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Carbonyl Oxide Chemistry. 4.[1] Novel Observations on the Behavior of 1-Methoxy-2,3,7-trioxabicyclo[2.2.1]hept-5-ene

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Several years ago, in an extensive study of the dye-sensitized photooxygenation of furan and of 2-substituted or 2,5-disubstituted furans, Gollnick et al.[2] isolated or at least spectroscopically characterized the corresponding 2,3,7-trioxabicyclo[2.2.1]hept-5-enes, such as **2**, deriving from singlet oxygen addition to each of the furans. In particular, the 1-methoxy derivative **2a** was identified by ^{1}H NMR data, though it was obtained only in $CFCl_3$ solution at −78 °C and at higher temperature gave only resinous material. The *endo*-peroxide **2a** reacted with alcohols, e.g., methanol, to give addition products believed to be 2-alkoxy-5-hydroperoxy-2-methoxy-2,5-dihydrofurans, e.g., **3a**.[2]

More recently, we observed that the thermal rearrangement of 1-methoxy-4-phenylfuran *endo*-peroxides **2** leads to furanodioxetanes[3] or 3*H*-1,2-dioxoles[4] depending on the nature of the substituents at C-5 and C-6. Both series of *endo*-peroxides add methanol to give dihydrofurans such as **3**.[5] In contrast, the 1-methoxy-4-phenylfuran *endo*-peroxides bearing a hydrogen atom at C-5, e.g., **2b**, under the same conditions add methanol to give quantitatively hemiperacetals, e.g., **6b**, *via* intermediate carbonyl oxides,[6] e.g., **5b**.[7,8]

In connection with a program on the preparation and use of organic peroxides,[1,3−5,7,8] we have now systematically investigated the behavior of the *endo*-peroxide **2a**.

Results and Discussion

We confirmed that photooxygenation of the furan **1a** in $CDCl_3-CFCl_3$ in the presence of tetraphenylporphyrin at −78 °C provides peroxide **2a**, which undergoes thermal conversion into resinous material,[2] both in apolar and in polar solvents and also at very low concentration.[9] Dye-sensitized photooxygenation of **1a** in methanol gave, almost quantitatively, an oily compound which had the ^{1}H and ^{13}C spectral data as previously reported.[2] However, the lately recorded IR spectrum indicated the presence of a carbonyl group (1723 cm^{-1}); in addition, a carefully recorded ^{1}H NMR spectrum showed coupling splittings characterized by constants ($J = 11.5$ Hz and $J = 6.8$ Hz for the unsaturated and saturated H−H couplings, respectively) which fit an open rather than a cyclic structure.[10] The ^{13}C NMR showed the signal due to a quaternary carbon at a value (δ 165.7 ppm) compatible with an ester rather than an orthoester function.[12] Therefore, these spectral data allowed us to exclude a structure such as **3a** for the product obtained by photooxygenation in methanol of **1a**; they are in total agreement with hemiperacetal structure **6a** (Scheme 1).[13]

Formation of the hemiperacetal **6a** indicated the intermediacy of carbonyl oxide **5a** which was confirmed by performing the dye-sensitized photooxygenation of **1a** in acetone, ethyl vinyl ether, or methyl acrylate under the conditions used for **1b**.[11,7] As shown in Scheme 2, **1a** gave the 1,2,4-trioxolane **9a** in 50% yield,[14] the two stereoisomeric 5-ethoxy-1,2-dioxolanes **10a** and **11a** (in *ca.* 2:1 molar ratio, by ^{1}H NMR) in 95% yield,[14] and the two stereoisomeric forms of the regioisomers **12a**, **13a**, **14a**, and **15a** (in *ca.* 1:1:1:0.5 molar ratio, by ^{1}H NMR) in 75% yield,[14] respectively. The structures of the new products **9a**−**15a** were assigned on the basis of elemental analyses and/or spectral data. Indeed, the regiochemistry of dioxolanes **10a**−**15a** was readily established by spectroscopic techniques. In particular, in the ^{13}C NMR spectra of the 5-substituted dioxolanes **10a**, **11a**, and **14a** the signal for the methylene carbon in the ring appeared in the range δ 46−50 ppm while for both of the 4-substituted compounds **12a** and **13a** it was observed at δ 72.3 ppm, a value typical for an oxygenated methylene carbon. On the other hand, the ^{1}H NMR analysis of the partially purified minor compound **15a** clearly indicated that it is the C-3 stereoisomer of **14a**. The stereochemistry of compounds **10a**−**15a** was established by ^{1}H NMR with the aid of selective decouplings, taking into account the following observations: (1) the observed values of the coupling constants are closely related to those reported for other dioxolanes;[15] (2) the vicinal coupling constants between *cis* protons are larger than those between *trans* protons in five-membered rings;[16] and (3) a long range coupling exists between the H-3 and H-5 when they are in *trans* configuration.[15,17] Consistent with the assignment of the stereochemistry is the observed upfield

