0.5 H, CHO), 2.4–0.9 (m, 8 H), 1.72 (s, 3 H, =CCH_3), 1.03 (d, J = 6.4 Hz, 3 H, CH_3), 0.97 (d, J = 6.4 Hz, 3 H, CH_3); ^{13}C NMR δ 150.1, 149.2, 108.5, 108.2, 76.2, 70.8, 44.1, 40.5, 39.9, 38.6, 37.7, 36.0, 33.2, 31.3, 31.0, 29.6, 28.1, 20.8, 20.7, 18.3, 18.2; MS, m/z 154 (M^+).

(1*R*,3*S*,6*S*)- and (1*S*,3*S*,6*S*)-3-Isopropenyl-6-methylcyclohexyl Acetate (7). A mixture of 9.2 g (59.7 mmol) of alcohols **6** and 11.2 mL (0.118 mol) of acetic anhydride in 160 mL of pyridine was stirred at 85 °C for 3 h. The solution was cooled, poured into H_2O (400 mL), and extracted three times with ether (200 mL each). The combined extract was washed with 1 N HCl (100 mL), saturated $NaHCO_3$ (100 mL), and brine (50 mL), dried ($MgSO_4$), concentrated, and filtered through a small silica gel column to give 10.42 g (89% yield) of the two isomeric acetates **7**: IR (neat) 1725, 1640, 1450, 1370, 1240; ^1H NMR δ 5.05 (br s, 0.5 H, CHO), 4.7 (m, 2 H, =CH_2), 4.47 (br t, J = 10 Hz, 0.5 H, CHO), 2.2–1.1 (m, 8 H), 2.08 (s, 1.5 H, CH_3), 2.06 (s, 1.5 H, CH_3), 1.7 (s, 3 H, =CCH_3), 0.91 (d, J = 6.4 Hz, 1.5 H, CH_3), 0.88 (d, J = 6.8 Hz, 1.5 H, CH_3); ^{13}C NMR δ 170.7 (2 C), 149.6, 148.8, 108.8, 108.6, 78.1, 73.4, 43.6, 38.5, 37.0, 36.8, 35.5, 34.8, 33.0, 31.1, 30.8, 29.6, 29.0, 21.2, 21.1, 20.84, 20.77, 18.1, 18.0; MS, m/z 196 (M^+).

(1*R*,3*S*,6*S*)- and (1*S*,3*S*,6*S*)-3-Acetyl-6-methylcyclohexyl Acetate (8). Into a cold (−78 °C) solution of 7.2 g (36.7 mmol) of acetates **7** in 100 mL of MeOH and 500 mL of CH_2Cl_2 under argon was bubbled ozone until the solution became light blue (about 1 h). The ozone addition was stopped, and the solution was stirred under argon at −78 °C for 15 min and at 25 °C for 30 min. To the solution were added 45 g of zinc dust and 100 mL of acetic acid, and the resulting mixture was stirred at 25 °C for 30 min and filtered through Celite. The filtrate was neutralized with 5 N NaOH solution (340 mL), the organic layer was separated, and the aqueous layer was extracted twice with ether (400 mL). The organic layer and ether extracts were combined, washed with water (100 mL) and brine (100 mL), dried ($MgSO_4$), and concentrated to give 6.93 g (95% yield) of ketones **8**: IR (neat) 1725, 1700, 1440, 1360, 1240; ^1H NMR δ 5.07 (br s, 0.5 H, CHO), 4.44 (td, J = 10 Hz, 4 Hz, 0.5 H, CHO), 2.7–1.1 (m, 8 H), 2.15 (s, 1.5 H, CH_3), 2.14 (s, 1.5 H, CH_3), 2.09 (s, 1.5 H, CH_3), 2.06 (s, 1.5 H, CH_3), 0.92 (d, J = 6.5 Hz, 1.5 H, CH_3), 0.88 (d, J = 6.5 Hz, 1.5 H, CH_3); ^{13}C NMR δ 211.0, 209.5, 170.6, 170.4, 77.2, 72.3, 49.7, 45.2, 36.6, 34.5, 33.1, 32.4, 32.1, 28.1, 27.8, 27.5, 24.1, 20.9, 17.9, 17.7; MS, m/z 198 (M^+).

