Multifunctional Compounds from the 2,5-Peroxide of Methyl Furan-3-carboxylate

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Thermal rearrangement of the title compound (**1**) leads to the corresponding diepoxide (**3**) in apolar solvents and to the Δ^2-butenolide (**4**) in basic solvents, whereas the formation of the epoxide (**5**) is independent of solvent; these conversions represent convenient entries to the syntheses of multifunctional compounds which are structurally related to biologically active products.

Recently, we reported that the 2,5-peroxides of 2,5-diarylfurans, by thermal conversion in organic solvents other than alcohols, lead to *cis* 1,2-diaroyloxiranes,[1,2] *cis* 2-aroylenol esters,[1,3] and parent furans,[1,4] the actual products being temperature, solvent, and concentration dependent. In contrast, thermal conversion in solution of 2,5-peroxides of 2,5-dialkylfurans takes a different course yielding diepoxides and/or polymeric material.[4,5]†

We have now found that methyl 2,3,7-trioxabicyclo[2.2.1]hept-5-ene-5-carboxylate (**1**),‡ prepared in quantitative yield by dye-sensitized photo-oxygenation at −40 °C of the 2,5-unsubstituted furan (**2**), at room temperature in chloroform

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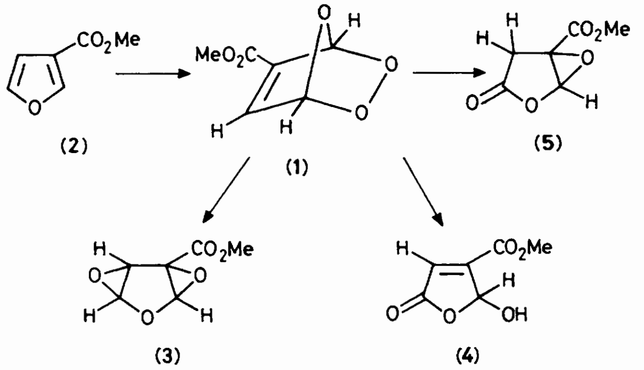
† Gollnick[6] suggests that the 2,5-peroxide of 2,5-dimethylfuran yields the diepoxide *via* a dimeric 2,5-peroxide.

‡ Isolated as previously described for similar peroxides (ref. 4). M.p. 53—58 °C, i.r. ν(CHCl$_3$) 1725 and 1612 cm^{-1}; n.m.r. δ (^{1}H) (CDCl$_3$) 3.82 (s, 3H, OMe), 6.51 (d, *J* 1.1 Hz, 1H, 1-H), 6.88 (d, *J* 1.1 Hz, 1H, 4-H), and 7.05 (t, *J* 1.1 Hz, 6-H). Molecular weight (MW) (benzene freezing point (f.p.) depression) 153 (required 158). Satisfactory active oxygen analysis was obtained.

Table 1. % Yields of the products of thermal conversion of the 2,5-peroxide (**1**) at 35 °C.

Entry	Solvent	Reaction time[a]	Yield/%[b]			Polymeric material/%
			(**3**)	(**4**)	(**5**)	
1	Chloroform	70 min	80	—	11	9
2	Benzene	90 min	77	—	23	—
3	Nitromethane[c]	5 min	45	—	20	35
4	Acetonitrile[c]	30 min	25	20	30	25
5	Acetone[c]	30 min	—	50	18	32
6	Methanol[c]	30 min	—	50	10	40
7	THF[c,d]	5 min	—	50	10	40
8	DMF[d]	immediate	—	54	—	46
9	Triethylamine	immediate	—	—	—	100

[a] Based on the disappearance of peroxide (**1**) (^{1}H n.m.r.). [b] Deduced on the basis of the ^{1}H n.m.r. spectrum. [c] Sometimes a compound, assigned as methyl 5-hydroxy-5*H*,2-furanone-3-carboxylate [$\delta(^1H)$ (CD_3CN) 6.13 (d, *J* 1.1 Hz, 1H, 5-H) and 7.85 (d, *J* 1.1 Hz, 1H, 4-H)] was detected, but this rapidly polymerised. [d] THF = tetrahydrofuran, DMF = dimethylformamide.