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[1] Part 3: Iesce, M. R.; Cermola, F.; Giordano, F.; Scarpati, R.; Graziano, M. L. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3295.

[2] Gollnick, K.; Griesbeck, A. *Tetrahedron* **1985**, *41*, 2057.

[3] Iesce, M. R.; Graziano, M. L.; Cermola, F.; Scarpati, R. *J. Chem. Soc., Chem. Commun.* **1991**, 1061.

[4] Iesce, M. R.; Cermola, F.; Graziano, M. L.; Cimminiello, G.; Scarpati, R. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1855.

[5] Iesce, M. R.; Cermola, F.; Graziano, M. L.; Scarpati, R. *Synthesis* **1994**, 944.

[6] Carbonyl oxides are known as elusive intermediates in the reaction of alkenes with ozone and of diazo compounds with singlet oxygen. They were evidenced by trapping reactions with methanol, carbonyl compounds, and vinyl ethers (Bunnelle, W. H. *Chem. Rev.* **1991**, *91*, 335).

[7] (a) Graziano, M. L.; Iesce, M. R.; Cermola, F.; Giordano, F.; Scarpati, R. *J. Chem. Soc., Chem. Commun.* **1989**, 1608. (b) Iesce, M. R.; Graziano, M. L.; Cermola, F.; Cimminiello, G.; Scarpati, R. *Gazz. Chim. Ital.* **1990**, *120*, 629.

[8] Iesce, M. R.; Cermola, F.; Graziano, M. L.; Scarpati, R. *J. Chem. Soc., Perkin Trans. 1* **1994**, 147.

[9] In contrast, under the same conditions, the peroxide **2b** and its derivatives substituted on the phenyl gave well-defined compounds.[7,8]

[10] For some alkoxy-2,5-dihydrofurans the unsaturated and saturated J_{H-H} couplings are reported to be 5.6−6.0 Hz and 1.0−1.2 Hz, respectively, (Batterham, T. J. *NMR Spectra of Simple Heterocycles*; Taylor, E. C., Weissberger, A., Eds.; John Wiley & Sons: New York, 1973; Chapter 5, p 378). On the other hand, a value of 12.9 Hz was found for the unsaturated J_{H-H} coupling in a (*Z*)-acrylate derivative.[11]

[11] Graziano, M. L.; Iesce, M. R.; Cimminiello, G.; Scarpati, R. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1699.

[12] The chemical shifts of polyoxygenated carbons for dihydrofurans **3** are reported in the range δ 121−122 ppm.[11]

[13] Chemical behavior of the product appeared not conclusive for the assignment of the structure. Although the absence of **4a**[5] in the hydrolysis mixture supported structure **6a**, compound **7a** obtained by Et_2S reduction (Iesce, M. R.; Cermola, F.; Piazza, A.; Graziano, M. L.; Scarpati, R. *Synthesis* **1995**, 439) and compound **8a** obtained by acid hydrolysis[5] could be formed both from **3a** and from **6a**.

