[3',2':6,7][1]benzopyrano[3,4-c]pyridine-5,11-dione (21; 3.9 mg, 0.011 mmol) in 1 mL of a saturated solution of HCl in methanol was gently heated on a steam bath for 1 h. The reaction mixture was diluted with water (1 mL), neutralized with saturated aqueous sodium bicarbonate, and then extracted with ethyl acetate (5 mL × 3). The extract was dried ($MgSO_4$) and evaporated, and the residue was separated by preparative TLC (1000-μm plate, 10:1 $CHCl_3$/acetic acid) to give 12-hydroxy-9-methyl-5*H*,11*H*-pyrano[3',2':6,7][1]benzopyran[3,4-c]pyridine-5,11-dione (2, isoschumanniophytine) (1.4 mg, 0.0047 mmol, 43%) as a pale yellow solid which was obtained as pale-yellow crystals, mp 305–308 °C dec, after recrystallization from $CHCl_3$: ^1H NMR ($CDCl_3$) δ 2.46 (3 H, d, J = 0.6 Hz), 6.21 (1 H, q, J = 0.6 Hz), 6.88 (1 H, s), 8.89 (1 H, d, J = 5.7 Hz), 8.96 (1 H, d, J = 5.7 Hz), 9.55 (1 H, s), 15.03 (1 H, s); MS m/z (rel intensity) 295 (M^+, 100), 267 (12); exact mass calcd for $C_{16}H_{10}NO_5$ $[M + H]^+$ 296.0559, found 296.0556. The ^1H NMR and low-resolution mass spectra are in agreement with those recorded[2,3,17] for natural isoschumanniophytine. Synthetic and natural 2 were also identical by TLC using co-spotting and a variety of solvent systems.

Acknowledgment. We thank Professor P. J. Houghton for authentic samples of schumanniophytine and isoschumanniophytine, ^1H NMR spectra of them and their acetates, and other helpful information.

Registry No. 1, 69735-24-6; 2, 96889-79-1; 6, 500-22-1; 8, 138459-35-5; 9, 138459-36-6; 10, 138459-37-7; 11, 20052-28-2; 12, 138459-38-8; 13, 138459-39-9; 14, 138459-40-2; 15, 138459-41-3; 16, 138459-42-4; 17, 138459-43-5; 18, 138459-44-6; 19, 138459-45-7; 20, 138459-46-8; 21, 96889-80-4; 24, 1162-81-8; 25, 1013-69-0; 2,4,6-trihydroxyacetophenone, 480-66-0; 7-hydroxy-8-iodo-5-methoxy-2-methyl-4*H*-1-benzopyran-4-one, 83805-64-5.

(17) The resonances at δ 8.89, 8.96, and 15.03 are incorrectly reported in ref 2. The ^1H NMR spectrum we report is in agreement with a copy of the spectrum furnished (see Acknowledgment) by Professor Houghton.

Fluorinated Chirons for Vitamin D_3 Syntheses. A Serendipitous Synthesis of a 9α-Hydroxy Derivative of (7*Z*)-Vitamin D_3

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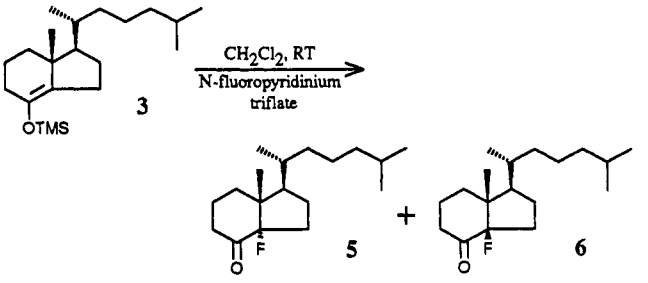
With the discoveries of various biological activities of vitamin D and its metabolites, the development of vitamin D analogues as drugs to be used in the treatment of various diseases has been actively pursued.[1-4] One approach to the discovery of useful vitamin D analogues is to develop analogues that bind strongly to the receptors involved in calcium homeostasis but do not elicit a calcium biological response, thus blocking the vitamin D receptor site from analogues which do elicit a calcium biological response. This is the case of 6-fluorovitamin D_3 (6-F-D_3),[5] which does not display any biological activity in either intestinal calcium absorption (ICA) (Chart I) or bone mobilization (BCM) assays. However, it is the first vitamin D_3 analogue found that binds to the 1,25-$(OH)_2D_3$ receptor in vitro and antagonizes 1,25-$(OH)_2D_3$ activity in vivo.[6] It was assumed that the binding affinity shown by 6-F-D_3 for the receptor is the effect of the fluorine on the triene system of vitamin D_3. The synthesis of 9-fluoro and 14-fluorovitamin D_3 was initiated in order to observe which effects placing fluorine in other positions around the triene system would have on the binding of such compounds to the various vitamin D receptors.