(1*R*,6*S*)- and (1*S*,6*S*)-3-(α-Acetoxyethylidene)-6-methylcyclohexyl Acetate (9). A solution of 6 g (30.3 mmol) of ketones **8** and 5.82 g (30.6 mmol) of *p*-TsOH in 225 mL of acetic anhydride was heated at 90 °C for 6 h under argon. About 30 mL of acetic anhydride (containing generated acetic acid) was distilled from the mixture under reduced pressure (30 mmHg) at the end of each hour. The mixture was then cooled to room temperature, diluted with ether (400 mL), washed with H_2O (100 mL), saturated $NaHCO_3$ (50 mL), and brine (50 mL), and dried ($MgSO_4$). The solvent was evaporated, and the residue was column chromatographed to give 4.36 g (60% yield) of enol acetates **9** as four isomers and 2.1 g (35% recovery) of ketones **8** and their C-3 epimers.

9: IR (neat) 1725, 1425, 1360, 1225; ^1H NMR δ 4.91 (m, 0.25 H, CHO), 4.80 (m, 0.25 H, CHO), 4.42 (td, J = 10.3 Hz, 4.6 Hz, 0.25 H, CHO), 4.33 (td, J = 10.1 Hz, 4.6 Hz, 0.25 H, CHO), 2.9–1.0 (m, 7 H), 2.14 (s, CH_3), 2.13 (s, CH_3), 2.09 (s, CH_3), 2.06 (s, CH_3), 2.05 (s, CH_3), 2.03 (s, CH_3), 1.88 (s, 0.75 H, =CCH_3), 1.87 (s, 0.75 H, =CCH_3), 1.86 (s, 0.75 H, =CCH_3), 1.80 (s, 0.75 H, =CCH_3), 0.920 (d, J = 6.4 Hz, 0.75 H, CH_3), 0.917 (d, J = 6.4 Hz, 0.75 H, CH_3), 0.912 (d, J = 6.8 Hz, 0.75 H, CH_3), 0.911 (d, J = 6.8 Hz, 0.75 H, CH_3); ^{13}C NMR δ 171.1, 170.9, 170.5, 170.4, 169.3, 169.2, 169.0, 168.97, 139.2, 138.8, 138.7, 122.3, 122.0, 121.0, 120.7, 77.07, 76.7, 74.1, 73.8, 62.7, 37.0, 36.8, 36.7, 34.6, 34.4, 33.9, 32.5, 32.4, 32.2, 32.0, 30.8, 29.5, 29.3, 27.5, 27.4, 26.0, 21.1, 20.9, 20.7, 20.6, 18.0, 17.7, 17.0, 16.7, 15.8, 15.7, 15.5; MS m/z 240 (M^+).

(3*R*,4*S*)- and (3*S*,4*S*)-3-Acetoxy-4-methylcyclohexanone (10). The mixture of enol acetates **9** was subjected to the same conditions as described above for the reaction of **7** with ozone. The titled compounds (85% yield; ratio of 1:1) were separated by column chromatography.

(3*R*,4*S*)-*cis*-3-Acetoxy-4-methylcyclohexanone: more polar isomer, $[\alpha]^{23}_D$ + 47.3° (*c* 0.127, $CHCl_3$); IR (neat) 1725, 1460, 1420, 1375, 1240; ^1H NMR δ 5.27 (m, 8 Hz wide, 1 H, CHO, equatorial H), 2.6–1.8 (m, 7 H), 2.05 (s, 3 H, CH_3CO), 1.01 (d, J = 6.8 Hz, 3 H, CH_3); ^{13}C NMR δ 208.2, 169.9, 74.5, 45.2, 39.8, 33.4, 28.1, 20.5, 16.3; MS, m/z 170 (M^+).