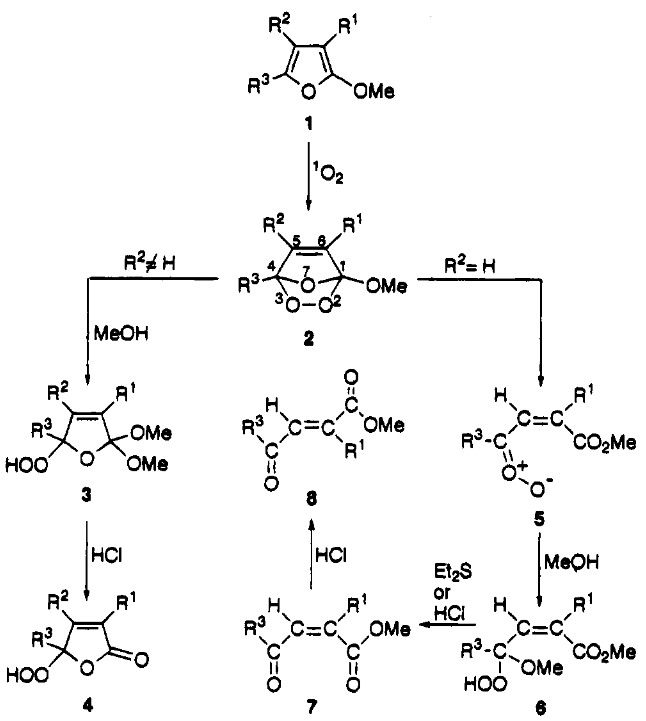
[14] Quantification was based on the relative areas of the distinct signals of each compound and the methoxy signals of the whole mixture (^{1}H NMR).

[15] Keul, H.; Choi, H.; Kuczkowski, R. L. *J. Org. Chem.* **1985**, *50*, 3365.

[16] Abraham, R. J.; Fisher, J.; Loftus, P. *Introduction to NMR Spectroscopy*; J. Wiley and Sons: New York, 1988; p 44.

0022-3263/95/1960-5324$09.00/0

Scheme 1



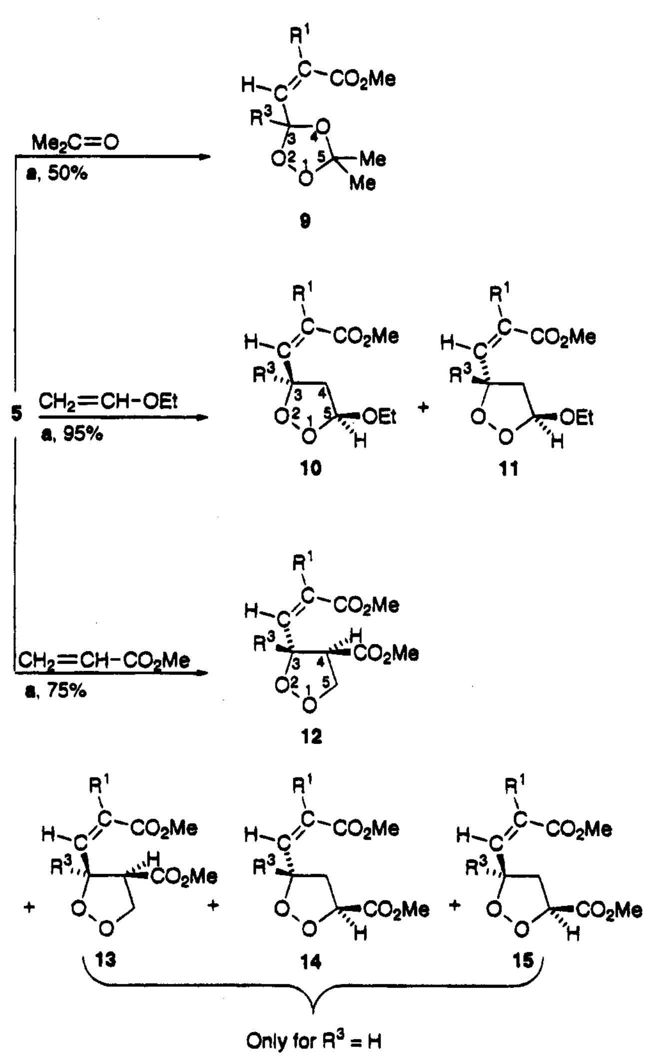
a; $R^1 = R^2 = R^3 = H$
b; $R^1 = CO_2Me$, $R^2 = H$, $R^3 = Ph$