In the synthetic scheme, a suitably fluorinated C/D-ring piece would be coupled to an A-ring piece at the 7,8-bond using a Wittig-type condensation. This path was chosen because the A-ring and C/D-ring carbon skeletons are readily available.[7] Furthermore, the 1α- and 25-hydroxyl groups could easily be incorporated into the synthesis, if desired. The fluorine would be incorporated into the C/D-ring by allowing N-fluoropyridinium triflate[8] to react with the appropriate C/D-ring silyl enol ether (Scheme I).

Treatment of Grundmann's ketone (1)[7] with LDA at −20 °C gave the kinetic enolate which was quenched with trimethylsilyl chloride to give the kinetic silyl enol ether 2 in 82% yield. Conversion of Grundmann's ketone to the thermodynamic silyl enol ether 3 was accomplished by heating the ketone, triethylamine, and trimethylsilyl chloride in DMF at 130 °C for 93 h (73%).

Treatment of the kinetic silyl enol ether 2 with *N*-fluoropyridinium triflate[8] in refluxing methylene chloride for 2 h gave the desired 9α-fluoro C/D-ring ketone 4 in 27% yield (Scheme II). However, the reaction also yielded the 14α-fluoro C/D-ring ketone 5 (9%), the 14β-fluoro C/D-ring ketone 6 (14%), *cis*-Grundmann's ketone (7, 7%), and the α,β-unsaturated ketone 8 (7%). The stereochemistry of the above-described compounds was assigned on the basis of ^1H NMR data.

Treatment of the thermodynamic silyl enol ether 3 with *N*-fluoropyridinium triflate[8] gave the 14α-fluoro C/D-ring ketone 5 in 16% yield and the 14β-fluoro C/D-ring ketone 6 in 27% yield. Again, *cis*-Grundmann's ketone (7) and the α,β-unsaturated ketone 8 were byproducts. It should be noted that the large amount of 14β-fluoro product 6 was quite unexpected. No 9β-fluoro product could be detected in the product mixture when the kinetic silyl enol ether 2 was fluorinated.



Lythgoe and co-workers have shown with model compounds and a total synthesis of vitamin D_3 that coupling of an A-ring phosphine oxide with Grundmann's ketone (1) gives the 7,8-double bond in the proper trans orientation without any cis byproduct.[9] Accordingly, the A-ring phosphine oxide 9[7] was condensed with the C/D-ring ke-

