



## Photochemical reactions of 2,6-bis(trimethylsilyl)-4*H*-pyran with $\alpha$ -ketoesters

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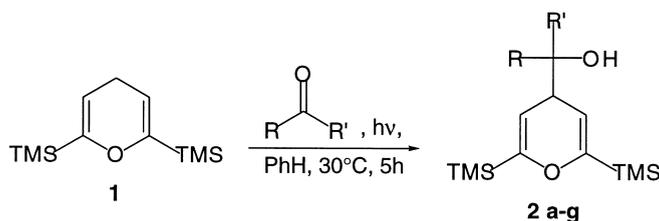
Received 14 April 2000; accepted 19 May 2000

### Abstract

The photochemical reaction of 2,6-bis(trimethylsilyl)-4*H*-pyran with various  $\alpha$ -ketoesters gave moderate to good yields of new bis(silylated) 4*H*-pyrans functionalized in position 4. In some cases, an oxidation by-product was also isolated. © 2000 Elsevier Science Ltd. All rights reserved.

Pyrans are interesting intermediates in organic synthesis.<sup>1</sup> Recently, we have found that 2,6-bis(trialkylsilyl)-4*H*-pyrans can be prepared by cyclodehydration of 1,5-bis(acylsilanes) under acid catalysis.<sup>2</sup> Thus, a mixture of 1,5-bis(trimethylsilyl)pentanedione and a catalytic amount of *p*-toluenesulfonic acid was thermolysed under reduced pressure, using a Kugelrohr apparatus to give the 2,6-bis(trimethylsilyl)-4*H*-pyran **1** (yield: 80%).<sup>2</sup> Except for our synthesis, such silylated heterocycles seem to be unprecedented. In order to functionalize the methylenic position of the 4*H*-pyran **1**, we tried to condense activated carbonyl compounds such as ethyl pyruvate using various bases (*n*-BuLi, *t*-BuLi, LDA at different temperatures) according to the literature.<sup>3</sup> Unfortunately, we recovered quantitatively the starting material. These observations could be explained by some kind of antiaromatic character of an intermediate anion. Based on this experience, we tried to use single electron transfer processes to generate a radical cationic species of 2,6-bis(trimethylsilyl)-4*H*-pyran. The electron transfer was carried out photochemically. Thus, the mixture of **1** and carbonyl compound in benzene was irradiated at  $\lambda = 350$  nm, at 30°C, during 5 h (Scheme 1). The first attempt with benzaldehyde gave a low yield (12%) of the corresponding pyran **2a** (Table 1, entry 1). On the other hand, the reaction with acetone and benzoquinone failed. Next, we applied the photochemical reaction to more activated carbonyl derivatives such as bis(acetyl) or  $\alpha$ -ketoesters.  $\alpha$ -Ketoesters (entries 4, 6 and 7) were prepared by oxydation of the corresponding methyl ketones (R-CO-CH<sub>3</sub>) by KMnO<sub>4</sub>.<sup>4a-c</sup> The resulting  $\alpha$ -ketoacids were esterified according to Steglich's method (using DCC as dehydrating agent).<sup>4d</sup> Irradiation of **1** in