chemical shift of the substituent at C-4 when it is at the shielding zone of the unsaturated chain attached to C-3. For example, the signal of 4-H appeared at δ 3.58 ppm for **12a** and at δ 4.19 ppm for **13a**; concomitantly, the signal of the CO_2Me appeared at δ 3.81 ppm for **12a** and at δ 3.64 ppm for **13a**.

The phenyl-substituted carbonyl oxide **5b** was reported to lead regioselectively to the 5-ethoxydioxolanes **10b** and **11b** by reaction with ethyl vinyl ether and to the 4-(methoxycarbonyl)dioxolane **12b** by reaction with methyl acrylate.[7] The finding that methyl acrylate reacts with the carbonyl oxide **5a** to give the regioisomers **14a** and **15a** together with **12a** and **13a** shows that the observed regioselectivity for **5b** is due to the presence, at the carbonyl oxide carbon, of a further conjugating substituent such as phenyl which makes dominant the interaction HOMO(dipole)–LUMO(dipolarophile) for the electron-poor alkene. On the basis of these new results it is evident that, in the absence of the phenyl substituent effect, the cycloaddition of carbonyl oxides is both HOMO- and LUMO-controlled by the dipole, as previously reported on the basis of theoretical calculations.[18]

In summary, we have found that *endo*-peroxide **2a**, in participating solvents, leads to acyclic or cyclic adducts *via* carbonyl oxide **5a**. The general behavior of **5a** is similar to that of the disubstituted carbonyl oxide **5b**. However, [3 + 2] cycloaddition of the latter to the electron-poor methyl acrylate is regioselective, while **5a** leads to the two stereoisomeric forms of both the regioisomers **12a**–**15a**, providing more information concerning the reactivity of the 1,3-dipolar system. Work is underway in our laboratories to further explore this area and to study the use of the carbonyl oxides in the synthesis of organic peroxides.

Scheme 2



a; $R^1 = R^3 = H$
b; $R^1 = CO_2Me$, $R^3 = Ph$

Experimental Section

General. IR spectra were recorded with chloroform as solvent. ^1H and ^{13}C NMR spectra were run in $CDCl_3$ at 400 and 100.6 MHz, unless otherwise stated. Chemical shifts are reported in ppm referenced to the TMS. Coupling constants were measured by homonuclear decoupling experiments. DEPT techniques were employed to determine the multiplicity in the ^{13}C spectra. HPLC was performed using a Merck Lichrosorb Si-60 (10 μm) column with a 5 mL min^{-1} flow rate of elution. The solvents used in photooxygenation reactions were anhydrous. Ethyl vinyl ether (Aldrich) and methyl acrylate (Fluka) were freshly distilled. 2-Methoxyfuran (Aldrich), tetraphenylporphyrin (TPP) (Fluka), and methylene blue (MB) (Fluka) were used without purification. Silica gel (0.063–0.2 mm Macherey-Nagel) and light petroleum (bp 40–60 °C) were used for column chromatography.

General Procedure for the Dye-Sensitized Photooxygenation of 2-Methoxyfuran (1a) in Various Solvents. Each solution of the furan **1a**, after addition of the sensitizer (TPP 3.6×10^{-4} mmol or MB 8×10^{-3} mmol for 1 mmol of **1a**) was irradiated with a halogen-superphot lamp (Osram, 650W). During the irradiation, dry oxygen was bubbled through the solution which was kept at the temperature pointed out below.

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(17) The coupling was measurable (J = 0.8 Hz) only for **11a**; for **12a**, **13a**, and **14a** it was apparent through selective decoupling experiments, in which irradiation of H-5 removed the line broadening of the signal for the coupled proton H-3.

(18) Houk, K. N.; Yamaguchi, K. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; J. Wiley and Sons: New York, 1984; Vol. 2, Chapter 13, p 435.

