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PHOTOOXYGENATION OF 3- AND 2-SILYLOXYBENZOFURANS: REARRANGEMENT OF DIOXETANES VIA α-SILYLPEROXY KETONES TO KETOESTER CLEAVAGE PRODUCTS

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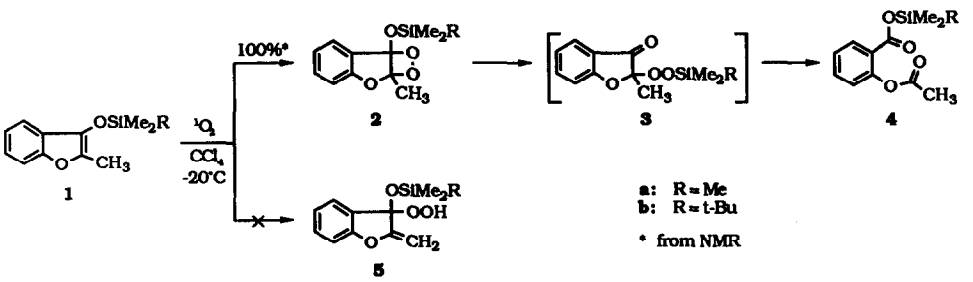
Abstract: Photooxygenation of 2-methyl-3-silyloxybenzofurans **1** afforded isolable dioxetanes **2**, the latter rearranged *via* α-silylperoxy ketones **3** to cleavage products **4**; 2-silyloxy-3-methylbenzofuran **6** with $^1O_2$ gave the more stable dioxetane **7**.

Photooxygenation of silyl ketene acetals afforded dioxetanes, which rearranged on warming into α-silylperoxy esters. [1] Now we found for the first time an analogous pathway in the reaction of the silyl enol ether **1a** with $^1O_2$ (Eq. 1). The difference in this case is that the rearrangement product, namely the α-silylperoxy ketone



(Eq. 1)

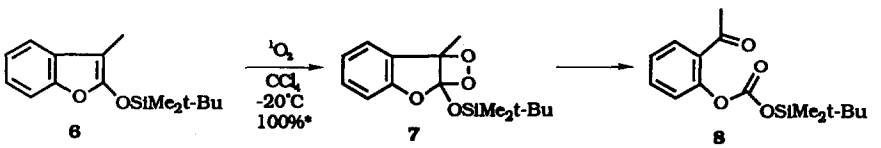
3a, was unstable and rearranged further into cleavage product **4a**. Previously, such cleavage products were considered to arise exclusively directly from the corresponding dioxetanes **2** without trespassing α-silylperoxy ketones **3**.

2-Methyl-3-silyloxybenzofurans **1** were prepared from 2-methylbenzofuran-3-one [2] according to published methods [3] and characterized [4] by NMR, IR, MS and CH analysis. A solution of benzofuran **1a** and catalytic amounts of TPP (tetraphenylporphin) in CCl_4 under an oxygen atmosphere was irradiated at -20 °C and the reaction was monitored by ^1H NMR. After about 1h, benzofuran **1a** was converted completely into dioxetane **2a**, which was confirmed by ^1H and ^{13}C NMR, [5] IR, and peroxide test (KI/HOAc). At 35 °C during about 1h the dioxetane **2a** rearranged to the known ester **4a**. [6] When dioxetane **2a** was allowed to stand at -20 °C, besides ketoester **4a** the α-silylperoxy ketone **3a** [7] was observed by its characteristic ^{13}C NMR signal at δ 197.5 (C=O). At this temperature, after 20-30 d the dioxetane **2a** was completely converted into silylperoxy ketone **3a** and ketoester **4a** (**3a** : **4a** = 65 : 35). When the reaction mixture was warmed up from -20 to 35 °C, all silylperoxy ketone **3a** was converted into ketoester **4a** in a period of 4h. These results imply that dioxetane **2a** rearranged *via* the intermediary silylperoxy ketone **3a** into the ketoester **4a**. During

this process no prototropic ene reaction product **5a** was detected.

The photooxygenation of benzofuran **1b** gave under the same conditions as employed for benzofuran **1a** the dioxetane **2b**, which was characterized [8] by ^1H and ^{13}C NMR, IR, and the peroxide test. Similarly, no prototropic ene reaction product **5b** was detected. The dioxetane **2b** rearranged at ambient temperature into the ketoester **4b**, which was characterized [9] by ^1H and ^{13}C NMR, IR and MS. The difference in the rearrangement of dioxetanes **2b** *versus* **2a** is that no α-silylperoxy ketone **3b** was observed during NMR monitoring. If the reaction course of dioxetane **2b** to ketoester **4b** is the same as that of **2a** to **4a**, presumably the intermediary silylperoxy ketone **3b** appears to be too unstable for NMR detection.