(3*S*,4*S*)-*trans*-3-Acetoxy-4-methylcyclohexanone: less polar isomer, $[\alpha]^{23}_D$ +18.5° (*c* 0.13, $CHCl_3$); IR (neat) 1725, 1700, 1458, 1250; ^1H NMR δ 4.80 (td, J = 10 Hz, 4.8 Hz, 1 H, CHO, axial H), 2.8–1.4 (m, 7 H), 2.06 (s, 3 H, CH_3), 1.07 (d, J = 6.5 Hz, 3 H, CH_3); ^{13}C NMR δ 207.4 (s), 169.7 (s), 75.4 (d), 45.3 (t), 39.2 (t), 34.6 (q), 28.3 (d), 20.7 (t), 16.5 (q); MS, m/z 170 (M^+).

(*S*)-(−)-4-Methyl-2-cyclohexen-1-one (1). A mixture of 2.80 g (16.5 mmol) of a mixture of 3(*R*),4(*S*)- and 3(*S*),4(*S*)-3-acetoxy-4-methylcyclohexanone and 4.6 mL (33 mmol) of triethylamine in 65 mL of toluene was stirred under argon at 25 °C for 3 h. The mixture was poured into H_2O (100 mL) and extracted three times with ether (100 mL each). The combined extracts were washed with H_2O (50 mL) and brine (50 mL), dried ($MgSO_4$), concentrated, and column chromatographed to give 1.71 g (94% yield) of enone **1**: $[\alpha]^{22}_D$ −119° (*c* 0.37, EtOH) (lit.[4] $[\alpha]^{22}_D$ +112°, in EtOH; for *R* configuration); IR (neat) 3020, 2960, 1670; ^1H NMR δ 6.81 (d, J = 10.1 Hz, 1 H, =CH), 5.95 (d, J = 10.1 Hz, 1 H, =CH), 2.6–1.6 (m, 5 H), 1.76 (d, J = 7.1 Hz, CH_3); ^{13}C NMR[11] δ 199.16 (s), 155.94 (d), 128.12 (d), 36.43 (d), 30.66 (t), 30.45 (t), 19.77 (q); MS, m/z 110 (M^+).

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Electron Transfer Induced Desilylation of Trimethylsilyl Enol Ethers

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The trimethylsilyl moiety is now widely used as a protecting group for alcohols through the formation of trimethylsilyl ethers and for aldehydes and ketones through the formation of trimethylsilyl enol ethers. The trimethylsilyl protecting group has routinely been removed with fluoride ion,[1] acid,[2] or base.[3] Unfortunately, these reagents offer little in the way of selectively between trimethylsilyl enol ethers and trimethylsilyl ethers. We now report a selective method for the deprotection of trimethylsilyl enol ethers in the presence of trimethylsilyl ethers. This method is based on the photoinduced single-electron transfer[4,5] from the easily oxidized tri-

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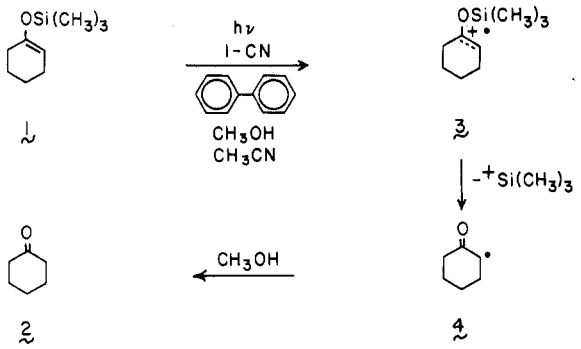
methylsilyl enol ether.

In general, organic substrates with an $E_{1/2}$ for oxidation vs a saturated calomel electrode (SCE) of ca. 2.2 V or less are very susceptible to oxidation by a photoinduced single electron transfer process. Comparison of the $E_{1/2}^{ox}$ of a typical trimethylsilyl enol ether with that of a simple trimethylsilyl ether show them to differ by at least 1 V.[6] On the basis of this difference, we decided to explore the possibility of selective photoinduced deprotection of trimethylsilyl enol ethers in the presence of trimethylsilyl ethers.

