Formation of Novel Photoadducts from Irradiation of 5(*S*)-5-*O*-*tert*-Butyldimethylsiloxymethylfuran-2(5*H*)-one

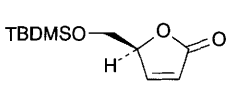
David Brown, Christine J. Cardin and John Mann*

Department of Chemistry, Reading University, Whiteknights, Reading, UK RG6 2AD

Irradiation of 5*S*-5-*O*-*tert*-butyldimethylsiloxymethylfuran-2(5*H*)-one **1** in acetonitrile yields the *C*2-symmetric bis(lactone), 1*S*,2*S*,6*S*,7*S*-[3*S*,10*S*]-bis-*tert*-butyldimethylsiloxymethyl-4,9-dioxatricyclo[5.3.0.0^{2,6}]deca-5,8-dione **6**, and a 3-substituted intramolecular product resulting from an apparent 8-*endo-trig* cyclisation.

We have been exploring the photocatalysed additions of alcohols[1] and amines[2] to stereochemically defined 5-substituted-furan-2(5*H*)-ones, *e.g.* **1**, and had demonstrated that ethylene glycol would add under irradiation (254 nm) to yield a mixture of diastereoisomers **2a** and **2b** [(4*R*,5*S*)-5-*tert*-butyldimethylsiloxymethyl-4-(*R*,*S*)-dihydroxyethyltetrahydrofuran-2(5*H*)-one] which could be separated after conversion into the respective acetonides. Alternatively, irradiating **1** in the presence of 2,2-dimethyl-1,3-dioxolane yields the adducts **3a** and **3b**† {(4*R*,5*S*)-5-*tert*-butyldimethylsiloxymethyl-4-[*O*-isopropylidene-(*R*,*S*)-dioxyethyl]tetrahydrofuran-2(5*H*)-one} directly (13, 17% respective isolated yields after chromatography).

Variable quantities of other products were also obtained, and we initially believed that these might be further addition products between adducts **3** and butenolide **1**. In order to try to improve the synthesis of these adducts, butenolide **1** was irradiated (MeCN, 254 nm) in the presence of an excess of the (*S*)-isomer **3a**, and after 16 h two new products were formed. From the NMR data, one of these was clearly a butenolide dimer, and the other an intramolecular photoaddition product, which after close inspection of the NMR data was assigned the structure **4**.‡ Such an addition is, to our knowledge, the first example of a photochemically-induced intramolecular addition to 5-substituted-furan-2(5*H*)-ones, and of a photochemical addition that occurs at the 3 (rather than 4) position. The reaction presumably occurs by the mechanism shown in Scheme 1. The initial 1,3-biradical abstracts a hydrogen from the *tert*-butyl group and the resultant primary radical, which is stabilised by the β-silicon atom, reacts with the incipient radical at C-3 to form compound **4**. Subsequent hydrolysis (aqueous AcOH in THF) provides compound **5**.§



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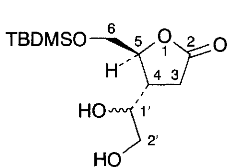
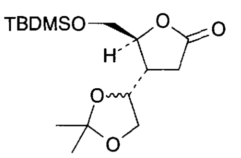
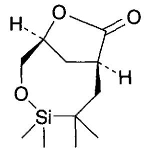


2a,b



3a,b



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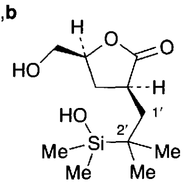

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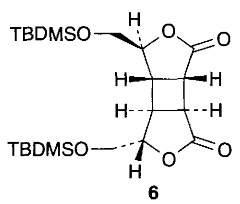
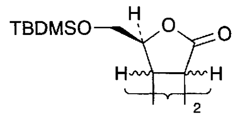