Progress of the reaction was checked by periodically monitoring the disappearance of the furan **1a** (^{1}H NMR).

1-Methoxy-2,3,7-trioxabicyclo[2.2.1]hept-5-ene (2a). A 5×10^{-2} M solution of the furan **1a** (0.5 mmol) in $CFCl_3$/$CDCl_3$ (1:1 v/v) (TPP as sensitizer) was photooxygenated at −78 °C. When the reaction was complete (120 min), the ^{1}H NMR spectrum, recorded at −78 °C at 200 MHz, showed the presence of **2a**[2] which at higher temperatures underwent rapid polymerization, as indicated by the appearance, in the ^{1}H NMR spectrum, of only broad signals. Evaporation of the solvent yielded only resinous material which was not characterized.

Methyl (*Z*)-4-Hydroperoxy-4-methoxy-2-butenoate (6a). A 2×10^{-2} M solution of the furan **1a** (98 mg, 1 mmol) in MeOH (MB as sensitizer) was photooxygenated at −20 °C. When the reaction was complete (150 min), MeOH was removed under reduced pressure at rt. The residue, which according to spectral analysis was the hemiperacetal **6a**, was taken up in dry ether and filtered to remove MB. Evaporation of the filtrate gave pure **6a** as a colorless oil (158 mg, 97%). All the attempts to separate **6a** from the MB chromatographically failed since, according to the behavior of other hemiperacetals **6**,[8,11] compound **6a** partly polymerized and partly hydrolyzed on contact with the adsorbents: IR 3519, 3415, 1723, 1664 cm^{-1}; ^{1}H NMR δ 3.59 (s, 3 H), 3.76 (s, 3 H), 5.97 (dd, $J = 11.5$, 0.7 Hz, 1 H), 6.19 (dd, $J = 6.8$, 0.7 Hz, 1 H), 6.28 (dd, $J = 11.5$, 6.8 Hz, 1 H), 9.29 (br s, 1 H); ^{13}C NMR δ 51.6 (q), 56.2 (q), 102.6 (d), 122.7 (d), 140.6 (d), 165.7 (s).[19] Anal. Calcd for $C_6H_{10}O_5$: C, 44.44; H, 6.22. Found: C, 44.61; H. 6.12.

Methyl (*Z*)-4-Oxo-2-butenoate (7a). A solution of **6a** (162 mg, 1 mmol) in CCl_4 (20 mL) was treated with Et_2S (180 mg, 2 mmol). When the reduction was complete (120 min) the ^{1}H NMR showed the presence of the *Z*-isomer **7a** in addition to Et_2S and Et_2SO. Removal of the solvent and of the unreacted Et_2S gave a residue which was chromatographed on silica gel using light petroleum/ether (4:1) as eluent to give 71 mg (62%) of **7a**[20] as a colorless oil: IR 1728, 1687, 1636 cm^{-1}; ^{1}H NMR δ 3.85 (s, 3 H), 6.34 (dd, $J = 11.7$, 7.4 Hz, 1 H), 6.65 (d, $J = 11.7$ Hz, 1 H), 10.55 (d, $J = 7.4$ Hz, 1 H). Anal. Calcd for $C_5H_6O_3$: C, 52.63; H, 5.30. Found: C, 52.61; H, 5.21.

Methyl (*E*)-4-Oxo-2-butenoate (8a). A solution of **6a** (162 mg, 1 mmol) in acetone (30 mL) was treated with 2 M HCl (0.3 mL) and kept at rt. After 1 h the solvent of a sample (1 mL) was evaporated and the ^{1}H NMR spectrum of the residue showed **6a** almost unchanged. After 36 h, the acetone was removed in vacuo from the remainder of the solution and the residue treated with H_2O (4 mL) and extracted three times with $CHCl_3$. The organic layers were dried over $MgSO_4$ and evaporated to a residue whose ^{1}H NMR spectrum showed, in addition to broad signals, the presence of **8a** (25%). No spectral evidence was obtained to support the presence of the lactone **4a**. Column chromatography of the residue on silica gel with light petroleum/ether (4:1) gave 24 mg (21%) of **8a**:[21] mp 38−39 °C (from light petroleum); IR 1733, 1704, 1646 cm^{-1}; ^{1}H NMR δ 3.85 (s, 3 H), 6.73 (d, $J = 15.9$ Hz, 1 H), 6.97 (dd, $J = 15.9$, 7.3 Hz, 1 H), 9.77 (d, $J = 7.3$ Hz, 1 H). Control experiments showed that, under the conditions used for the hydrolysis of **6a**, the *Z*-isomer **7a** partly isomerizes into *E*-isomer **8a** and partly polymerizes.