behaves in the same way as the 2,5-peroxides of the 2,5-dialkylfurans yielding methyl 3,5,7-trioxatricyclo-[4.1.0.0^{2,4}]heptane-1-carboxylate, (**3**).§ In contrast, when acetone was used as solvent a drastic change of reaction pathway was observed and methyl 5*H*,2-furanone-5-hydroxy-4-carboxylate (**4**)¶ was obtained. In both solvents some methyl 3-oxo-2,6-dioxabicyclo[3.1.0]hexane-5-carboxylate, (**5**),** was detected which was isolated by silica gel chromatography. Table 1 shows % yields of the rearrangement products of the peroxide (**1**) at 35 °C in various solvents. The formation of one or both the major products is independent of dielectric constant of the solvent, but it is related to its basicity.[7] Furthermore, the product ratios were invariant with concentration, the reaction course was uninfluenced by 2,6-di-t-butyl *p*-cresol addition, and no interconversions of compounds (**3**), (**4**), or (**5**) were observed under these reaction conditions. Therefore, we suggest that all the three isomerization processes involve an intramolecular synchronous rearrangement with, in particular, the solvent assisting breakage of the C–H α-bond and inducing the formation of the Δ^2-butenolide (**4**).

The good yields together with the mild reaction conditions make the conversion of the furan (**2**) into furanone (**4**) a convenient entry to the synthesis of functionalized Δ^2-butenolides. Also, epoxides of the type (**5**) are interesting multifunctional compounds which have been obtained only occasionally[8] and for which no general preparative method or general properties are reported. In this connection, it is noteworthy that the compounds (**3**)—(**5**) are structurally related to compounds which play a significant role both in biochemistry and/or phytochemistry.[5,9—11]

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§ From entry 1: m.p. 87—90 °C (from light petroleum); i.r. $\nu(CHCl_3)$ 1745 cm^{-1}; n.m.r. δ (^{1}H) ($CDCl_3$) 3.87 (s, 3H, OMe), 4.27 (d, *J* 1.5 Hz, 1H, 2-H), 5.61 (dd, *J* 1.5 and 2.2 Hz, 1H, 4-H), and 5.71 (d, *J* 2.2 Hz, 1H, 6-H); δ (^{13}C) ($CDCl_3$) 50.2 (d, C-2), 53.1, (q, OMe), 56.7 (s, C-1), 91.6 (d, C-4), 93.6 (d, C-6), and 165.2 (s, C=O). MW (benzene f.p. depression) 150 (required 158). Satisfactory elemental analyses were obtained.

¶ Isolated from entry 8 by dissolution in diethyl ether; liquid; i.r. $\nu(CHCl_3)$ 3565, 1795, 1745, and 1620 cm^{-1}; n.m.r. δ (^{1}H) ($CDCl_3$) 3.91 (s, 3H, OMe), 5.25 (bs, 1H, OH), 6.41 (d, *J* 1.1 Hz, 1H, 5-H), and 6.74 (d, *J* 1.1 Hz, 1H, 3-H); δ (^{13}C) ($CDCl_3$) 52.9 (q, OMe), 97.3 (d, C-5), 128.7 (d, C-3), 153.3 (s, C-4), 161.1 [s, C=O (ester)], and 169.1 [s, C=O (lactone)]; satisfactory elemental analyses were obtained.

** M.p. 85—87 °C (from light petroleum); i.r. $\nu(CHCl_3)$ 1818 and 1747 cm^{-1}; n.m.r. δ (^{1}H) ($CDCl_3$) 2.98 (dd, *J* 19.5 and 0.7 Hz) and 3.38 (d, *J* 19.5 Hz, together 2H, 4-H), 3.86 (s, 3H, OMe), and 5.75 (d, *J* 0.7 Hz, 1H, 1-H); δ(^{13}C) ($CDCl_3$) 33.2 (t, C-4), 53.1 (q, OMe), 57.1 (s, C-5), 80.3 (d, C-1), 164.6 [s, C=O(ester)], and 171.3 [s, C=O (lactone)]; satisfactory elemental analyses were obtained.

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