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## Triphenylphosphine Reduction of Thiophene Endoperoxides: Nucleophilic Attack on Sulfur versus Biphilic Insertion into the Peroxide Bond

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Abstract: The thiophene endoperoxide 2a, obtained by photooxygenation of thiophene 1a, led with triphenylphosphine to the furan 3a and betaine 4, while the 5-phenyl derivative 2b produced quantitatively furan 3b; two independent reaction pathways are proposed which entail nucleophilic attack on sulfur by triphenylphophine to afford entrione 5a and betaine 4 and biphilic insertion into the peroxide bond to generate furan 3a.

The [4+2] cycloaddition of thiophenes with singlet oxygen leads to the corresponding endoperoxides<sup>[1]</sup>, which constitute thiaozonide structures. Although these interesting bicyclic sulfur-substituted peroxides possess a variety of opportunities to undergo chemical reactions, only the thermolysis of thiophene endoperoxides has so far been investigated<sup>[1]</sup>. Presently we report on the novel reaction of the two acylthiophene endoperoxides 2a,b with triphenylphosphine, in which we demonstrate that triphenylphosphine attacks both the sulfur and oxygen sites of the endoperoxides 2a,b to promote unprecedented chemistry (Scheme 1).



Photooxygenation of thiophenes 1a,b was performed with tetraphenylporphine as sensitizer in CDCl<sub>3</sub> at - 30 °C and led to endoperoxides 2a,b, which were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy at - 20 °C. The chemical shifts of the two carbon atoms substituted by the heteroatoms are typical for such compounds<sup>[1b]</sup> (2a:  $\delta$  105.7, 106.5; 2b:  $\delta$  105.6, 107.0).

Treatment of endoperoxide 2a with three equivalents of triphenyphosphine at room temperature yielded furan 3a and betaine 4 in a ratio of 55: 45 (Scheme 1), whereas endoperoxide 2b is transformed entirely to the

corresponding furan 3b. The product ratio was determined by integration of characteristic signals in the crude <sup>1</sup>H NMR spectrum (by comparison with authentic material). The betaine structure 4 is consistent with all chemical shifts (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR) and all phosphorus coupling constants.

The mechanism of the formation of betaine 4 from endoperoxide 2a is presented in Scheme 1. The first step (Scheme 1, step a) involves nucleophilic attack of triphenylphosphine on the sulfur atom of the endoperoxide 2a and elimination of triphenylphosphine sulfide, which was detected by <sup>31</sup>P NMR spectroscopy ( $\delta = 43.4$ ), to afford the enetrione 5a. A subsequent 1,5 H shift (Scheme 1, step b) transforms the vinylic methyl group into the exomethylene group and the resulting enone is in equilibrium with its cyclic hemiacetal 6 (Scheme 1, step c). Michael-type addition of another triphenylphosphine leads to the intermediary betaine which converts to the observed betaine 4 by H shift (Scheme 1, steps d and e). Experimental evidence in support derives from independent synthesis of betaine 4 by starting from entrione 5a<sup>[2]</sup> (62% yield of isolated material) or hemiacetal 6 and by monitoring the reaction progress by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy.

In the reactions of enertione 5a or hemiacetal 6 with triphenylphosphine, no furan 3a was observed. Thus, there appears to exist an independent reaction channel. We postulate the biphilic insertion of triphenylphosphine into the peroxide bond of the endoperoxide 2a (Scheme 1, step f), a well-established reaction mode for endoperoxides<sup>[3]</sup> and dioxetanes<sup>[4]</sup>. Subsequent extrusion of triphenylphosphine oxide  $[\delta(^{31}P) 29.1]$  results in thiones, which are desulfurized by triphenylphosphine to the furan 3a (Scheme 1, steps g and h).

The steps b to e are not possible for the endoperoxide 2b because of the phenyl group at the C-5 position and, hence, furan 3b is the only product in the reaction of endoperoxide 2b with triphenylphosphine. Since furan 3b results when independently prepared enerrione 5b is treated with triphenylphosphine<sup>[2]</sup> and both S attack and 0-0 insertion are expected to take place in the reaction of triphenylphosphine with the endoperoxide 2b, the sequences of steps f to h and of steps i and j (Scheme 1) are suggested for the formation of furan 3b. In contrast, for entrione 5a, the more favorable alternative is generation of betaine 4.

The present results uncover a novel reaction type of thiophene endoperoxides and provide valuable mechanistic insight into their ambident behavior towards triphenylphosphine. The thiaozonides may be attacked either at the sulfur atom or at the peroxide bond.

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