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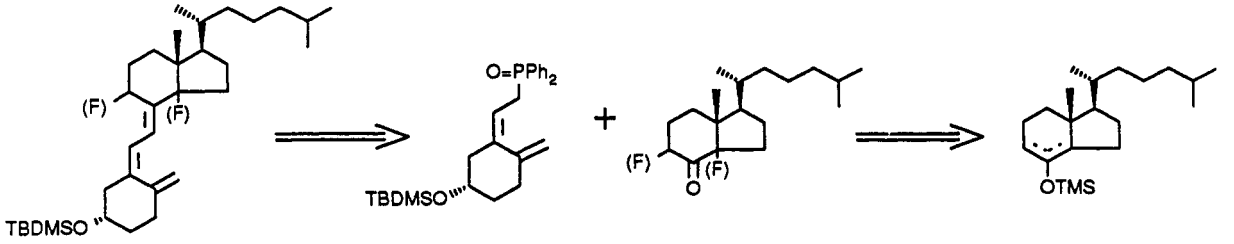
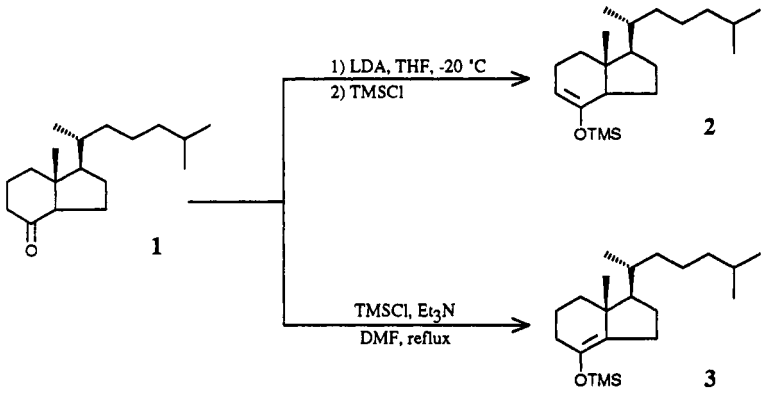
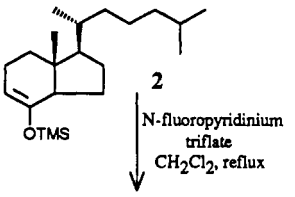
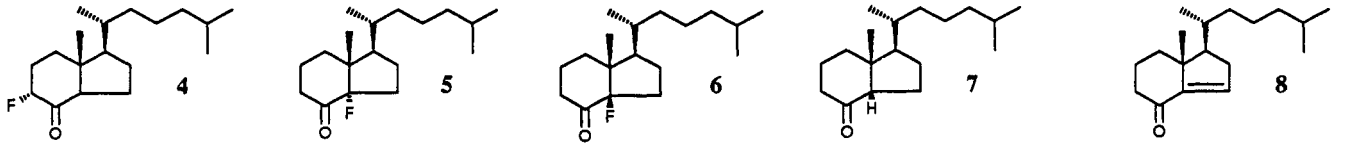
Scheme I



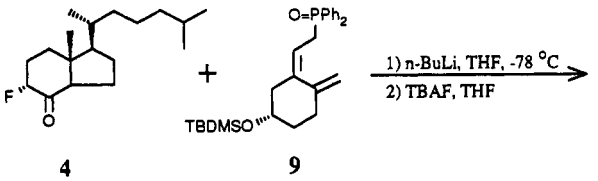
Scheme II



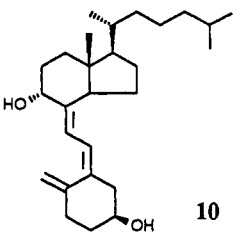




tone 4 under standard conditions[10] and gave a coupled product in 24% yield. The silyl blocking group was removed with TBAF to give the hydroxy compound **10** in 53% yield. These latter two materials gave acceptable combustion analyses with regard to carbon and hydrogen. However, in the ^{1}H NMR spectrum, the coupling pattern seen with the C-9 proton was not commensurate with the presence of geminal fluorine atom. In order to evaluate this conclusion, a gated-decoupling spectrum was obtained and no enhancement in the signal for the C-9 proton was found. Thus, it had to be concluded that the two synthetic coupled products did not contain a fluorine on C-9. The mass spectrum of the materials suggested that a hydroxyl groups had replaced the fluorine atom and the combustion analysis was compatible with this conclusion. Consequently, the product **10** would appear to be a C-9 hydroxy derivative of the vitamin D nucleus.

