An Improved Photosensitizer for the Photoinduced Electron-Transfer Deoxygenation of Benzoates and *m*-(Trifluoromethyl)benzoates

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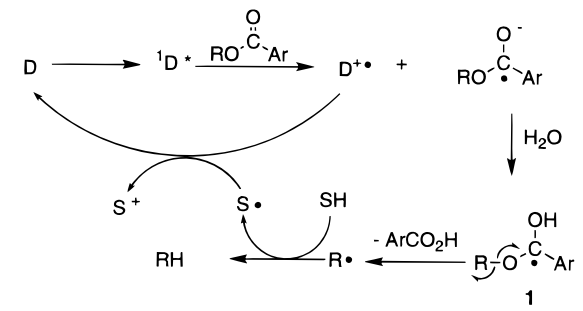
In 1975 Barton and McCombie introduced the deoxygenation of secondary alcohols via a free radical chain mechanism.[1,2] This procedure involved the tin hydride reduction of thionocarbonyl derivatives of the alcohol such as xanthates, thionobenzoates, and thionocarbonylimidazolides. Since this time, other derivatives have been developed for this process.[3]

Saito and co-workers reported the deoxygenation of benzoates and *m*-(trifluoromethyl)benzoates via a photoinduced electron-transfer mechanism in which 9-methylcarbazole (MCZ, **2**) was used as the photosensitizer.[4] We have recently used this reaction as the key step in a stereocontrolled, *de novo* synthesis of β-2′-deoxyribonucleosides.[5] The mechanism is shown in Scheme 1.[4] Photoinduced electron transfer from MCZ (D) to the benzoyl group gives a radical ion pair. Solvent cage escape, which is promoted by salts such as $Mg(ClO_4)_2$, and protonation of the radical anion gives radical **1** which undergoes β-scission to give the deoxygenated radical. Hydrogen atom abstraction from solvent (SH, i.e., 2-propanol) gives the deoxygenated product. The solvent radical is then oxidized by the donor radical cation. In principle, the photosensitizer (D) could be used in substoichiometric amounts since it is regenerated; however, in practice at least 1 equiv is generally used.[6] We report here the development of a new photosensitizer which shows turnover in its function and can be used in substoichiometric amounts.

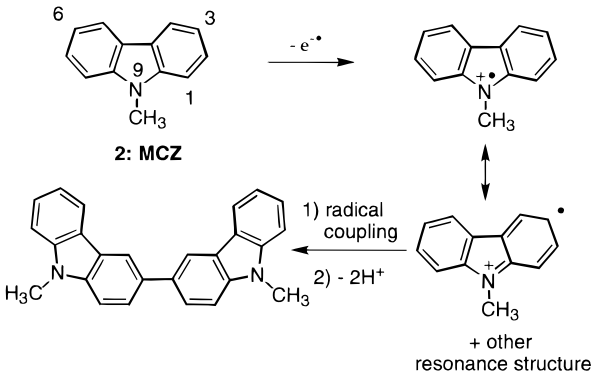
The radical cation chemistry of carbazoles ($D^{+\bullet}$ in Scheme 1) has been studied electrochemically by Ambrose.[7] Cyclic voltammetric analysis showed that 9-methylcarbazole (**2**) is irreversibly oxidized, indicating that the radical cation undergoes further reaction or degradation. After bulk electrolysis, a bicarbazole as a result of radical coupling at the 3-positions was isolated; the mechanism of this process is shown in Scheme 2.[7] The electrochemical oxidation of many 9-alkylcarbazoles substituted at the 3- and 6-positions showed improved reversibility, indicating that their radical cations were longer lived and did not undergo degradation on the CV time scale.

We reasoned that the turnover properties of the carbazole photosensitizer in the deoxygenation of benzoyl derivatives could be improved by blocking the 3- and 6-positions. Importantly, we needed to choose groups that would not significantly change the redox potential or chromophore of the photosensitizer so as not to alter its excited-state electron-transfer properties. We chose to study 3,6-dimethyl-9-ethylcarbazole (**3**, DMECZ), which was synthesized according to a known procedure from commercially available 9-ethylcarbazole-3-carboxalde-

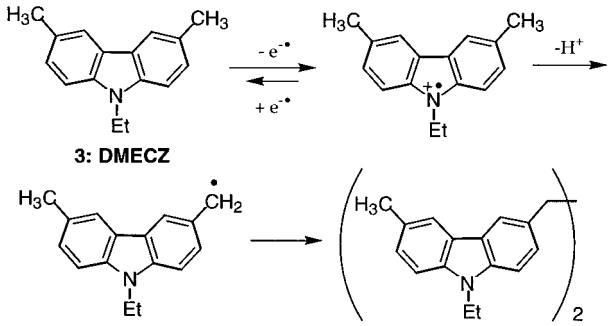
Scheme 1



Scheme 2



Scheme 3



(1) Barton, D. H. R; McCombie, S. W. *J. Chem. Soc. Perkin Trans 1* **1975**, 1574.