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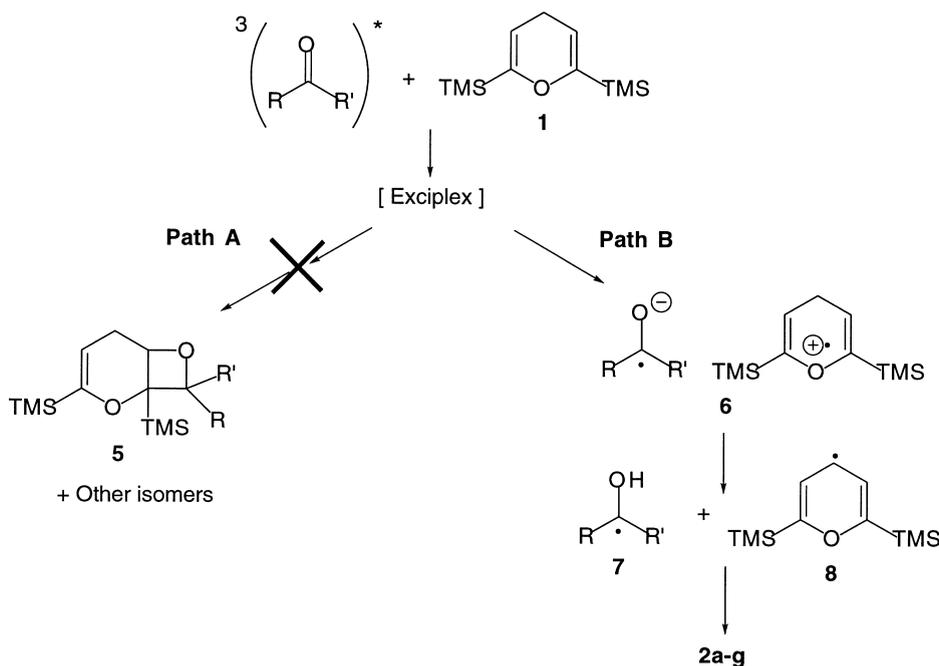
Scheme 1. <sup>5</sup>Table 1  
Photochemical reactions of the 4*H*-pyran **1** with carbonyl compounds<sup>6</sup>

Entry	R	R'	Conv. (%)	4-Substituted pyran (%)	Selectivity (%)	By-product (%)
1	Ph	H	40	<b>2a</b> (12)	30	-
2	Me	COMe	69	<b>2b</b> (42) <sup>7</sup>	61	 <b>3</b> (10) <sup>8</sup>
3	Me	CO <sub>2</sub> Et	88	<b>2c</b> (62) <sup>7</sup>	70	-
4	<i>t</i> Bu	CO <sub>2</sub> Et	56	<b>2d</b> (38) <sup>7</sup>	68	-
5	Ph	CO <sub>2</sub> Me	83	<b>2e</b> (52) <sup>7</sup>	63	-
6	<i>p</i> -MeO(C <sub>6</sub> H <sub>4</sub> )	CO <sub>2</sub> Me	77	<b>2f</b> (49) <sup>7</sup>	64	 <b>4</b> (16) <sup>9</sup>
7	1-naphthyl	CO <sub>2</sub> Me	60	<b>2g</b> (44) <sup>7</sup>	73	-

the presence of bis(acetyl) gave moderate yield (42%) of the desired compound **2b** which was accompanied with the oxidation by-product **3** (Table 1, entry 2). The best results were obtained with  $\alpha$ -ketoesters. The reaction of ethyl pyruvate furnished the  $\alpha$ -hydroxyester **2c** in 62% yield (Table 1, entry 3) whereas the more hindered *tert*-butyl analogue (entry 4) gave the corresponding **2d** in 38% yield. The reaction rate was lower in the latter case. The photochemical reaction was also performed with aromatic  $\alpha$ -ketoesters such as methyl phenyl- and methyl naphthylglyoxylates (Table 1, entries 5–7). The functionalized 4*H*-pyrans **2e–g** were obtained in moderate yield (44–52%). With *p*-methoxyphenyl  $\alpha$ -ketoester (entry 6), we were able to isolate the coupling product **4**. When the irradiation time was increased, more 4*H*-pyran **2** was not formed but we observed a slow degradation of the starting material. Nevertheless, the 4*H*-pyrans **2** were obtained in moderate to good yield. It is worth noting that the selectivity of the photochemical reaction (except compound **2a**) was quite high (Table 1: 61–73%).

Attempts were also performed with  $\alpha$ -ketonitriles (benzoylcyanide and (*p*-methoxy)benzoyl cyanide) but we obtained low yields (10–25%) of the desired compounds which were accompanied with the oxidation by-product **3** (10–15%).