Furthermore, the regioisomeric silyloxybenzofuran, namely 2-dimethyl-t-butylsilyloxy-3-methylbenzofuran (**6**), was prepared from 3-methylbenzofuran-2-one [10] according to published methods [3] and characterized by NMR [11] IR, MS and CH analysis. The photooxygenation of benzofuran **6** gave under the same conditions as used for the regioisomeric benzofurans **1** the dioxetane **7** (Eq. 2) within 30 min, which was



6 **7** **8** (Eq. 2)

* from NMR

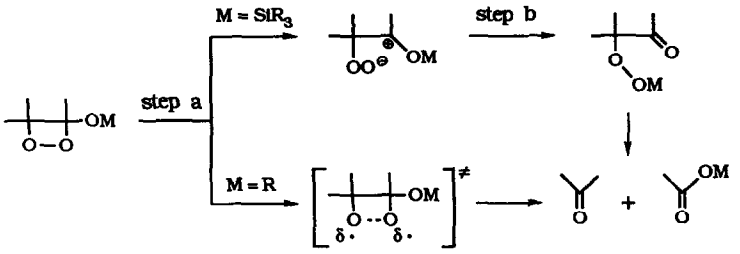
confirmed by NMR, [12] IR and the peroxide test (KI/HOAc). No ene product was detected; moreover, dioxetane **7** was more stable than its regioisomer **2**. At about 20 °C dioxetane **7** was converted slowly within about 9 d to the ketoester **8**, the usual dioxetane cleavage product. In this process no intermediary α-silylperoxy lactone analogous to the α-silylperoxy ketone **3a** was detected.

It was previously reported [13] that the photooxygenation of 2- or 3-methylbenzofurans did not lead to ene products. Similarly, neither did we observe that the photooxygenation of the silyloxy derivatives **1a,b** and **6** afforded any prototropic ene products. The significant difference in the cases of 2- or 3-methylbenzofurans is that ketoester products were formed, postulated to arise *via* ring opening of the corresponding dioxetanes, [13a] while the silyloxy derivatives **1a,b** and **6** gave isolable dioxetanes **2a,b** and **7** as primary products. Furthermore, the study of deuterium incorporation in the photooxygenation of 3-methylbenzofuran indicated that the observed ketoester could not derive from ene reaction followed by Hock cleavage of the resulting hydroperoxide. [13a] However, the process **2a** → **3a** → **4a** (Eq. 1) conclusively establishes that the isolable dioxetane **2a** rearranged *via* silyl migration into the α-silylperoxy ketone **3a**, the latter undergoing subsequent Hock-Criegee cleavage [14] into the ketoester **4a**. Such Hock-Criegee cleavage of silyl peroxides into dicarbonyl products was recently documented [15] in the photooxygenation of the O-silylated cyclic enediols.

The present case of the photooxygenation of 3-silyloxybenzofuran **1** (Eq. 1) and the previously reported photooxygenation of the silyl ketene acetals [1] and ene diols [15] clearly demonstrate that the resulting silyloxy-substituted dioxetanes rearrange very readily into the corresponding α-silylperoxy carbonyl products. Such transformations are rare for alkoxy-substituted dioxetanes; in fact, only recently [16] was an

example documented.

At least two reasons may be offered to rationalize the greater propensity of silyloxylated *versus* alkoxylated dioxetanes to rearrange into α-peroxy carbonyl compounds. On one hand, an α-silyloxy group stabilizes a carbocationic center substantially better than an α-alkoxy group, so that opening of the dioxetane ring by C-O bond heterolysis leading to a 1,4-dipole is facilitated over the more usual O-O bond homolysis affording cleavage products (Eq. 3, step a). On the other hand, silyl groups like the proton migrate more readily to



(Eq. 3)

anionic sites than the corresponding alkyl groups (Eq. 3, step b), in view of the fact that silicon accommodates more effectively positive charge compared to carbon.

The unusual feature in the present case is the fact that the resulting α-silylperoxy carbonyl compounds subsequently fragment into the dioxetane cleavage product *via* a Hock-Criegee rearrangement (Eq. 1). Fortunately, monitoring the progress of the photooxygenation by low temperature ^{1}H NMR uncovered the intermediary dioxetanes and their α-silylperoxy carbonyl rearrangement products, which otherwise would have remained unnoticed. We suspect that the pathway **1** → **2** → **3** → **4** (Eq. 1) occurs in the photooxygenation of enol type substrates more generally than presently recognized. Apparently, any substituent on the enol oxygen that is capable of stabilizing cationic centers and shows propensity to migrate to anionic sites should qualify. The prototype would be an enol itself, for which $^1O_2$ addition would produce hydroxy-substituted dioxetanes and subsequent rearrangement would lead to α-hydroperoxy carbonyl products *via* transposition of a proton instead of a silyl group in step b of Eq. 1.

