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INTRAMOLECULAR SILYL MIGRATION IN THE SINGLET OXYGENATION OF 2-METHYL-5-TRIMETHYLSILYLFURAN

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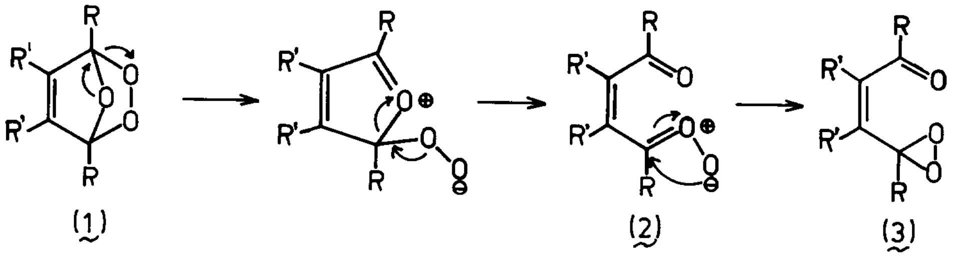
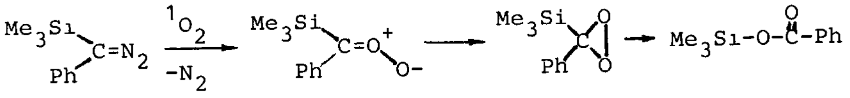
SUMMARY: Tetraphenylporphyrin-sensitized photooxygenation of 2-methyl-5-trimethylsilylfuran (4) affords quantitatively trimethylsilyl 2-oxo-4-pentenoate (5), presumably via intramolecular Baeyer-Villiger rearrangement of the intermediary dioxirane (3a).

Recently we reported[1] that the furan endoperoxides (1) oxidize olefins to epoxides, sulfides to sulfoxides and adamantanone to its lactone. The oxygen transfering ability of this novel oxidant was rationalized in terms of the carbonyl oxide and/or dioxirane intermediates (2) and (3), as illustrated in Eq.1. Attempts to differentiate between these highly reactive species by intermolecular trapping experiments with dipolarophiles such as aldehydes (PhCHO and CH_3CHO)[2] and ketones (CF_3COCF_3 and adamantanone)[3] unfortunately failed; intermolecular Baeyer-Villiger oxidation of the carbonyl dipolarophiles occurred. The latter results suggest that an intermediate of (1) is responsible for these oxygen transfer reactions; they do not, however enable us to differentiate between the proposed carbonyl oxide (2) and dioxirane (3) possibilities. Moreover, very recently it was argued[4] that the stable endoperoxide of 1,3-di-tert-butylisofuran epoxidizes olefins and hydroxylates aromatic rings via the diradical rather than the dipolar form of the resulting carbonyl oxide intermediate.



(1)

Since intermolecular trapping experiments failed to define the nature of the oxidizing species derived from the furan endoperoxides (1), we turned to intramolecular probes. For example, it was previously shown[5] that the singlet oxygenation of α-silyl diazoalkanes affords silyl esters (Eq.2); a preference for the dioxirane intermediate was expressed. Similarly, the