Photochemical excited carbonyl compounds can form more or less stable exciplexes with electron rich alkenes. Two types of reactions of these intermediates are frequently observed.<sup>10</sup> They yield 1,4-biradicals which are intermediates in the formation of oxetanes **5** (Scheme 2, path A: Paternò–Büchi reaction).<sup>10a,11</sup> On the other hand, the exciplex species react via single electron transfer to yield the radical ion pair **6** (Scheme 2, path B). After a proton exchange, the resulting radicals **7** and **8** combine to give stable products. Obviously, in our case, the path B was favored to form exclusively the compounds **2a–g**.



**Conclusion.** We describe a new photochemical reaction between the 2,6-bis(trimethylsilyl)-4H-pyran **1** and various  $\alpha$ -ketoesters. This reaction proceeds exclusively via a radical coupling leading to the 4-substituted bis(silylated) 4H-pyrans **2b–g** (path B). Paternò–Büchi reaction, usually observed with enolethers, do not compete here. This functionalization was not possible using classical anionic chemistry.

## Acknowledgements

The authors thank H. Baïlla and Dr. J. M. Nuzillard for the determination of compound **4**.

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5. *Typical experiment*: a mixture of 4*H*-pyran **1** (200 mg, 0.88 mmol) and ethyl pyruvate (1.77 mmol, 2.0 equiv.) in benzene (30 ml) was irradiated at 350 nm (Rayonet, T = 30°C) during 5 h. After evaporation in vacuo, the residue was purified by flash chromatography (petroleum ether:ethyl acetate 90:10) to give the  $\alpha$ -hydroxy ester **2c** (185 mg, 62%).
6. All new compounds gave satisfactory analyses (IR, MS,  $^1\text{H}$  and  $^{13}\text{C}$  NMR).
7. Selected data for compounds **2b–g**. Oil. Compound **2b**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm/TMS): 0.07 (s, 9H), 0.09 (s, 9H), 1.30 (s, 3H), 2.17 (s, 3H), 2.99 (dd, 1H,  $J=4.2, 3.8$  Hz), 3.73 (brs, OH), 4.92 (dd, 1H,  $J=3.8, 2.7$  Hz), 4.99 (dd, 1H,  $J=3.4, 3.1$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): -2.9 ( $2\times\text{SiMe}_3$ ), 21.1 ( $\text{CH}_3$ ), 25.5 ( $\text{CH}_3$ ), 38.3 (CH), 82.1 ( $\text{C}_4$ ), 107.7 (CH), 108.6 (CH), 159.7 ( $\text{C}_4$ ), 160.2 ( $\text{C}_4$ ), 212.3 (CO). IR (film,  $\text{cm}^{-1}$ ): 3468, 1709, 1608.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm/TMS): 0.10 (s, 9H), 0.11 (s, 9H), 1.27 (t, 3H,  $J=6.9$  Hz), 1.36 (s, 3H), 2.97 (dd, 1H,  $J=4.2, 3.8$  Hz), 3.14 (brs, OH), 4.21 (q, 2H,  $J=6.9$  Hz), 4.91 (dd, 1H,  $J=3.4, 3.1$  Hz), 5.02 (dd, 1H,  $J=3.8, 2.7$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): -2.8 ( $2\times\text{SiMe}_3$ ), 14.2 ( $\text{CH}_3$ ), 20.9 ( $\text{CH}_3$ ), 39.0 (CH), 61.6 ( $\text{CH}_2$ ), 77.5 ( $\text{C}_4$ ), 107.7 (CH), 108.1 (CH), 159.5 ( $\text{C}_4$ ), 159.9 ( $\text{C}_4$ ), 175.8 (CO). IR (film,  $\text{cm}^{-1}$ ): 3508, 1727, 