(2) (a) Hartwig, W. *Tetrahedron* **1983**, *39*, 2609. (b) McCombie, S. W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; pp 811−833.

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(4) Saito, I.; Ikehira, H.; Kasatani, R.; Watanabe, M.; Matsuura, T. *J. Am. Chem. Soc.* **1986**, *108*, 3115.

(5) (a) Park, M.; Rizzo, C. J. *J. Org. Chem.* **1996**, *61*, 6092. (b) Huang, Z.; Schneider, K. C.; Benner, S. A. *J. Org. Chem.* **1991**, *56*, 3869.

(6) (a) Barvian, M. R.; Barkley, R. M.; Greenberg, M. M. *J. Am. Chem. Soc.* **1995**, *117*, 4894. (b) Myers, A. G.; Condroski, K. R. *J. Am. Chem. Soc.* **1995**, *117*, 3057. (c) Matray, T. J.; Greenberg, M. M. *J. Am. Chem. Soc.* **1994**. *116*, 6931. (d) Barvian, M. R.; Greenberg, M. M. *J. Org. Chem.* **1993**, *58*, 6151. (e) Ireland, R. E.; Armstrong, J. D.; Lebreton, J.; Meissner, R. S.; Rizzacasa, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 7152. (f) Barvian, M. R.; Greenberg, M. M. *Tetrahedron Lett.* **1992**, *33*, 6057. (g) Myers, A. G.; Condroski, K. R. *J. Am. Chem. Soc.* **1993**, *115*, 7926. (h) Clive, D. L. J.; Daigneault, S. *J. Org. Chem.* **1991**, *56*, 3801. (i) Almond, M. R.; Collins, J. L.; Reitter, B. E.; Rideout, J. L.; Freeman, G. A.; St Clar, M. H. *Tetrahedron Lett.* **1991**, *32*, 5745. (j) Suzuki, M.; Koyano, H.; Noyori, R. *J. Org. Chem.* **1987**, *52*, 5583. (k) Clive, D. L. J.; Daigneault, S. *J. Chem. Soc. Chem. Commun.* **1989**, 332.

(7) (a) Ambrose, J. F.; Nelson, R. F. *J. Electrochem. Soc.* **1968**, *115*, 1159. (b) Ambrose, J. F.; Carpenter, L. L.; Nelson, R. F. *J. Electrochem. Soc.* **1975**, *122*, 876.

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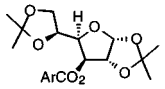
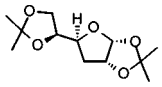
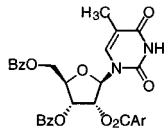
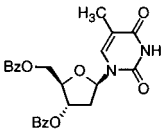
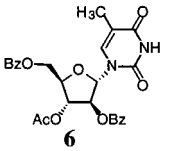
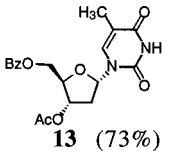
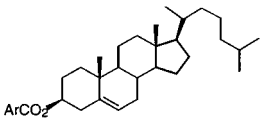
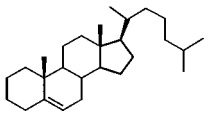
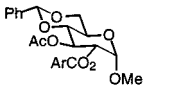
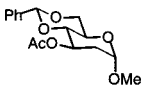
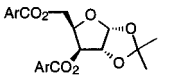
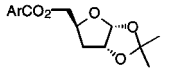
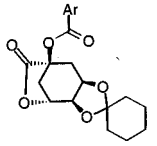
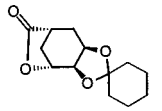
Table 1