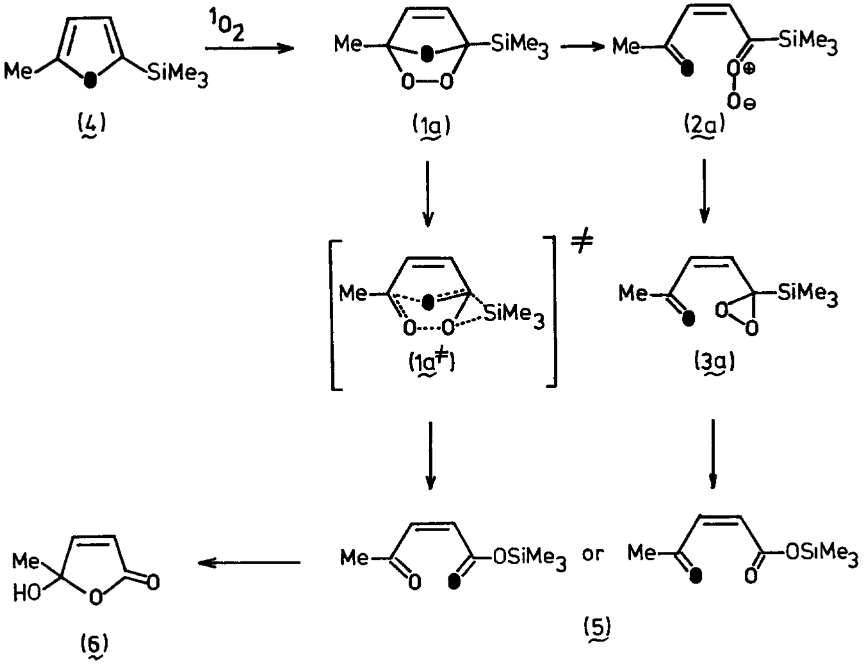


(2)

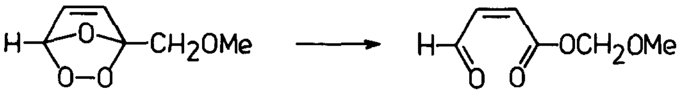
formation of silyl formate in the ozonolysis of silylketenes was rationalized in terms of a related dioxirane structure.[6] These interesting intramolecular Baeyer-Villiger rearrangements served as incentive to prepare the silylfuran endoperoxide (1a) and examine its singlet oxygenation. The results of this investigation are herein reported.

Tetraphenylporphyrin-sensitized photooxygenation of a 0.08 M solution of 2-methyl-5-trimethylsilylfuran[7] (4) in CCl_4 at 0°C as described[11], afforded a quantitative yield of silyl ester (5), cf. Scheme I, characterized on the basis of the following spectral data: ^{1}H NMR (CCl_4) δ(ppm) 0.35 (9H, s, Me_3Si) 2.30 (3H, s, CH_3), 5.80-6.00 (1H, d, J = 12 Hz, =C-H) and 6.30-6.50 (1H, d, J = 12 Hz, =C-H); IR (CCl_4) ν(cm^{-1}) 3100 (=C-H), 2980-2900 (aliphatic CH), 1720 (CO_2SiMe_3), 1700 (CH_3CO) and 1625 (C=C). Oxygen, sensitizer and light were all necessary to effect this oxidation. On methanolysis the silyl ester (5) was quantitatively converted to the known γ-hydroxy-γ-lactone (6), whose spectral data were identical to the reported ones.[8]

SCHEME I



Attempts to trap the silylfuran endoperoxide (**1a**) by low temperature (-60°C) reduction with diimide[9] led to a complex and undefined product mixture. Trapping (**1a**) with methanol[10], by carrying out the photooxygenation of the furan (**4**) directly in CH_3OH at low temperature (-70°C) afforded exclusively the γ-lactone (**6**). Clearly, the intramolecular silatropic shift in the rearrangement (**1a**) → (**5**) takes place faster than external intervention by methanol. In analogy to previous work[5,6], it is tempting to conclude that the dioxirane intermediate (**3a**), derived from cyclization of the carbonyl oxide intermediate (**2a**) is the immediate precursor to the silyl ester (**5**). Nevertheless, recently[11] it has been claimed that furan endoperoxides (**1b**) undergo intramolecular Baeyer-Villiger rearrangement directly into methoxymethyl cis-4-oxo-2-butenoate (**7**), the so-called "anomalous ozonide" product[12], without intervention of carbonyl oxide or dioxirane intermediates (Eq.3). Although the evidence in support of this interpretation is modest, in fact, recent results on the ozonization of α,β-enones[13] speak against such a direct mechanism, analogously the formation of silyl ester (**5**) via the sequence (**1a**) → (**1a**$^{\neq}$) → (**5**) can be proposed. Oxygen labeling experiments (Scheme I), by tagging the furan oxygen with O-18, should unequivocally permit differentiation between the direct path via the activated complex (**1a**$^{\neq}$) versus stepwise path via the intermediates (**2a**) and/or (**3a**). Such experiments are currently in progress. However, the question whether carbonyl oxides (**2**) or dioxiranes (**3**) are the immediate precursors in such intramolecular Baeyer-Villiger rearrangements must be answered using other mechanistic probes, e.g. intramolecular trapping with built-in carbonyl dipolarophiles.[14] Such an experiment is presented in the accompanying paper.



(**1b**) (**7**) (3)

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