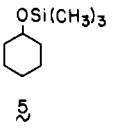
In initial experiments, it was necessary to establish that photoinduced single-electron transfer would occur from a simple trimethylsilyl enol ether to generate an intermediate cation radical, which would then be converted into the precursor aldehyde or ketone. This was accomplished through the facile photoinitiated conversion of the trimethylsilyl enol ether of cyclohexanone,[7] **1**, into cyclohexanone (**2**). In a typical experiment, a solution of **1** (2



equiv), biphenyl (1 equiv) and 1-cyanonaphthalene (1-CN, 1 equiv) in 40:60 methanol/acetonitrile was irradiated in a Pyrex vessel with a bank of 16 300-nm lamps in a Rayonet photoreactor for 5 h. Workup gave an isolated yield of 60% of **2** (GLC yield = 70%). Control experiments showed that only trace amounts of **1** were converted into **2** in the absence of irradiation with all other conditions being comparable to those in the photochemical experiment. When the solvent system was 3:1 acetonitrile/water, a 74% yield of **2** was obtained.

From a mechanistic point of view, the initial excitation involves 1-CN, which in its excited state is a sufficiently powerful oxidant ($E_{1/2}^{red*}$ = 1.84 V) to remove an electron from **1** ($E_{1/2}^{ox}$ = 1.29 V) to produce the cation–radical **3**.[8,9] The details of the conversion of **3** into **2** have not been elucidated. However, a reasonable mechanistic postulate would involve loss of the trimethylsilyl cation from **3** to give **4**,[10] followed by hydrogen transfer from methanol to **4** to yield **2**. It is interesting to note that the fluorescence quenching rate constant, k_q, for 1-CN in this reaction was 7.6×10^{10} L mol^{-1} s^{-1}. Since this is slightly in excess of what might be expected for a diffusion-controlled process, a weak ground state complex between **1** and 1-CN might be implicated. However, no direct evidence for such a ground state complex could be found.

In contrast to the ease with which **1** was photodeprotected through irradiation in the presence of a suitably powerful excited state oxidant, its saturated analogue, the trimethylsilyl ether of cyclohexanol, **5**,[11] was very unreactive under the conditions where **1** was completely deprotected. Under the same reaction conditions, 96% of **5** remained after 5 h.



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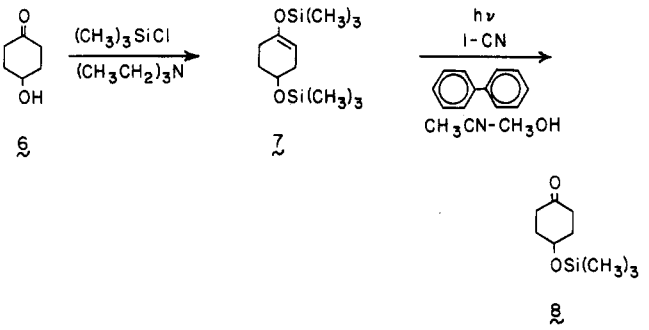
The most meaningful test of the use of selective photoinitiated deprotection of silyl ethers is whether one type of silyl ether can be removed in the presence of the other. In order to answer this question, 4-hydroxycyclohexanone (**6**)[12] was diprotected in one step through treatment with excess trimethylsilyl chloride and trimethylamine in *N,N*-dimethylformamide at reflux for 4.5 h. When **7** was



6 **7** **8**

subjected to the same photochemical reaction conditions as was used for the deprotection of **1**, **8**[13] was obtained in 63% yield. Less than 3% of **6** could be detected by GLC. Thus, the trimethylsilyl group could be removed from the enol ether function while leaving the silyl group on the unactivated hydroxyl function intact.

As noted, the yields of the desired products in the photodeprotections described above were far from quantitative. A complex mixture of higher molecular weight materials was also observed, but not characterized. The disappearance of the photosensitizer, 1-CN, in these reactions leads us to speculate that photoadducts may have been formed through addition of the silyl enol ether to excited state 1-CN.[9]

Although the yields observed for the photodeprotection of sily enol ethers are marginal from a synthetic point of

(5) For earlier studies of photoinduced single-electron transfer reactions from our laboratory, see: Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977. Gassman, P. G.; Olson, K. D. *Ibid.* **1982**, *104*, 3740. Gassman, P. G.; Olson, K. D. *Tetrahedron Lett.* **1983**, *24*, 19. Roth, H. D.; Schilling, M. L. M.; Gassman, P. G.; Smith, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2711. Gassman, P. G.; Hay, B. A. *Ibid.* **1985**, *107*, 4075. Gassman, P. G.; Hay, B. A. *Ibid.* **1986**, *108*, 4227.