Methyl (*Z*)-3-(5,5-Dimethyl-1,2,4-trioxolan-3-yl)propenoate (9a). A 2×10^{-2} M solution of the furan **1a** (98 mg, 1 mmol) in acetone (MB as sensitizer) was photooxygenated at −20 °C. When the reaction was complete (150 min), the acetone was removed under reduced pressure at rt. The residue, whose ^{1}H NMR showed the presence of **9a** (50%[14]) as the only identifiable compound, was chromatographed over silica gel using light petroleum/ether (17:3) as eluent to give 94 mg (50%) of the trioxolane **9a** as a colorless oil: IR 1725, 1658 cm^{-1}; ^{1}H NMR δ 1.51 and 1.52 (2 × s, 6 H), 3.76 (s, 3 H), 6.04 (dd, $J = 11.5$, 0.5 Hz, 1 H), 6.16 (dd, $J = 11.5$, 7.1 Hz, 1 H), 6.70 (dd, $J = 7.1$, 0.5 Hz, 1 H); ^{13}C NMR δ 24.2 (two overlapping q), 51.8 (q), 97.3 (d), 109.2 (s), 124.7 (d), 141.0 (d), 165.3 (s). Anal. Calcd for $C_8H_{12}O_5$: C, 51.06; H, 6.43. Found: C, 51.21; H, 6.40.

Methyl (*Z*)-3-(*cis*-5-Ethoxy-1,2-dioxolan-3-yl)propenoate (10a) and Methyl (*Z*)-3-(*trans*-5-Ethoxy-1,2-dioxolan-3-yl)propenoate (11a). A 2×10^{-2} M solution of the furan **1a** (98 mg, 1 mmol) in ethyl vinyl ether (TPP as sensitizer) was photooxygenated at −20 °C. When the reaction was complete (150 min), the ether was removed under reduced pressure at rt. The residue, which consisted of only the stereoisomeric dioxolanes **10a** and **11a** (95%,[14] in *ca.* 2:1 molar ratio by ^{1}H NMR), was rapidly chromatographed on a short column of silica gel using light petroleum/ether (9:1) to give 141 mg (70%[22]) of a mixture of the two isomers. Chromatography of this mixture by HPLC with a mobile phase of *tert*-butyl methyl ether/hexane (3:22) led to the isolation of the only minor isomer **11a** which was characterized by analytical and spectral data. For the isomer **10a**, which was still obtained in a mixture with **11a**, the spectral data were deduced by those of the mixture, the signals of **11a** being subtracted.

11a: colorless oil; HPLC $t_R = 26.2$ min; IR 1718, 1646 cm^{-1}; ^{1}H NMR δ 1.24 (t, $J = 7.1$ Hz, 3 H), 2.57 (ddd, $J = 12.9$, 5.5, 3.5 Hz, 1 H), 3.09 (ddd, $J = 12.9$, 8.2, 1.2 Hz, 1 H), 3.51 (dq, $J = 9.3$, 7.1 Hz, 1 H), 3.74 (s, 3 H), 3.83 (dq, $J = 9.3$, 7.1 Hz, 1 H), 5.27 (ddd, $J = 5.5$, 1.2, 0.8 Hz, 1 H), 5.81 (dd, $J = 11.5$, 1.5 Hz) and 5.86 (m, $J = 8.2$, 7.1, 3.5, 1.5, 0.8) together 2 H, 6.47 (dd, $J = 11.5$, 7.1 Hz, 1 H); ^{13}C NMR δ 14.9 (q), 49.7 (t), 51.5 (q), 63.8 (t), 76.7 (d), 102.0 (d), 119.3 (d), 149.9 (d), 166.1 (s). Anal. Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.32; H, 6.81.