Substrate	Product and Yield
 **4a:** Ar= *m*-$CF_3C_6H_4$- **b:** Ar= C_6H_5-	 **11** (84% from **4a**) (86% from **4b**)
 **5** Ar= *m*-$CF_3C_6H_4$-	 **12** (51%)
 **6**	 **13** (73%)
 **7a:** Ar= *m*-$CF_3C_6H_4$- **b:** Ar= C_6H_5-	 **14** (92% from **7a**) (90% from **7b**)
 **8a:** Ar= *m*-$CF_3C_6H_4$- **b:** Ar= C_6H_5-	 **15** (85% from **8a**) (84% from **8b**)
 **9a:** Ar= *m*-$CF_3C_6H_4$- **b:** Ar= C_6H_5-	 **16a** (64% from **9a**) **16b** (70% from **9b**)
 **10** Ar= *m*-$CF_3C_6H_4$-	 **17** (60%)

hyde.[8] Ambrose showed that DMECZ (**3**) undergoes quasi-reversible oxidation, indicating that the stability of the radical cation was improved over MCZ but still undergoes slow reaction on the time scale of the cyclic voltammetry experiment. After bulk electrolysis, a dimer of DMECZ arising from radical coupling at the C3 methyl group was isolated (Scheme 3).

The results of our deoxygenation study using DMECZ as the photosensitizer is summarized in Table 1. Deoxygenations were carried out with a Hanovia 450 W medium-pressure Hg lamp in a Pyrex reaction vessel and the temperature of the reaction was maintained by a coldfinger. The substrate concentration was approximately 1.5 mM in degassed 10% water in 2-propanol with 3.0 mM $Mg(ClO_4)_2$. The *m*-(trifluoromethyl)benzoate derived from diacetone glucose (**1a**) was smoothly deoxygenated with DMECZ within 2 h using 10 mol % of DMECZ. We found that the deoxygenation of *m*-(trifluoromethyl)benzoates did not require $Mg(ClO_4)_2$, although its inclusion increased the rate of deoxygenation. For protected 5-methyluridine derivative **5,** in which there is a competition between the 3′-benzoate and 2′-[*m*-(trifluoromethyl)benzoate], we obtained the protected thymidine (**12**) in 51% yield along the corresponding 2′,3′-dideoxy derivative in 16% yield; no 3′-deoxy-5-methyluridine was observed. Optimal conditions for selective 2′-deoxygenation required $Mg(ClO_4)_2$, 15 mol % photosensitizer, and a reaction temperature of 0 °C maintained by a circulating temperature bath. We previously found that the *m*-(trifluoromethyl)benzoate of **5** could be selectively deoxygenated using *N*-methylcarbazole (MCZ) as the photosensitizer.[5a] It would appear that DMECZ shows both turnover and improved reactivity as a photosensitizer.

To examine the reactivity of DMECZ, we also synthesized the corresponding benzoates of the secondary alcohols shown in Table 1 (**4b**, **7b**−**9b**) and found they are easily deoxygenated in the presence of $Mg(ClO_4)_2$ using 10 mol % photosensitizer. In previous work by us and others,[5,6] the photodeoxygenation of *m*-(trifluoromethyl)benzoates with MCZ required reaction times from 5 to 16 h and benzoates are still slower. With DMECZ (**3**), the deoxygenation of *m*-(trifluoromethyl)benzoates and benzoates are usually complete within 2 h at room temperature. The only exception were cholesterol derivatives **7,** which required 9 h. In the case of long photolysis times, a second portion of photosensitizer is added after about 3−4 h.

We have developed 3,6-dimethyl-9-ethylcarbazole (**3**) as a new photosensitizer for the photoinduced electron-transfer deoxygenation of *m*-(trifluoromethyl)benzoates and benzoates. By examining the radical cation chemistry of carbazoles, a substitution pattern was chosen to slow the rates of potential degradation pathways. The increased lifetime of the radical cation of carbazole **3** allows for the photosensitizer to be regenerated (Scheme 1) and thus it can be used in substoichiometric amounts. Importantly, it appears that **3** is a more reactive photosensitizer. An advantage of the photodeoxygenation over the Barton and related deoxygenation reactions is that toxic tin species are avoided. In addition, the deoxygenation is carried at at room temperature or below, and benzoyl derivatives are attractive due their easy synthetic access under mild and neutral conditions.

