

## A Photochemically-generated Acyl-Vinyloxy Biradical as a Synthetic Precursor of a 2,3-Dihydrofuran and a Butyrolactone

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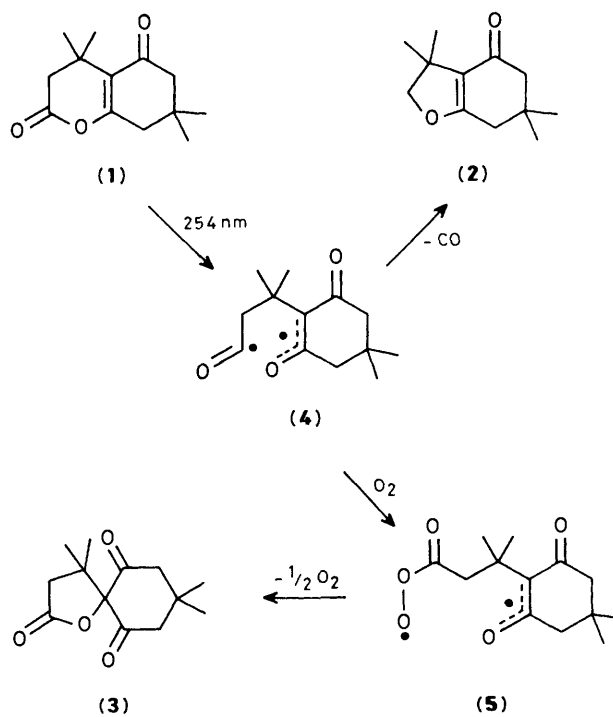
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Photolysis of 4,4,7,7-tetramethyl-4,6,7,8-tetrahydro-2*H*-1-benzopyran-2,5(3*H*)-dione (1) gives the acyl-vinyloxy biradical (4) which can be trapped with oxygen to give the spiro lactone (3) before losing CO to form the 2,3-dihydrofuran (2).

Biradicals are frequent intermediates in light-induced reactions of carbonyl compounds. While 1,4-biradicals generated by a Norrish type II photoprocess have been successfully trapped with oxygen to give furans<sup>1</sup> or hydroperoxides,<sup>2</sup> acyl-alkyl biradicals from a Norrish type I reaction of cycloalkanones have only been intercepted by nitric oxide.<sup>3</sup> We now report that the photoreaction of the enol lactone (1)<sup>4,5</sup> gives 3,3,6,6-tetramethyl-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-one (2) in degassed solution, but affords 4,4,8,8-tetramethyl-1-oxaspiro[4,5]decan-2,6,10-trione (3) in the presence of oxygen.

Irradiation ( $\lambda = 254 \text{ nm}$ ) of (1) ( $10^{-1} \text{ M}$ ) in argon degassed methanol gave 2,3-dihydrofuran (2) [m.p. 63–65 °C; i.r. (KBr): 1660, 1640  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ ):  $\delta$  4.24 (s, 2H), 2.35 (s, 2H), 2.27 (s, 2H), 1.38 (s, 6H), 1.14 (s, 6H);  $^{13}\text{C}$  n.m.r. ( $\text{CDCl}_3$ ):  $\delta$  195, 175, 119, 86, 52, 42, 38, 34, 28, 26;  $m/z$ : 194 ( $M^+$ ), 83 (100%)] in 75% yield. Irradiation of a similar aerated solution of (1) afforded spiro lactone (3) [m.p. 68–70 °C; i.r. (KBr): 1770, 1740, and 1705  $\text{cm}^{-1}$ ;  $m/z$ : 238 ( $M^+$ ), 83 (100%);  $^1\text{H}$  n.m.r. and  $^{13}\text{C}$  n.m.r. corresponding to those reported for 2,2-dialkyldimedones<sup>6</sup>] in 59% yield. Both compounds were purified by chromatography ( $\text{SiO}_2\text{-CH}_2\text{Cl}_2$ ).

Enol lactones are obtained by photoisomerization of non-enolizable 1,3-diketones<sup>7,8</sup> using light of  $\lambda = 300 \text{ nm}$ . In contrast, one example of irradiation of an endocyclic enol lactone with light of  $\lambda = 254 \text{ nm}$  with loss of carbon monoxide from the carbonyl part of the intermediate acyl-vinyloxy



biradical and subsequent cyclopropane formation has been reported.<sup>9,10</sup> While 2-substituted 2,3-dihydrofurans similar to (2) have been synthesized by electrochemical reduction of 2,2-dibromodimedone in the presence of alkenes,<sup>11</sup> the formation of (3) represents the first example of a reaction wherein an acyl-vinyloxy biradical (4) is trapped with oxygen [most probably giving intermediate (5) which then affords (3) by redox chemistry<sup>1</sup>] prior to decarbonylation.

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### References

- 1 M. Yoshioka, M. Oka, Y. Ishikawa, H. Tomita, and T. Hasegawa, *J. Chem. Soc., Chem. Commun.*, 1986, 639.
  - 2 R. D. Small, Jr., and J. C. Scaiano, *J. Am. Chem. Soc.*, 1978, **100**, 4512.
  - 3 P. Maruthamuthu and J. C. Scaiano, *J. Phys. Chem.*, 1978, **82**, 1588.
  - 4 S. Gelin and B. Chantegrel, *C. R. Acad. Sci., Sér. C*, 1971, **273**, 635.
  - 5 P. Margaretha, *Tetrahedron Lett.*, 1970, 1449.
  - 6 J. R. Mahagan, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1434.
  - 7 J. Eriksen and P. E. Plith, *Tetrahedron Lett.*, 1982, 481.
  - 8 H. J. Wüthrich, A. Siewunsky, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 1973, **56**, 239.
  - 9 A. Yogev and Y. Mazur, *J. Am. Chem. Soc.*, 1965, **87**, 3520.
  - 10 D. Bellus, *Adv. Photochem.*, 1971, **8**, 109.
  - 11 J. Yoshida, M. Yamamoto, and N. Kawabata, *Tetrahedron Lett.*, 1985, 6217.
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