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(7) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

(8) The anion radical of 1-CN would be formed as the counterion. The conversion of **3** into product would be competitive with back electron transfer from 1-CN$^-$ to **3** to produce starting materials.

(9) The reaction of excited state 1-CN with silyl enol ethers has been studied previously in benzene. Cycloaddition products of 1-CN and the enol ethers were the major products. Pac, C.; Mizuno, K.; Okamoto, H.; Sakurai, H. *Synthesis* **1978**, 589.

(10) It was presumed, but not proven, that attack of the nucleophilic solvent methanol on **3** transferred the trimethylsilyl cation from **3** to methanol to produce the protonated trimethylsilyl ether of methanol. Loss of a proton from this intermediate would have given the very volatile trimethylsilyl methyl ether, which was not isolated. An alternate, reasonable mechanism would involve back electron transfer from 1-CN$^{-\bullet}$ to **4** to yield the enolate anion of cyclohexanone. Protonation of this enolate anion by methanol would give **2**.

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(12) The authors thank Dr. Robert Rosen for supplying a sample of **6**, which was prepared by the literature procedure. Haslanger, M.; Lawton, R. G. *Synth. Commun.* **1974**, *4*, 155.

(13) Gray, R. T.; Spangler, R. J.; Djerassi, C. *J. Org. Chem.* **1970**, *35*, 1525.

view, our procedures do offer a very selective method for the removal of the protecting silyl group from an enol ether in the presence of a silyl ether of an alcohol.

Experimental Section[14]

1-(Trimethylsiloxy)cyclohexene (1). This compound was prepared in 89% yield from cyclohexanone and trimethylsilyl chloride according to the literature procedure: bp 76 °C (20 mm) [lit.[7] bp 74–75 °C (20 mm)].

Photosensitized Deprotection of 1-(Trimethylsiloxy)-cyclohexene (1). A solution of 1 (190.8 mg, 1.12 mmol), biphenyl (86.2 mg, 0.56 mmol), 1-CN (85.7 mg, 0.56 mmol), methanol (3.2 mL), and acetonitrile (4.8 mL) contained in a 14-mm, 35-mL Pyrex tube was irradiated in a Rayonet photochemical reactor fitted with 16 300-nm lamps for 5 h, while the disappearance of 1 was monitored by GLC analysis of the reaction mixture. When the starting material was completely consumed, the reaction mixture was concentrated by careful removal of the solvent by distillation. The residue was purified by preparative GLC with use of a 10-ft, 10% SE 30 on Chromosorb W column to give a 60% yield (65.8 mg, 0.67 mmol) of cyclohexanone. The ^1H NMR spectrum was identical with a commercially available sample of cyclohexanone.

Photosensitized Deprotection of 1-(Trimethylsiloxy)-cyclohexene (1). GLC Yields. (a) To a 5-mm Pyrex tube, which had been presoaked in a potassium hydroxide/isopropyl alcohol solution overnight was added 1-(trimethylsiloxy)cyclohexene (1) (44.6 mg, 0.262 mmol), biphenyl (21.6 mg, 0.14 mmol), 1-CN (21.5 mg, 0.14 mmol), 1.2 mL of acetonitrile, and 0.8 mL of methanol. The tube was irradiated for 32.8 min in a Rayonet photochemical reactor fitted with 16 300-nm lamps. After irradiation was complete, 18.0 mg of nonane was combined with the reaction solution, and the solution was analyzed by GLC on an 8-m capillary column coated with an OV-101 liquid phase. The yields of the products were calculated by integration of the peaks for products and the nonane standard. The yield of cyclohexanone was found to be 70%.

(b) The procedure was identical with that described in a, with the following exceptions: 1-(trimethylsiloxy)cyclohexene (1; 48.2 mg, 0.283 mmol), 1.5 mL of acetonitrile, and 0.5 mL of distilled water rather than methanol. The solution was irradiated for 175 min, and 14.4 mg of nonane was added. The yield of cyclohexanone was found to be 74%.