Experimental Section

All commercially obtained chemicals were used as received. HPLC grade 2-propanol (99.5%) was purchased from Aldrich in a Sure-seal bottle and used as received. *m*-(Trifluoromethyl)-benzoates and benzoates **4**, **7a,** and **9** were prepared from the corresponding commercially available alcohol by standard methods. Cholesterol benzoate (**7b**) was purchased from Aldrich. *m*-(Trifluoromethyl)benzoate **10** was prepared from the corresponding alcohol, which is available from quinic acid.[9] Benzoyl derivatives **8a** and **8b** were prepared from commercially available methyl 4,6-*O*-benzylidene-α-D-glucopyranose (Aldrich) by formation of the 2,3-*O*-dibutylstannylene (Bu_2SnO, toluene, $-H_2O$) followed by regioselective esterification with 1.1 equiv of the appropriate benzoyl chloride in the presence of 1 equiv of Bu_4NF (1.0 M in THF) in CH_2Cl_2 to give the corresponding 2-*O*-benzoyl derivative;[10] esterification with acetyl chloride gave **8a** and **8b**. Protected nucleoside derivatives **5** and **6** were prepared by Vorbruggen glycosylation of the corresponding protected ribose 1-*O*-benzoate[5a] and arabinose 1-*O*-acetate, respectively, with bis(trimethylsilyl)thymine and $SnCl_4$ in acetonitrile. 3,6-

(8) Buu-Hoi, N. P.; Hoan, N. *J. Org. Chem.* **1951**, *16*, 1327.

(9) Elliot J. D.; Kelson, A. B.; Purcell, N.; Stoodley, R. J.; Palfreyman, M. N. *J. Chem. Soc., Perkin Trans I* **1983**, 2441.

(10) (a) David, S.; Hanessian, S. *Tetrahedron* **1985**, *41*, 643. (b) Holzapfel, C. W.; Koekemoer, J. M.; Marais, C. F. *S. Afr. J. Chem.* **1984**, *37*, 19.

Dimethyl-9-ethylcarbazole (**3**) was prepared as previously described starting from commercially available 9-ethlcarbazole-3-carboxaldehyde (Aldrich).[8] All reactions were performed under an argon atmosphere. Proton and carbon-13 NMR data were recorded at 300 and 75 MHz, respectively, in $CDCl_3$ unless otherwise noted. Chemical shifts are reported in ppm downfield from TMS ($\delta = 0$); coupling constants are given in hertz.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-[3-(trifluoromethyl)benzoyl]-α-D-glucofuranose (4a): ^{1}H NMR ($CDCl_3$) δ 8.26 (s, 1H), 8.20 (d, $J = 7.8$ Hz, 1H), 7.85 (d, $J = 7.8$ Hz, 1H), 7.61 (t, $J = 7.8$ Hz, 1H), 5.97 (d, $J = 3.7$ Hz, 1H), 5.52 (d, $J = 2.1$ Hz, 1H), 4.64 (d, $J = 3.7$ Hz, 1H), 4.37−4.29 (m, 2H), 4.16−4.05 (m, 2H), 1.56 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H), 1.26 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 164.0, 132.8, 131.2 (q, $J_{C-F} = 33$ Hz), 130.4, 130.0, 129.3, 126.5, 123.5 (q, $J_{C-F} = 275$ Hz), 112.4, 109.5, 105.1, 83.3, 79.9, 77.2, 72.5, 67.4, 26.8, 26.6, 26.1, 25.1.

3-*O*-Benzoyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (4b):[11] ^{1}H NMR ($CDCl_3$) δ 8.02 (d, $J = 7.2$ Hz, 2H), 7.57−7.62 (m, 2H), 7.46 (t, $J = 7.5$ Hz, 2H), 5.95 (d, $J = 3.6$ Hz, 1H), 5.50 (d, $J = 2.5$ Hz, 1H), 4.63 (d, $J = 3.6$ Hz, 1H), 4.39−4.31 (m, 2H), 4.17−4.06 (m, 2H), 1.56 (s, 3H), 1.41 (s, 3H), 1.32 (s, 3H), 1.27 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 165.1, 133.5, 129.7, 129.5, 128.5, 112.3, 109.4, 105.1, 83.4, 79.9, 76.6, 72.6, 67.2, 26.8., 26.7, 26.2, 25.2.