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4. **1a**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.28 (s, 9H), 2.34 (s, 3H), 7.12-7.44 (m, 4H);
   ^{13}C NMR (63 MHz, $CDCl_3$): δ = 0.3 (q), 11.0 (q), 110.9 (d), 117.8 (d), 121.9 (d), 123.2 (d),

125.1 (s), 133.2(s), 140.8 (s), 152.0 (s);
MS (70 eV): m/z (%) = 220 (67) [M+], 205 (17) [M+ - CH_3], 177 (13), 151 (14), 121 (16), 73 (100).
1b: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.20 (s, 6H), 1.10 (s, 9H), 2.38 (s, 3H), 7.12-7.48 (m, 4H);
^{13}C NMR (63 MHz, $CDCl_3$): δ = -4.3 (q), 11.1 (q), 18.1 (s), 25.7 (q), 111.0 (d), 117.8 (d), 122.0 (d), 123.2 (d), 125.1 (s), 133.5 (s), 140.6 (s), 152.1 (s);
MS (70 eV): m/z (%) = 262 (100) [M+], 247 (4) [M+ - CH_3], 205 (96), 177 (58), 73 (51).

5. **2a**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.36 (s, 9H), 1.82 (s, 3H), 7.0-7.38 (m, 4H);
^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.7 (q), 17.1 (q), 111.0 (s), 111.9 (d), 117.7 (s),122.6 (d), 123.1 (d), 126.5 (s), 132.1 (d), 160.4 (s).
6. **4a**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.37 (s, 9H), 2.31 (s. 3H), 7.06 (d, 1H), 7.28 (d, 1H), 7.49 (dd, 1H), 8.01 (d, 1H);
^{13}C NMR (50 MHz, $CDCl_3$): δ = -0.4 (q), 20.9 (q), 123.5 (d), 125.7 (d), 132.2 (d), 133.6 (d), 138.4 (s), 150.8 (s), 164.3 (s), 169.2 (s).
7. **3a**: ^{1}H NMR (200 MHz, $CDCl_3$, -20 °C): δ = 0.16 (s, 9H), 1.58 (s, 3H), 7.0-7.7 (m, 4H);
^{13}C NMR (50 MHz, $CDCl_3$, -20 °C): δ = -1.5 (q), 18.3 (q), 108.7 (s), 112.7 (d), 118.9 (s), 122.0 (d), 124.7 (d), 138.9 (d), 170.0 (s), 197.5 (s).
8. **2b**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.35 (s, 3H), 0.47 (s, 3H), 1.04 (s, 9H), 1.84 (s, 3H), 6.9-7.4 (m, 4H);
^{13}C NMR (50 MHz, $CDCl_3$): δ = -3.2 (q), -2.6 (q), 17.0 (q), 17.7 (s), 25.2 (q), 111.0 (s), 111.8 (d), 117.6 (s), 122.5 (d), 122.9 (d), 126.1 (s), 132.0 (d), 160.1 (s).
9. **4b**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.40 (s, 6H), 1.05 (s, 9H), 2.36 (s, 3H), 7.0-8.1 (m, 4H);
^{13}C NMR (50 MHz, $CDCl_3$): δ = -4.8 (q), 17.8 (s), 21.0 (q), 25.6 (q), 123.7 (d), 124.5 (s), 125.7 (d), 132.0 (d), 133.6 (d), 151.2 (s), 163.9 (s), 169.4 (s).
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11. **6**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.29 (s, 6H), 1.01 (s, 9H), 2.02 (s, 3H), 7.06-7.29 (m, 4H);
^{13}C NMR (50 MHz, $CDCl_3$): δ = -4.4 (q), 6.5 (q), 18.0 (s), 25.5 (q), 87.9 (s), 109.8 (d), 117.5 (d), 121.2 (d), 122.2 (d), 131.4 (s), 148.1 (s), 155.3 (s);
MS (70 eV): m/z (%) = 262 (38) [M+], 177 (8), 148 (47), 120 (32), 91 (31), 73 (100).
12. **7**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.20 (s, 3H), 0.31 (s, 3H), 0.98 (s, 9H), 1.83 (s, 3H), 6.70-7.40 (m, 4H);
^{13}C NMR (50 MHz, $CDCl_3$): δ = -3.6 (2 × q), 16.3 (q), 17.7 (s), 25.4 (q), 94.5 (s), 110.6 (s), 111.1(d), 122.3 (d), 123.9 (d), 130.7 (s), 131.7 (d), 159.3 (s).
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