6



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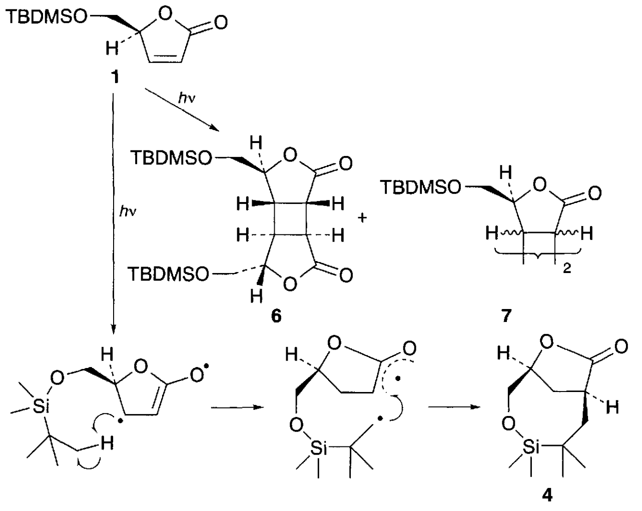
The dimer was more efficiently prepared by irradiation of butenolide **1** alone (0.06 mol dm^{-3} solution in MeCN, 254 nm, 16 h). This resulted in the formation of major **6**¶ and minor **7**‖ dimeric products (24, 12% respective isolated yields after chromatography), and the intramolecular photoadduct **4** (9%). As the major dimer **6** contained magnetically equivalent monomeric units, the structure was determined by X-ray crystallography (Fig. 1) and shown to be the head-to-head (HH), *cis-anti-cis* isomer.** Although residual disorder in the TBDMS sidechain containing Si(13) precluded refinement to a lower *R* factor, the stereochemistry of the cyclobutane ring was clearly established.

Despite extensive NMR studies, signal overlap has so far precluded structure determination of the minor dimeric product **7**. Work is being carried out to improve the yield of the *C*2-symmetric bis(lactone), which has considerable synthetic



Scheme 1

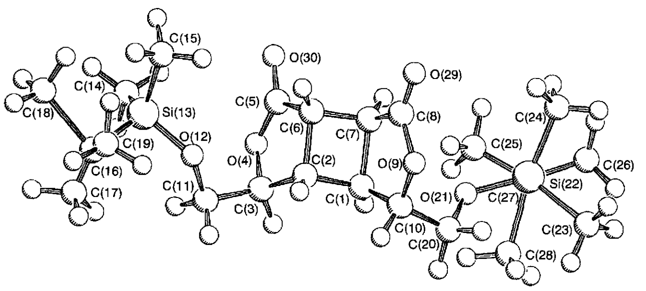


Fig. 1 X-Ray structure of **6**

potential, and to investigate the potential of the intramolecular photocyclisation reacton, which to our knowledge is unprecedented.

