 03.00