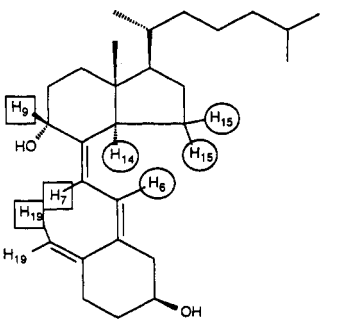


4 9



10

In addition to the different coupling pattern at C–9, the chemical shift position of the protons of carbons 7 and 19 were different from those usually found for the (7*E*)-triene structure of the natural vitamin. The configuration of the protons on carbons 6, 7, and 9 were established by a 2D-NOESY experiment. The protons in squares show an



Critical observed NOE interactions for Compound **10**

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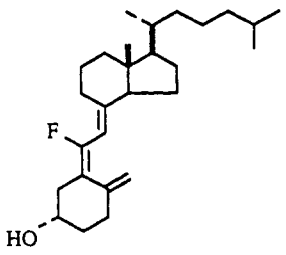
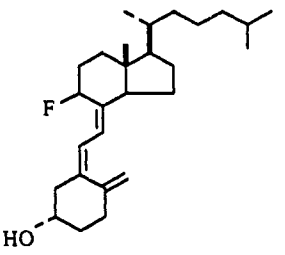
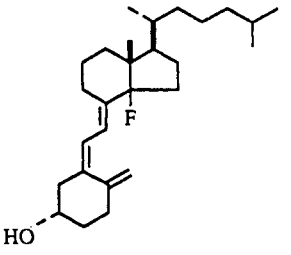
Chart I



6-Fluorovitamin D_3



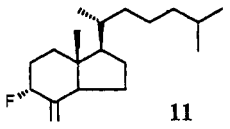
9-Fluorovitamin D_3



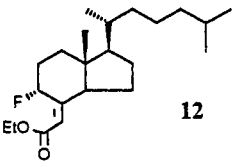
14-Fluorovitamin D_3

NOE enhancement with H-7 and those in circles with H-6. These effects not only establish the presence of the unnatural 7Z configuration of the vitamin D_3 nucleus[11] but also the 9α-configuration of the C-9 hydroxyl group (there was no NOE enhancement between H-9 and H-14). During the course of this study, Mouriño reported a synthesis of (7Z)-9α-hydroxyvitamin D_3.[12] The properties of the material synthesized, serendipitously, are in agreement with those reported.

This finding of the replacement of the 9α-fluorine substituent by a hydroxyl substituent under the phosphine oxide reaction conditions is surprising, but the exact mechanism has not been investigated. However, two alternate synthetic approaches to the coupling sequence have been studied. First, a Wittig condensation was evaluated and it was found that methylylide gave the 9α-fluoro methylene C/D-ring compound 11 in 50% yield with no trace of the 9α-hydroxy product. Since the reaction workup was identical to that used in the phosphine oxide reaction, it appears that instability of the allylic fluoride did not lead to the hydroxyl substitution. Attempts to couple the ylide equivalent of the phosphine oxide 9 to the 9α-fluoro C/D-ring ketone 4 were unsuccessful. The A-ring ylide did not react with compound 4 at low temperature and isomerized 4 at room temperature.



11



12

Finally, the coupling of a Horner–Emmons reagent, triethyl phosphonoacetate, with ketone 4 was investigated using the Masamune–Roush nonenolizing method.[13] The coupled product 12 was obtained in 65% yield. When the phosphonate equivalent of the phosphine oxide 9 was coupled to ketone 4, the reaction proceeded in ~40% yield; however, the phosphonate did not eliminate to give the triene system. Attempts to induce the elimination by heating the coupled product in DMF with sodium hydride resulted in decomposition of the material.

The coupling of the 14α- and 14β-fluoro C/D-ring ketones 5 and 6 with the phosphine oxide 9 resulted in both cases with elimination of HF to give the α,β-unsaturated ketone 8.

The 9α-hydroxy derivative of (7Z)-vitamin D_3 was tested for vitamin D activity and showed no in vivo activity (ICA and BCM) and no binding to the chick intestinal receptor in vitro.

(11) It is to be noted that the 9α-hydroxyl group reverses the stereochemical nomenclature of the double bond at C-7 with respect to the vitamin D system. For simplicity, this compound will be named as a derivative of (7Z)-vitamin D_3.

(12) Maestro, M. A.; Sardina, F. J.; Castedo, L.; Mouriño, A. *J. Org. Chem.* **1991**, *56*, 3582.

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Experimental Section

General. Reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. All solvents were dried and/or distilled prior to use when dry conditions were necessary: THF was distilled from sodium and benzophenone, triethylamine was distilled from calcium hydride, DMF and methylene chloride were stored over 3A sieves. Reactions requiring dry conditions were run under an atmosphere of argon or nitrogen.