D. B. thanks the EPSRC for a studentship.

Received, 9th January 1995; Com. 5/00151J

Footnotes

† The two anomers were separable by flash chromatography (diethyl ether–light petroleum, 3:2) to give two eluted anomers. First eluted anomer isolated as a white crystalline solid: mp 55–56 °C; δ_H ($CDCl_3$, 250 MHz; *J*/Hz) 0.07 (3H, s, $SiCH_3$), 0.08 (3H, s, $SiCH_3$), 0.89 [9H, s, $C(CH_3)_3$], 1.35 (3H, s, acetonide CH_3), 1.43 (3H, s, acetonide CH_3), 2.52 (1H, dd, J_{gem} 20.7, $J_{3,4}$ 8.9, H-3a), 2.61–2.73 (2H, m, H-3b, H-4), 3.59 (1H, dd, J_{gem} 8.3, $J_{2',1'}$ 6.4, H-2a′), 3.70 (1H, dd, J_{gem} 11.2, $J_{6,5}$ 2.8, H-6a), 3.87 (1H, dd, J_{gem} 11.3, $J_{6,5}$ 3.4, H-6b), 4.08 (1H, dd, J_{gem} 8.3, $J_{2',1'}$ 6.5, H-2b′), 4.18–4.25 (1H, m, H-1′), 4.37–4.40 (1H, m, H-5). Second eluted anomer isolated as a colourless oil: δ_H ($CDCl_3$, 250 MHz) 0.06 (3H, s, $SiCH_3$), 0.07 (3H, s, $SiCH_3$), 0.89 [9H, s, $C(CH_3)_3$], 1.34 (3H, s, acetonide CH_3), 1.42 (3H, s, acetonide CH_3), 2.19 [1H, dd, J_{gem} 20.7, $J_{3,4}$ 8.9, H-3a), 2.64–2.66 (1H, m, H-4), 2.74 (1H, dd, J_{gem} 16.9, $J_{3,4}$ 9.8, H-3b), 3.62–3.65 (1H, m, H-2′a), 3.69 (1H, dd, J_{gem} 11.3, $J_{6,5}$ 2.6, H-6a), 3.93 (1H, dd, J_{gem} 11.3, $J_{6,5}$ 2.8, H-6b), 4.05–4.13 (2H, m, H-1′, H-2b′), 4.54–4.58 (1H, m, H-5).

‡ 4,4,5,5-Tetramethyl-3,9-dioxa-4-sila-bicyclo[5.2.1]decan-8-one **4** isolated as a white crystalline solid: mp 87–88 °C; ν_{max} (Nujol mull)/cm^{-1} 2923vs, 2853vs, 1757vs, 1342s, 1185s, 1154s; δ_H ($CDCl_3$, 400 MHz) 0.11 (3H, s, $SiCH_3$), 0.29 (3H, s, $SiCH_3$), 0.84 (3H, s, CCH_3), 1.09 (3H, s, CCH_3), 1.82 (1H, dd, J_{gem} 15, $J_{6,7}$ 3.7, H-6a), 1.97–2.05 (2H, m, H-6b, H-10a), 2.65–2.74 (1H, m, H-10b), 2.84–2.91 (1H, m, H-7b), 3.74 (1H, dd, J_{gem} 12.5, $J_{1,2}$ 0.7, H-2a), 4.19 (1H, dd, J_{gem} 12.5 $J_{1,2}$ 2.6, H-2b), 4.53–4.57 (1H, m, H-1); *m*/*z* (GC-MS/EI) 229 (MH^+).

§ (3*R*,5*S*)-Hydroxymethyl-3-[2′-dimethylsilylhydroxy-2′,2′-dimethylethyl]tetrahydrofuran-2(5*H*)-one **5** isolated as a white crystalline solid: mp 97–98 °C; ν_{max} (Nujol mull)/cm^{-1} 3306s, br, 3220s, br, 2920vs, 2852vs, 1753vs, 1296w, 1254s, 1203s, 1176w, 1112w, 1057s, 866s, 829w; δ_H ($CDCl_3$, 400 MHz) 0.13 (3H, s, $SiCH_3$), 0.15 (3H, s, $SiCH_3$), 0.93 (3H, s, CCH_3), 0.96 (3H, s, CCH_3), 1.34 (1H, dd, J_{gem} 14, $J_{1'a,3}$ 8.6, H-1′a), 1.79 [1H, br s, $Si(CH_3)_2OH$], 1.82–1.88 (1H, m, H-4a), 2.2 (1H, dd, J_{gem} 14, $J_{1'b,3}$ 2.8, H-1′b), 2.33 (1H, br s, CH_2OH), 2.46–2.53 (1H, m, H-4b), 2.77–2.85 (1H, m, H-3), 3.62 (1H, dd, J_{gem} 12, $J_{6,5}$ 4.5, H-6a), 3.62 (1H, dd, J_{gem} 12, H-6b), 4.46–4.52 (1H, m, H-5).