10a (^{1}H NMR integration indicated an approximate 4:1 molar ratio with **11a**): HPLC $t_R = 27.2$ min; ^{1}H NMR δ 1.23 (t, $J = 7.1$ Hz, 3 H), 2.33 (ddd, $J = 12.9$, 6.5, 1.2 Hz, 1 H), 3.21 (ddd, $J = 12.9$, 8.4, 5.5 Hz, 1 H), 3.50 (dq, $J = 9.3$, 7.1 Hz, 1 H), 3.74 (s, 3 H), 3.82 (dq, $J = 9.3$, 7.1 Hz, 1 H), 5.32 (dd, $J = 5.5$, 1.2 Hz, 1 H), 5.69 (m, $J = 8.4$, 7.1, 6.5, 1.5 Hz, 1 H), 5.89 (dd, $J = 11.5$, 1.5 Hz, 1 H), 6.38 (dd, $J = 11.5$, 7.1 Hz, 1 H); ^{13}C NMR δ 15.0 (q), 48.5 (t), 51.5 (q), 63.7 (t), 76.8 (d), 102.8 (d), 121.1 (d), 145.6 (d), 166.0 (s).

Methyl (*Z*)-3-[*trans*-4-(Methoxycarbonyl)-1,2-dioxolan-3-yl]propenoate (12a) and Methyl (*Z*)-3-[*cis*-4-(Methoxycarbonyl)-1,2-dioxolan-3-yl]propenoate (13a); Methyl (*Z*)-3-[*trans*-5-(Methoxycarbonyl)-1,2-dioxolan-3-yl]propenoate (14a) and Methyl (*Z*)-3-[*cis*-5-(Methoxycarbonyl)-1,2-dioxolan-3-yl]propenoate (15a). A 2×10^{-2} M solution of the furan **1a** (98 mg, 1 mmol) in methyl acrylate (TPP as sensitizer) was photooxygenated at −20 °C. After completion of the reaction (150 min), the acrylate was removed at rt under reduced pressure, using a solid CO_2−acetone trap. The residue, which showed the presence of the four isomers **12a**–**15a** [75%[14] (**12a**:**13a**:**14a**:**15a** in *ca.* 1:1:1:0.5 molar ratio by ^{1}H NMR)], was rapidly chromatographed on a short column of silica gel, using light petroleum/ether (3:1) to give a fraction (110 mg) composed of **12a**, **13a**, **14a**, and **15a** and a fraction (38 mg) composed of **12a**, **13a**, and **14a** (total yield 69%[22]). Chromatography of the latter fraction by HPLC with a mobile phase of *tert*-butyl methyl ether/hexane (1:3) led to the isolation of **12a**, **13a**, and **14a** which were characterized by analytical and spectral data. All the attempts to isolate the regioisomer **15a** by HPLC of the first fraction failed owing both to its small amount and to its transformation on contact with the adsorbent.[22] However, it was obtained partially purified in mixture with **13a**, and its spectral data were deduced by those of this mixture, the signals of **13a** being subtracted.

12a: oil; HPLC $t_R = 22.6$ min; IR 1743, 1719, 1649 cm^{-1}; ^{1}H NMR δ 3.58 (ddd, $J = 7.8$, 6.8, 3.9 Hz, 1 H), 3.72 (s, 3 H), 3.81 (s, 3 H), 4.13 (dd, $J = 7.8$, 6.8, Hz, 1 H), 4.42 (br t, $J = 7.8$ Hz, 1 H), 5.91 (dd, $J = 11.7$, 1.5 Hz, 1 H), 6.00 (ddd, $J = 6.8$, 3.9, 1.5 Hz, 1 H), 6.39 (dd, $J = 11.7$, 6.8 Hz, 1 H); ^{13}C NMR δ 51.5 (q), 52.5 (q), 60.8 (d), 72.3 (t), 80.5 (d), 120.6 (d), 147.3 (d), 165.7 (s), 170.9 (s). Anal. Calcd for $C_9H_{12}O_6$: C, 50.00; H, 5.60. Found: C, 49.86; H, 5.65.