1605. Compound **2d**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm/TMS): 0.10 (s, 9H), 0.12 (s, 9H), 1.07 (s, 9H), 1.31 (t, 1H,  $J=7.3$  Hz), 3.21 (brs, OH), 3.32 (dd, 1H,  $J=5.0, 4.6$  Hz), 4.33 (q, 2H,  $J=7.3$  Hz), 4.78 (dd, 1H,  $J=4.6, 2.7$  Hz), 5.16 (dd, 1H,  $J=4.6, 2.7$  Hz). IR (film,  $\text{cm}^{-1}$ ): 3515, 1723, 1603. Compound **2e**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm/TMS): 0.02 (s, 9H), 0.12 (s, 9H), 3.31 (brs, OH), 3.67 (t, 1H,  $J=3.8$  Hz), 3.79 (s, 3H), 4.52 (t, 1H,  $J=3.1$  Hz), 4.82 (dd, 1H,  $J=3.4, 2.7$  Hz), 7.3–7.4 (m, 3H), 7.61 (d, 2H,  $J=7.3$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): -2.8 ( $2\times\text{SiMe}_3$ ), 39.3 (CH), 52.8 ( $\text{CH}_3$ ), 80.7 ( $\text{C}_4$ ), 107.0 (CH), 107.2 (CH), 125.9 (CH), 127.6 (CH), 128.0 (CH), 138.4 ( $\text{C}_4$ ), 160.4 ( $\text{C}_4$ ), 161.6 ( $\text{C}_4$ ), 173.9 (CO). IR (film,  $\text{cm}^{-1}$ ): 3492, 1725, 1609. Compound **2f**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm/TMS): 0.04 (s, 9H), 0.12 (s, 9H), 3.25 (brs, OH), 3.63 (dd, 1H,  $J=3.8, 3.4$  Hz), 3.79 (s, 3H), 3.82 (s, 3H), 4.55 (dd, 1H,  $J=3.4, 2.7$  Hz), 4.80 (t, 1H,  $J=3.1$  Hz), 6.89 (d, 2H,  $J=9.2$  Hz), 7.53 (d, 2H,  $J=9.2$  Hz). IR (KBr,  $\text{cm}^{-1}$ ): 3499, 1725, 1609. Compound **2g**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm/TMS): 0.03 (s, 9H), 0.16 (s, 9H), 3.49 (brs, OH), 3.68 (s, 3H), 4.15 (t, 1H,  $J=3.8$  Hz), 4.74 (t, 1H,  $J=2.7$  Hz), 5.08 (t, 1H,  $J=3.1$  Hz), 7.4–7.5 (m, 3H), 7.72 (d, 1H,  $J=7.3$  Hz), 7.8–7.9 (m, 2H), 8.38 (m, 1H). IR (film,  $\text{cm}^{-1}$ ): 3494, 1732, 1651, 1603.
8. Selected data for compound **3**: oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm/TMS): 0.23 (s, 9H), 6.22 (d, 1H,  $J=9.2$  Hz), 6.34 (d, 1H,  $J=6.5$  Hz), 7.19 (dd, 1H,  $J=9.2, 6.5$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): -2.9 ( $\text{SiMe}_3$ ), 113.3 (CH), 116.4 (CH), 141.2 (CH), 163.6 ( $\text{C}_4$ ), 174.5 ( $\text{C}_4$ ). IR (film,  $\text{cm}^{-1}$ ): 1727, 1611. This oxidation by-product **3** was also observed when a solution of 4*H*-pyran **1** in AcOEt was stored at room temperature, under air atmosphere, during several days.
9. Selected data for compound **4**. Oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm/TMS): -0.08 (s, 9H), 0.06 (s, 9H), 0.07 (s, 9H), 0.11 (s, 9H), 3.19 (dd, 1H,  $J=5.0, 4.6$  Hz), 3.74 (s, 3H), 3.79 (s, 3H), 4.04 (brs, OH), 4.43 (dd, 1H,  $J=4.7, 2.6$  Hz), 4.86 (dd, 1H,  $J=4.7, 2.6$  Hz), 4.96 (d, 1H,  $J=3.0$  Hz), 5.07 (d, 1H,  $J=3.0$  Hz), 6.82 (d, 2H,  $J=9.0$  Hz), 7.72 (d, 2H,  $J=9.0$  Hz). IR (film,  $\text{cm}^{-1}$ ): 3486, 1717, 1651, 1605. This compound was fully assigned by  $^1\text{H}$ - $^1\text{H}$  correlations and  $^1\text{H}$ - $^{13}\text{C}$  correlations ( $^1J$  and  $^nJ$ ) at 500 MHz spectrometer.
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