Trimethylsilyl Cyclohexyl Ether (5). This compound was prepared in 52% yield from cyclohexanol and trimethylsilyl chloride according to the literature procedure: bp 74–75 °C (30 mm) [lit.[11] bp 59–61 °C (13 mm)].

Determination of the Stability of Trimethylsilyl Cyclohexyl Ether (5) to the Irradiation Conditions. A mixture of 5 (45.6 mg, 0.26 mmol), biphenyl (21.6 mg, 0.14 mmol), 1-CN (12.5 mg, 0.14 mmol), methanol (0.8 mL), and acetonitrile (1.2 mL) was irradiated for 5 h and analyzed by GLC in the same manner as described for the irradiation of 1. Less than 4% of 5 had been converted to cyclohexanol.

1,4-Bis(trimethylsiloxy)cyclohexene (7). To a dry, 100-mL, round-bottomed flask under a nitrogen atmosphere, equipped with a water condenser, magnetic stirbar, and sidearm fitted with a septum were added 4.6 mL of triethylamine (freshly distilled from lithium aluminum hydride), 4-hydroxycyclohexanone (6; 0.785 g, 6.88 mmol),[12] and 5.5 mL of *N,N*-dimethylformamide (distilled from calcium hydride). Trimethylsilyl chloride (2.09 mL, 1.79 g, 16.5 mmol) was then syringed into the stirred solution. The solution was refluxed over a period of 4.5 h and allowed to cool to room temperature. The solution was then diluted with 10 mL of pentane, washed successively with three 4-mL portions of cold, dilute sodium bicarbonate, 4 mL of cold, dilute hydrochloric acid, and again with 4 mL of cold, dilute sodium bicarbonate. The organic layer was dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under reduced pressure to afford 1.429 g (5.53 mmol, 80.4%) of 7, which was further purified before use, via MPLC with use of 1.5% ethyl acetate/petroleum ether (60–70 °C) as eluent. This gave 1.210 g (4.68 mmol, 68%) of pure 7: IR (neat) 2955, 1667, 1376, 1250, 1185, 1095, 960, 895, 840, 755 cm^{-1}; ^1H NMR ($CDCl_3$/TMS) δ 4.76 (m, 1 H), 3.84 (m, 1 H), 2.30–1.89 (m, 4 H), 1.88–1.57 (m, 2 H), 0.18 (s, 9 H), 0.12 (s, 9 H); ^{13}C NMR ($CDCl_3$) 149.60 (s), 100.96 (d), 67.33 (d), 33.11 (t), 31.74 (t), 28.33 (t), 0.06 (q) ppm; mass spectrum, *m/e* 258.1473, calcd for $C_{12}H_{26}O_2Si_2$ 258.1471. Anal. Calcd for $C_{12}H_{26}O_2Si_2$: C, 63.09; H, 11.18. Found: C, 63.11; H, 11.13.

4-(Trimethylsiloxy)cyclohexanone (8). A 100-mL, round-bottomed flask equipped with a septum-capped sidearm, water reflux condenser, and magnetic stirbar was charged with triethylamine (0.824 g, 8.14 mmol), 4-hydroxycyclohexanone (6; 0.465 g, 4.074 mmol), and *N,N*-dimethylformamide (3.3 mL). Stirring was commenced, and chlorotrimethylsilane (0.440 g, 0.514 mL, 4.08 mmol) was syringed into the reaction mixture. The solution was refluxed over a period of 4.5 h and allowed to cool to ambient temperature. At this time, the reaction mixture was diluted with petroleum ether (30–60 °C, 6 mL) and washed with three 3-mL portions of cold, dilute sodium bicarbonate, 3 mL of cold, dilute hydrochloric acid (rapidly), and once again with 3 mL of cold, dilute sodium bicarbonate. The organic portion was dried over anhydrous magnesium sulfate and filtered, and the filtrate was concentrated under reduced pressure. The residue was purified via MPLC with use of 5% ethyl acetate/petroleum ether (60–70 °C) as eluent to give 0.202 g of 8 (1.09 mmol, 27%) as a clear colorless oil: mass spectrum, *m/e* (relative intensities) 186 (15.6), 171 (36.5), 129 (55.5), 115 (19.4), 79 (14.5), 75 (100), 73 (61.7), 45 (10.5) [lit.[13] *m/e* 186]; IR (neat) 2950, 1720, 1252, 1097, 1040, 1007, 880, 840, 745 cm^{-1}; ^1H NMR ($CDCl_3$/TMS) δ 4.18 (m, 1 H), 2.34–1.90 (m, 8 H), 0.15 (s, 9 H); ^{13}C NMR ($CDCl_3$) 200.60 (s), 66.60 (d), 36.93 (t), 34.02 (t), 0.08 (q) ppm.