2′-*O*-[3-(Trifluoromethyl)benzoyl]-3′,5′-di-*O*-benzoyl-β-D-5-methyluridine (5):[5a] mp 92−95 °C; $[\alpha]^{21}_D$ −78.0° (*c*, 0.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 8.78 (br s, 1H), 8.17−7.99 (m, 4H), 7.93 (d, $J = 7.3$ Hz, 2H), 7.63−7.33 (m, 8H), 6.33 (d, $J = 6.1$ Hz, 1H), 5.84 (dd, $J = 3.8$, 6.0 Hz, 1H), 5.75 (t, $J = 6.1$ Hz, 1H), 4.70 (ABX, $J_{AB} = 12.3$, $J_{AX} = 2.6$, $J_{BX} = 3.5$, $\Delta\nu_{AB} = 69.5$ Hz, 2H), 4.65 (m, 1H), 1.54 (s, 3H); ^{13}C NMR δ 166.2, 165.7, 164.4, 163.7, 150.6, 135.1, 134.0, 133.4, 132.0 (q, $J_{C-F} = 30$ Hz), 130.6, 130.0, 129.9, 129.6, 129.4, 129.1, 128.9, 128.7, 127.0, 124.2 (q, $J_{C-F} = 270$ Hz) 112.5, 87.3, 80.8, 74.0, 71.6, 64.2, 12.4; IR (KBr) 3373, 3276, 3074, 1725, 1619, 1452, 1267, 1128, 1095, 713 cm^{-1}.

2′-*O*-Acetyl-2′,5′-*O*-dibenzoyl-α-D-arabinothymidine (6): ^{1}H NMR ($CDCl_3$) δ 8.52 (br s, 1H), 8.10−7.99 (m, 4H), 7.63−7.53 (m, 2H), 7.47−7.38 (m, 4H), 7.20 (d, $J = 1.5$ Hz, 1H), 6.18 (d, $J = 3.6$ Hz, 1H), 5.77 (t, $J = 3.6$ Hz, 1H), 5.54 (t, $J = 3.6$ Hz, 1H), 4.82−4.77 (m, 1H), 4.68−4.56 (m, 2H), 2.14 (s, 3H), 1.96 (d, $J = 1.5$ Hz, 3H); ^{13}C NMR δ 169.7, 166.1, 165.4, 163.3, 150.0, 135.9, 133.9, 133.4, 130.0, 129.8, 129.4, 128.7, 128.5, 128.3, 111.4, 90.8, 82.8, 80.3, 63.8, 20.7, 12.6.

[3-(Trifluoromethyl)benzoyl]cholesterol (7a): ^{1}H NMR ($CDCl_3$) δ 8.29 (s, 1H), 8.22 (d, $J = 7.8$ Hz, 1H), 7.80 (d, $J = 7.8$ Hz, 1H), 7.56 (t, $J = 7.8$ Hz, 1H), 5.42 (d, $J = 4.5$ Hz, 1H), 4.95−4.85 (m 1H), 2.47 (m, 2H), 2.05−0.95 (m, 26H), 1.08 (s, 3H), 0.92 (d, $J = 6.5$ Hz, 3H), 0.86 (d, $J = 6.6$ Hz, 6H), 0.69 (s, 3H); ^{13}C NMR δ 164.6, 139.4, 132.8, 131.7, 130.9 (q, $J_{C-F} = 33$ Hz), 129.3, 128.9, 126.5, 123.7 (q, $J_{C-F} = 273$ Hz), 123.0, 75.3, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.1, 37.0, 36.6, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.6, 21.0, 19.4, 18.7, 11.9.

Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-[3-(trifluoromethyl)benzoyl]-α-D-glucopyranoside (8a): ^{1}H NMR ($CDCl_3$) δ 8.32 (s, 1H), 8.22 (d, $J = 7.8$ Hz, 1H), 7.84 (d, $J = 7.8$ Hz, 1H), 7.61 (t, $J = 7.8$ Hz, 1H), 7.44−7.49 (m, 2H), 7.35−7.39 (m, 3H), 5.80 (t, $J = 9.8$ Hz, 1H), 5.55 (s, 1H), 5.14 (d, $J = 3.7$ Hz, 1H), 5.06 (dd, $J = 9.8$, 3.8 Hz, 1H), 4.34 (dd, $J = 10.2$, 4.7 Hz, 1H), 3.96−4.04 (m, 1H), 3.72−3.86 (m, 2H), 3.41 (s, 3H), 2.00 (s, 3H); ^{13}C NMR δ 169.9, 164.7, 136.9, 133.1, 131.2 (q, $J_{C-F} = 33$ Hz), 130.0, 129.4, 129.2, 128.3, 126.9, 126.2, 123.1 (q, $J_{C-F} = 273$ Hz), 101.7, 97.5, 79.0, 73.1, 68.9, 62.5, 55.5, 20.8.