Flash column chromatography was done on 230–400-mesh silica gel. Analytical GLC was performed using a DB1-30N fused silica capillary, 30 m × 0.249 mm. HPLC was performed using a Whatman M-9 column with 10/50 Partisil packing.

Melting points (Pyrex capillary) are uncorrected. Optical rotations ($[\alpha]_D$) were determined in a 1-d cell at 25 °C in the solvent indicated. ^1H NMR spectra were measured at 250 MHz. ^{13}C NMR spectra were measured at 51 MHz. ^{19}F NMR spectra were measured at 235 MHz. Chemical shifts are reported in δ values with internal reference $CHCl_3$ δ = 7.24 ppm, C_6H_6 δ = 7.15 ppm, or CH_2Cl_2 δ = 5.31 for ^1H; the middle $CDCl_3$ peak δ = 77 ppm, the middle C_6D_6 peak δ = 128 ppm, or the middle CD_2Cl_2 peak δ 53.8 ppm for ^{13}C; $CFCl_3$ δ = 0 ppm for ^{19}F. ^1H NMR data are tabulated in order: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet), number of protons, coupling constant(s) in hertz. Mass spectral data are tabulated as *m/z* (relative intensity). Elemental analyses were performed by the Microanalytical Laboratory operated by the College of Chemistry, University of California, Berkeley.

A standard aqueous workup consists of partitioning the reaction mixture between the solvent of choice and water, separating and washing the aqueous layer twice with solvent, combining the organic layers, washing them three times with brine, and then drying them with the drying agent of choice.

8-[(Trimethylsilyl)oxy]des-*A*,*B*-8(9)-cholestene (2). A solution of 2.30 g (3.20 mL, 22.7 mmol) of diisopropylamine, 45 mL of dry THF, and 14.2 mL (21.8 mmol) of *n*-butyllithium (1.54 M soln in hexanes) was stirred at room temperature for 15 min under argon and cooled to −20 °C. Grundmann's ketone (4.81 g, 18.2 mmol) in 45 mL of dry THF was added, dropwise. The mixture was stirred at −20 °C for 2 h. Trimethylsilyl chloride (2.57 g, 3.0 mL, 23.6 mmol) was added, the cooling bath was removed, and the solution was stirred for 1.5 h at room temperature. The solvent was removed on a rotary evaporator and the residue purified by flash chromatography (3% ethyl acetate/hexanes) to yield 5.00 g (82%) of a colorless oil: IR (thin film) 2970, 1664, 1256, 1211, 842 cm^{-1}; ^1H NMR (200 MHz, C_6D_6) δ 0.19 (s, 9), 0.81 (s, 3), 0.90 (s, 3), 0.93 (s, 4.5), 0.97 (s, 1.5), 1.14–2.37 (m, 18), 4.69 (q, 1, *J* = 3.0 Hz); ^{13}C NMR (C_6D_6) δ 0.54, 11.6, 19.0, 22.6, 22.8, 23.1, 23.8, 24.5, 28.4, 28.7, 36.6, 39.9, 44.0, 52.3, 55.3, 100.6, 128.3, 151.9. Anal. Calcd for $C_{21}H_{40}OSi$: C, 74.91; H, 12.00. Found: C, 74.73; H, 12.32.

8-[(Trimethylsilyl)oxy]des-*A*,*B*-8(14)-cholestene (3). A solution of 40 mL dry DMF, 2.1 g (2.8 mL, 20.6 mmol) of triethylamine, 2.19 g (8.28 mmol) of Grundmann's ketone, and 1.12 g (1.31 mL, 10.3 mmol) of trimethylsilyl chloride was heated at

130 °C for 93 h and poured into a saturated aqueous sodium bicarbonate solution. The aqueous layer was washed 4 times with ether. The combined organic layers were washed once with saturated aqueous sodium bicarbonate, once with 0.5 N hydrochloric acid, and once with water and dried with anhydrous $MgSO_4$. The solvent was removed on a rotary evaporator and the residue purified by flash chromatography (5% ethyl acetate/hexanes) to yield 2.05 g (73%) of a colorless oil: ^1H NMR ($CDCl_3$) δ 0.13 (s, 9), 0.83 (s, 3), 0.86, (s, 6), 0.92 (s, 3), 1.15–2.30 (m, 19); ^{13}C NMR ($CDCl_3$) δ 0.70, 18.4, 18.8, 20.3, 22.6, 22.8, 23.6, 23.8, 27.6, 28.0, 29.4, 34.9, 36.0, 37.4, 39.5, 43.7, 57.2, 128.0, 140.5.