Photosensitized Deprotection of 1,4-Bis(trimethylsiloxy)cyclohexene (7). A solution of 7 (32.2 mg, 0.124 mmol), biphenyl (10.5 mg, 0.068 mmol), 1-CN (10.4 mg, 0.068 mmol), methanol (0.2 mL), and acetonitrile (0.8 mL) contained in a 5-mm Pyrex tube, which had been presoaked in a potassium hydroxide/isopropyl alcohol solution overnight, was irradiated for 140 min in a Rayonet photoreactor fitted with 16 300-nm light bulbs. When the irradiation was complete, 15.6 mg of acetophenone (internal standard) was added, and the reaction mixture was analyzed by GLC with use of an 8-m, OV-101, capillary column. The yields of the products were calculated by electronic integration of the peaks for products and standard. The yield of 4-(trimethylsiloxy)cyclohexanone (8) was determined to be 63% while 4-hydroxycyclohexanone appeared in less than a 2% yield.

Dark Control Reaction for the Photosensitized Deprotection of 1,4-Bis(trimethylsiloxy)cyclohexene (7). A solution of 7, 1-CN, biphenyl, methanol, and acetonitrile contained in a 5-mm Pyrex tube was kept in the dark while being exposed in identical fashion to the other conditions present in the photosensitized deprotection of 7. Analysis by GLC determined that 8 was obtained in less than 3% yield.

Thermal Deprotection of 1,4-Bis(trimethylsiloxy)cyclohexene (7). A solution of 7, 1-CN, biphenyl, methanol, and acetonitrile was prepared in an identical fashion as for the photosensitized deprotection of 7. The solution was warmed to 50 °C (oil bath temperature) for 48 h and analyzed by GLC with use of an 8-m, OV-101, capillary column. The yields of the products were calculated by electronic integration of the peaks for products and an internal standard. The yield of 4-(trimethylsiloxy)-cyclohexanone (8) was determined to be 41% along with ca. 7–10% of 4-hydroxycyclohexanone. This demonstrated that under thermal conditions both the silyl enol ether and the silyl ether were deprotected at an approximate rate ratio of 4–5:1. This implied that the trace amounts of 6 found in the photodeprotection of 7 may be the result of a thermal deprotection of the silyl ether of the alcohol.

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(14) Boiling points are uncorrected. Routine proton and carbon nuclear magnetic resonance (NMR) spectra were recorded on Varian HF-T-80, Hitachi R24B, and Varian CFT-20 nuclear magnetic resonance spectrometers, respectively. High-field proton and carbon nuclear magnetic resonance spectra were recorded on a Nicolet NIC 1180E nuclear magnetic resonance spectrometer in magnetic field strengths of 300 and 75 MHz, respectively. Infrared spectra were recorded on a Beckman Model 4240 infrared spectrophotometer. Mass spectra were determined on AEI-MS30 (electron impact) and Finnigan 4000 (chemical ionization) instruments. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark. All methanol used in the experimental procedures was distilled from dimethoxymagnesium just prior to use.

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Preparation of a Prostanoid Intermediate from Loganin

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Iridoids[1,2] have been used successfully as optically active synthons for prostaglandins and prostaglandin analogues.[3] Moreover, the wide variety of iridoid substitution patterns available in nature suggests new and physiologically interesting prostaglandin analogues, such as relatives of the 11-deoxy-11-methyl group represented by the antiulcer agent **2**.[4] Here, we report the conservative conversion of loganin (1) into prostaglandin analogue intermediate **8**.