Methyl 3-*O*-acetyl-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (8b): ^{1}H NMR ($CDCl_3$) δ 8.03 (d, $J = 7.2$ Hz, 2H). 7.59 (t, $J = 7.2$ Hz, 1H), 7.50−7.43 (m, 4H), 7.39−7.34 (m, 3H), 5.80 (t, $J = 9.8$ Hz, 1H), 5.54 (s, 1H), 5.12 (d, $J = 3.7$ Hz, 1H), 5.05 (dd, $J = 9.8$, 3.6 Hz, 1H), 4.33 (dd, $J = 10.2$, 4.7 Hz, 1H), 4.04−3.95 (m, 1H), 3.82 (t, $J = 10.2$ Hz, 1H), 3.74 (t, $J = 9.6$ Hz, 1H), 3.40 (s, 3H), 1.99 (s, 3H); ^{13}C NMR δ 170.0, 166.0, 137.0, 133.5, 130.0, 129.1,128.6, 128.3, 126.2, 101.7, 97.7, 79.2, 76.6, 72.5, 68.9, 68.5, 62.5, 55.5, 20.9.

4,5-Bis-*O*-[3-(trifluoromethyl)benzoyl]-1,2-*O*-isopropylidene-α-D-xylofurnaose (9a): ^{1}H NMR ($CDCl_3$) δ 8.25 (s, 2H), 8.21−8.18 (m, 2H), 7.86−7.80 (m, 2H), 7.65−7.53 (m, 2H), 6.10 (d, $J = 3.7$ Hz, 1H), 5.65 (d, $J = 2.9$ Hz, 1H), 4.80−4.75 (m, 1H), 4.72 (d, $J = 3.7$ Hz, 1H), 4.65−4.62 (m, 2H), 1.58 (s, 3H), 1.36 (s, 3H); ^{13}C NMR δ 164.8, 164.0, 132.9, 132.3 (q, $J_{C-F} = 33$ Hz), 131.0, (q, $J_{C-F} = 33$ Hz), 130.2, 129.7, 129.4, 129.1, 126.6, 123.6 (q, $J_{C-F} = 273$ Hz), 123.4 (q, $J_{C-F} = 273$ Hz), 112.6, 105.1, 83.4, 77.2, 76.9, 62.2, 26.6, 26.1.

4,5-Di-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-xylofuranose (9b):[12] ^{1}H NMR ($CDCl_3$) δ 8.02 (d, $J = 8.0$ Hz, 4H), 7.61−7.51 (m, 2H), 7.46−7.37 (m, 4H), 6.07 (d, $J = 3.7$ Hz, 1H), 5.62 (d, $J = 3.0$ Hz, 1H), 4.81−4.75 (m, 1H), 4.69 (d, $J = 3.7$ Hz, 1H), 4.61 (dd, $J = 6.2$, 2.2 Hz, 2H), 1.56 (s, 3H), 1.31 (s, 3H); ^{13}C NMR δ 166.2, 165.3, 133.1, 132.8, 129.8, 129.5, 129.0, 128.6, 128.4, 112.4, 105.1, 83.5, 77.1, 76.8, 62.0, 26.8, 26.2.

[3-(Trifluoromethyl)benzoyl]lactone 10: ^{1}H NMR ($CDCl_3$) δ 8.29 (s, 1H), 8.23 (d, $J = 7.8$ Hz, 1H), 7.85 (d, $J = 7.8$ Hz, 1H), 7.61 (t, $J = 7.8$ Hz, 1H), 4.88 (dd, $J = 6.4$, 2.5 Hz, 1H), 4.62−4.57 (m, 1H), 4.40−4.36 (m, 1H), 3.20−3.14 (m, 1H), 2.71 (d, $J = 11.4$ Hz, 1H), 2.63 (ddd, $J = 14.5$, 7.4, 2.1 Hz, 1H), 2.54 (dd, $J = 14.5$, 4.4 Hz, 1H), 1.80−1.55 (m, 8H), 1.50−1.25 (m, 2H); ^{13}C NMR δ 173.1, 163.3, 133.1, 131.1 (q, $J_{C-F} = 33$ Hz), 130.1, 129.9, 129.2, 126.8, 123.0 (q, $J_{C-F} = 273$ Hz), 110.9, 77.2, 75.6, 72.1, 70.7, 36.9, 35.7, 33.7, 30.6, 25.0, 24.0, 23.5.