¶ 1*S*,2*S*,6*S*,7*S*-[3*S*,10*S*]-Bis-*tert*-butyldimethylsiloxymethyl-4,9-dioxatricyclo[5.3.0.$0^{2,6}$]deca-5,8-dione **6** isolated as a white crystalline solid: mp 180–181 °C; Satisfactory elemental analysis obtained; ν_{max} (Nujol mull)/cm^{-1} 2924vs, 2852vs, 1774s, 1758s, 1337s, 1252s, 1161s, 834s; δ_H ($CDCl_3$, 400 MHz) 0.04 (6H, s, $SiCH_3 \times 2$), 0.05 (6H, s, $SiCH_3 \times 2$), 0.85 [18H, s, $(CH_3)_3 \times 2$], 3.06 (2H, d, *J* 5.5), 3.22 (2H, d, *J* 5.5), 3.65 (2H, dd, J_{gem} 1.2, *J* 1.8), 3.85 (2H, dd, J_{gem} 11.2, *J* 2.7), 4.54 (2H, m, H-3, H-10); *m*/*z* (GC-MS/EI) 399 [$M^+ - C(CH_3)_3$].

‖ 5*S*,10*S*-Bis-*tert*-butyldimethylsiloxymethyl-4,9-dioxatricyclo[5.3.0.$0^{2,6}$]-deca-3,8-dione or 3*S*,10*S*-bis-*tert*-butyldimethylsiloxymethyl-4,9-dioxatricyclo[5.3.0.$0^{2,6}$]deca-5,8-dione **7** isolated as a white solid: mp 136–137 °C; satisfactory elemental analysis obtained; ν_{max} (Nujol mull)/cm^{-1} 2923vs, 2853vs, 1749vs, 1361s, 1336s, 1252s, 1176s, 1137s, 1098s, 1073s, 971s, 954s, 837s; δ_H ($CDCl_3$, 400 MHz) 0.04 (3H, s, $SiCH_3$), 0.06 (3H, s, $SiCH_3$), 0.12 (3H, s, $SiCH_3$), 0.12 (3H, s, $SiCH_3$), 0.86 [9H, s, $(CH_3)_3$], 0.91 [9H, s, $(CH_3)_3$], 3.16 (1H, dd, *J* 7.0, *J* 3.7, CHCO), 3.20–3.28 (2H, m, CHCO, C*H*CHO), 3.50 (1H, dd, *J* 6.6, *J* 2.2, CHCO), 3.67 (1H, dd, *J* 11.4, *J* 1.8, CH_2O), 3.89 (1H, dd, *J* 11.0, *J* 2.2, CH_2O), 3.97–4.06 (2H, m, CH_2O), 4.64 (1H, m, CHO), 4.68–4.72 (1H, m, CHO); *m*/*z* (GC-MS/EI) 399 [$M^+ - C(CH_3)_3$].

** *Crystal data* for **6**, 1*S*,2*S*,6*S*,7*S*-[3*S*,10*S*]-bis-*tert*-butyldimethylsiloxymethyl-4,9-dioxatricyclo[5.3.0.$0^{2,6}$]deca-5,8-dione: monoclinic, space group $P2_1$, a = 6.555(8), b = 11.619(8), c = 17.612(7) Å, β = 98.61(2)°, U = 1326.3(2) $Å^3$, Z = 2. The data was collected on a Marresearch Image Plate system, 95 frames at 2° intervals were measured for 2 min each. 3738 Reflections were measured, of which 3629 were independent in a monoclinic unit cell (R_{int} = 0.0404), Cell dimensions were determined from analysis of 492 independent reflections. The structure was solved by direct methods using SHELX86 (G. M. Sheldrick, SHELX86, *Acta Crystallogr., Sect. A*, 1990, **46**, 467). The structure was refined on F^2 using SHELXL (G. M. Sheldrick, SHELXL, program for crystal structure refinement, University of Göttingen). The conventional *R*-factor for the 1711 reflections with $I > 2\sigma(I)$ was 0.0865. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

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