Oxidation of an iridoid enol ether to a lactone has been accomplished in several ways, in particular by the method of D'Ascoli et al. (I_2/PDC, $Na_2S_2O_3$).[5,3h] Bromination with NBS and reduction of bromo lactone **4** with Zn/HOAc was also effective, giving lactone **5** in 83% yield, as shown in Scheme I. Ring opening, glucose cleavage, and decarboxylation were accomplished in one pot with 80% aqueous HOAc and gave the aldehyde ester **6** in 67% yield (after partial reesterification with diazomethane).

Wadsworth–Emmons reaction of aldehyde ester **6** with *gem*-dimethyl phosphonate reagent **7**[6] then gave the desired enone **8** as a 9/1 mixture of epimers in 81% yield. The epimers were cleanly separated by HPLC. The following evidence leads us to conclude that the major isomer has prostanoid-like trans side chains, and the minor isomer is cis substituted.

Table I. 15-Ketoprostanoids

$J_{12,13}$, Hz	H-13, ppm	H-14, ppm	ref
	trans-8,12		
8.0	6.69	6.20	3b
8.6	6.61	6.18	3h
8.9	6.77	6.19	3k
8	6.71	6.19	7a
8	6.80	6.22	7a
7.0	7.04	6.29	7b
7.5	6.84	6.29	7b
	cis-8,12		
11.0	7.03	6.19	3b
10.6	6.84	6.23	3k
10.3	6.74	6.16	3k
10.0	6.74	6.29	7b
	gem-Dimethyl Enone 8		
10.0 (minor isomer)	6.69	6.45	
8.8 (major isomer)	6.82	6.40	

The ^1H NMR (400 MHz) spectrum of the major product (8) of the Emmons–Horner reaction exhibited a doublet at 6.40 ppm with a coupling constant of J = 15.2 Hz, assigned to the vinyl proton at C-14, confirming the presence of a trans double bond, and a doublet of doublets at 6.82 ppm, assigned to the C-13 proton, with coupling constants of $J_{13,14}$ = 15.0 Hz and $J_{12,13}$ = 8.8 Hz. The minor component of the mixture showed peaks at 6.45 ppm ($J_{13,14}$ = 15.2 Hz) and 6.69 ($J_{13,14}$ = 15.0 Hz, $J_{12,13}$ = 10.0 Hz). A two-dimensional COSY ^1H NMR experiment allowed the estimation of $J_{8,12}$ = 8.3–9.8 Hz for the cis isomer, but no value was obtainable for the trans isomer.

Literature data as summarized in Table I[3k,q] indicate that $J_{12,13}$ values fall within the range of 7.0–8.9 Hz for the trans configuration of the side chains in 15-ketoprostaglandin analogues, while for the cis configuration the J values fall within the range of 10.0–11.0 Hz. By extension, the J value for the cis configuration is always higher than that of the corresponding trans epimer. Consequently, we assign the trans configuration to the major isomer isolated from the Wadsworth–Emmons reaction of **6** with **7**.

Experimental Section

Melting points are uncorrected. Routine proton spectra were obtained in the indicated solvent on a Varian EM 360 nuclear magnetic resonance (NMR) spectrometer, with use of tetramethylsilane as the internal standard. High-field proton and ^{13}C spectra were determined on an IBM Bruker WP-200-SY (200 MHz) or JEOL JMM-GX 400 (400 MHz) instrument. (We are indebted to M. Blumenstein of Hunter College for technical assistance). Infrared spectra (IR) were recorded on a Perkin-Elmer IR 598 instrument. High-performance liquid chromatography (HPLC) was conducted with a Waters Associates (Milford, MA) system consisting of two 4 mm × 30 cm μ-Porasil silica gel columns in series, a 6000 SDS pump, a U6K injector, and a Model 401 differential refractometer. Flash chromatography was carried out on E. Merck silica gel (230–400 mesh) according to the usual Still procedure. Preparative column chromatography was performed on E. Merck 7747 silica gel. Several separations were efficiently done with a Chromatotron (Harrison) apparatus with rotating plates coated with E. Merck 7749 silica gel. Thin-layer chromatography (TLC) was carried out on Machery-Nagel (MN)

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