General Procedure for the Photosensitized Deoxygenation Reaction. 3-Deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (11).[13] In a custom-made Pyrex reaction vessel equipped with a coldfinger, a solution of **4a** (61 mg, 0.14 mM), magnesium perchlorate hydrate (46 mg, 0.14 mM), and 3,6-dimethyl-9-ethylcarbazole (3 mg, 0.014 mM) in 100 mL of 10% deionized water/2-propanol was degassed by bubbling UHP argon through the solution for 30 min. The reaction was photolyzed with a Hanovia 450W medium-pressure Hg lamp while the temperature was maintained at 23 °C with a circulating temperature bath. After 2 h, the reaction was evaporated to remove the 2-propanol and the aqueous residue extracted three times with ethyl acetate. The organic phases were washed with saturated brine, dried over magnesium sulfate, filtered, and evaporated. Purification by flash chromatography on silica gave **11** as a clear oil (29 mg, 84% yield). ^{1}H NMR ($CDCl_3$) δ 5.80 (d, $J = 3.6$ Hz, 1H), 4.74 (t, $J = 4.2$ Hz, 1H), 4.19−4.06 (m, 3H), 3.84−3.77 (m, 1H), 2.17 (dd, $J = 4.0$, 13.3 Hz, 1H), 1.80−1.70 (m, 1H), 1.50 (s, 3H), 1.41 (s, 3H), 1.34 (s, 3H), 1.30 (s, 3H); ^{13}C NMR δ 111.3, 109.6, 105.6, 80.4, 78.6, 76.7, 67.2, 35.3, 26.7, 26.5, 26.1, 25.1.

3′,5′-Di-*O*-benzoyl-β-D-thymidine (12):[5a] mp 193−195 °C (lit.[14] mp 194−195 °C); ^{1}H NMR ($CDCl_3$) δ 8.50 (br s, 1H), 8.09−8.03 (m, 4H), 7.65−7.60 (m, 2H), 7.51−7.46 (m, 5H), 6.47 (dd, $J = 5.6$, 8.7 Hz, 1H), 5.66 (d, $J = 4.5$ Hz, 1H), 4.75 (ABX, $J_{AB} = 12.3$, $J_{AX} = 3.0$, $J_{BX} = 2.9$ Hz, $\Delta\nu_{AB} = 36.7$ Hz, 2H), 4.54 (d, $J = 2.0$ Hz, 1H), 2.73−2.67 (m, 1H), 2.37−2.35 (m, 1H), 1.62 (s, 3H); ^{13}C NMR δ 166.0, 163.2, 150.1, 134.4, 133.7, 129.8, 129.5, 129.3, 129.0, 128.8, 128.6, 111.7, 84.9, 82.7, 75.0, 64.3, 38.0, 12.7.

3′-*O*-Acetyl-5′-*O*-benzoyl-α-D-thymidine (13): ^{1}H NMR δ 8.74 (br s, 1H), 8.01 (d, $J = 7.3$ Hz, 2H), 7.65−7.57 (m, 1H), 7.47 (t, $J = 7.7$ Hz, 2H), 7.33 (d, $J = 0.9$ Hz, 1H), 6.32 (dd, $J = 7.2$, 2.3 Hz, 1H), 5.35 (d, $J = 6.4$ Hz, 1H), 4.73 (t, $J = 4.1$ Hz, 1H), 4.52−4.40 (m, 2H), 2.87 (dt, $J = 15.4$, 6.7 Hz, 1H), 2.30 (d, $J = 15.4$ Hz, 1H), 2.05 (s, 3H), 1.96 (d, $J = 0.9$ Hz, 3H); ^{13}C NMR δ 169.9, 166.1, 164.0, 150.3, 135.3, 133.5, 129.7, 129.3, 128.7, 110.3, 86.9, 84.6, 74.4, 64.1, 38.5, 20.9, 12.7