13a: oil; HPLC $t_R = 20.9$ min; IR 1738, 1725, 1650 cm^{-1}; ^{1}H NMR δ 3.64 (s, 3 H), 3.76 (s, 3 H), 4.19 (dt, $J = 7.8$, 4.9 Hz, 1 H), 4.29 (t, $J = 7.8$ Hz, 3 H), 4.48 (br dd, $J = 7.8$, 4.9 Hz, 1 H),

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[19] For completeness we report the NMR data previously assigned to a different structure.[2]

[20] The previously reported ^{1}H NMR data for **7a**, which were recorded at 60 MHz (Scharf, H. D.; Janus, J. *Chem. Ber.* **1978**, *111*, 2741), were inexact.

[21] Reported as oil; IR (film) and ^{1}H NMR (CCl_4, 60 MHz) data were consistent with those previously reported (Baltes, H.; Stork, L.; Schaefer, H. J. *Chem. Ber.* **1979**, *112*, 807).

[22] As previously reported for the 5-substituted dioxolanes **10b** and **11b**,[7b] **10a** and **11a** on contact with silica gel slowly lead to ethyl 2,5-dihydro-5-oxo-2-furanacetate (IR, ^{1}H NMR) while **14a** and **15a** slowly lead to methyl 2,5-dihydro-5-oxo-2-furanylpyruvate (IR, ^{1}H NMR).

5.95 (dd, $J = 11.7$, 1.5, 1 H), 6.08 (br dt, $J = 7.8$, 1.5 Hz, 1 H), 6.27 (dd, $J = 11.7$, 7.8, 1 H); ^{13}C NMR δ 51.5 (q), 52.0 (q), 57.8 (d), 72.3 (t), 78.7 (d), 121.7 (d), 142.7 (d), 165.7 (s), 169.9 (s). Anal. Calcd for $C_9H_{12}O_6$: C, 50.00; H, 5.60. Found: C, 50.25; H, 5.81.

14a: oil; HPLC $t_R = 24.3$ min; IR 1719, 1650 cm^{-1}; ^1H NMR δ 2.74 (ddd, $J = 12.9$, 9.1, 3.4 Hz, 1 H), 3.47 (ddd, $J = 12.9$, 8.3, 3.4 Hz, 1 H), 3.74 (s, 3 H), 3.81 (s, 3 H), 4.78 (br dd, $J = 9.1$, 3.4 Hz, 1 H), 5.86 [overlapping dd ($J = 11.5$, 1.5 Hz) and m ($J = 8.3$, 6.7, 3.4, 1.5 Hz), 2 H], 6.47 (dd, $J = 11.5$, 6.7 Hz, 1 H); ^{13}C NMR δ 46.1 (t), 51.6 (q), 52.4 (q), 76.8 (d), 77.4 (d), 119.7 (d), 148.9 (d), 165.9 (s), 170.5 (s). Anal. Calcd for $C_9H_{12}O_6$: C, 50.00; H, 5.60. Found: C, 50.11; H, 5.55.

15a (^1H NMR integration indicated an approximate 1:1 molar ratio with **13a**): HPLC $t_R = 20.1$ min; ^1H NMR δ 2.62 (ddd, $J = 12.7$, 5.9, 4.9 Hz, 1 H), 3.43 (ddd, $J = 12.7$, 8.8, 7.8 Hz, 1 H), 3.74 (s, 3 H), 3.79 (s, 3 H), 4.81 (dd, $J = 8.8$, 4.9 Hz, 1 H), 5.76 (m, $J = 7.8$, 7.1, 5.9, 1.5 Hz, 1 H), 5.92 (dd, $J = 11.5$, 1.5 Hz, 1 H), 6.36 (dd, $J = 11.5$, 7.1 Hz, 1 H).

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