Cholestene (14): ^{1}H NMR ($CDCl_3$) δ 5.28−5.26 (m, 1H), 2.33−2.15 (m 1H), 2.05−1.65 (m 4H), 1.60−0.95 (m, 25H), 1.00 (s, 3H), 0.91 (d, $J = 6.5$ Hz, 3H), 0.85 (d, $J = 6.6$ Hz, 6H), 0.67 (s, 3H); ^{13}C NMR δ 143.7, 119.0, 56.9, 56.2, 50.6, 42.3, 39.9, 39.8, 39.5, 37.5, 36.2, 35.8, 32.9, 31.9, 31.8, 28.3, 28.1, 28.0, 24.3, 23.8, 22.8, 22.6, 20.8, 19.5, 18.7, 11.9.

Methyl 2-deoxy-3-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside (15):[15] mp 120−122 °C (lit.[10] mp 124−125 °C); ^{1}H NMR ($CDCl_3$) δ 7.43−7.46 (m, 2H), 7.32−7.37 (m, 3H), 5.54 (s, 1H), 5.35−5.29 (m, 1H), 4.78 (d, $J = 3.2$ Hz, 1H), 4.25 (dd, $J = 10.2$, 4.8 Hz, 1H), 3.92−3.86 (m, 1H), 3.75 (t, $J = 10.2$ Hz, 1H), 3.65 (t, $J = 9.5$ Hz, 1H), 3.33 (s, 3H), 2.33 (ddd, $J = 12.5$, 5.2, 1.0 Hz, 1H), 2.03 (s, 3H), 1.74 (dt, $J = 12.5$, 3.8 Hz, 1H); ^{13}C

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NMR δ 170.2, 137.3, 129.1, 128.3, 127.0, 126.2, 101.8, 98.7, 80.4, 69.1, 68.0, 63.0, 54.9, 35.5, 21.2.

3-Deoxy-1,2-*O*-isopropylidene-5-*O*-[3-(trifluoromethyl)-benzoyl]-α-D-xylofuranose (16a): ^{1}H NMR ($CDCl_3$) δ 8.31 (s, 1H), 8.24 (d, J = 7.9 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 5.88 (d, J = 3.7 Hz, 1H), 4.80 (t, J = 4.3 Hz, 1H), 4.60−4.54 (m, 2H), 4.42−4.35 (m, 1H), 2.20 (dd, J = 13.3, 4.1 Hz, 1H), 1.79−1.69 (m, 1H), 1.54 (s, 3H), 1.34 (s, 3H); ^{13}C NMR δ 165.1, 133.0, 131.1 (q, J_{C-F} = 33 Hz), 129.6, 129.1, 126.6, 123.6 (q, J_{C-F} = 272 Hz), 111.4, 105.7, 80.2, 75.6, 65.9, 35.4, 26.7, 26.1.

3-Deoxy-1,2-*O*-isopropylidene-5-*O*-benzoyl-α-D-xylofuranose (16b):[16] ^{1}H NMR ($CDCl_3$) δ 8.05 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.0 Hz, 1H), 7.44 (t, J = 7.4 Hz, 2H), 5.88 (d, J = 3.7 Hz, 1H), 4.79 (t, J = 4.2 Hz, 1H), 4.61−4.51 (m, 2H), 4.39−4.33 (m, 1H), 2.18 (dd, J = 13.4, 4.3 Hz, 1H), 1.81−1.71 (m, 1H), 1.53 (s, 3H), 1.33 (s, 3H); ^{13}C NMR δ 166.4, 133.1, 129.8, 128.4, 111.4, 106.8, 80.3, 77.2, 75.8, 65.3, 35.4, 26.8, 26.2.

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Deoxylactone 17: ^{1}H NMR ($CDCl_3$) δ 4.72 (dd, J = 5.7, 2.5 Hz, 1H), 4.48−4.42 (m, 1H), 4.34−4.30 (m, 1H), 2.59 (dt, J = 6.3, 1.8 Hz, 1H), 2.41 (d, J = 12.2, 1H), 2.35−2.16 (m, 2H), 2.08 (ddd, J = 15.1, 6.4, 3.4 Hz, 1H), 1.75−1.40 (m, 10H); ^{13}C NMR δ 179.1, 110.2, 77.5, 72.4, 70.0, 37.0, 35.4, 33.8, 30.0, 28.1, 25.0, 24.0, 23.5.

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for compounds **4**−**17** (32 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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