9α-Fluoro-8-oxodes-*A*,*B*-cholestane (4). Under an argon atmosphere 1.87 g (7.10 mmol) of *N*-fluoropyridinium triflate (a gift from Onoda Cement Co., Japan) was added to 2.39 g (7.10 mmol) of kinetic silyl ether **2** in 36 mL of dry methylene chloride. The solution was refluxed for 2 h and subjected to a standard aqueous workup. The solvent was removed on a rotary evaporator and the residue was purified by flash chromatography (5% ethyl acetate/hexanes) to yield 139 mg (7%) of the α,β-unsaturated ketone 8,[14] 139 mg (7%) of *cis*-Grundmann's ketone (7),[14,15] 292 mg (14%) of 14β-fluoro ketone **6**, and 732 mg (36%) of a 3:1 mixture of 9α-fluoro ketone **4** and 14α-fluoro ketone **5**, all as colorless oils. Spectra for the 14-fluoro ketones will be given below. The 9α-fluoro ketone **4** was purified by HPLC (5% ethyl acetate/hexanes): IR (thin film) 2970, 1740, 1393, 1005 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.58 (s, 3), 0.82 (d, 3, J = 1.1 Hz), 0.85 (d, 3, J = 1.1 Hz), 0.91 (d, 3, J = 6.4 Hz), 1.00–2.30 (m, 17), 3.03 (dt, 1, J_{HF} = 11.6 Hz, J_{AB} = 6.8 Hz), 4.56 (dt, 1, J_{HF} = 50.6 Hz, J_{AB} = 2.5 Hz); ^{13}C NMR ($CDCl_3$) δ 11.9, 18.3, 18.7, 22.5, 22.8, 23.7, 27.5, 28.0, 30.3, 30.8, 33.9, 35.5, 35.9, 39.4, 51.3, 56.7, 57.8, 57.9, 91.3, 94.8, 206.4, 206.7; ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ −184.8 (t, J_{HF} = 47.5 Hz); MS m/z (relative intensity) 282 (11, M^+), 221 (100). Anal. Calcd for $C_{18}H_{31}FO$: C, 76.53; H, 11.08. Found: C, 76.28; H, 10.90.

14α- and 14β-Fluoro-8-oxodes-*A*,*B*-cholestane (5 and 6). Under an argon atmosphere 1.56 g (6.09 mmol) of *N*-fluoropyridinium triflate was added to 2.05 g (6.09 mmol) of the thermodynamic silyl ether **3** in 30 mL of dry methylene chloride. The mixture was stirred for 24 h at room temperature and then subjected to a standard aqueous workup. The solvent was removed on a rotary evaporator and the residue was purified by flash chromatography (5% ethyl acetate/hexanes) to yield 283 mg (16%) of the 14α-fluoro ketone **5** [IR (thin film) 2970, 1738, 1476, 1394, 918 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.65 (s, 3), 0.83 (d, 3, J = 1.1 Hz), 0.85 (d, 3, J = 1.1 Hz), 0.88 (d, 3, J = 6.0 Hz), 1.05–2.26 (m, 17), 2.83 (m, 2); ^{13}C NMR ($CDCl_3$) δ 13.7, 13.8, 18.6, 22.5, 22.8, 23.2, 23.8, 24.7, 25.2, 26.0, 27.9, 31.5, 31.7, 31.8, 34.7, 36.1, 37.6, 39.5, 51.6, 52.1, 52.5, 107.9, 111.3, 207.3, 207.9; ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ −151.6 (q, J = 20 Hz); MS m/z (relative intensity) 282 (20, M^+), 55 (100). Anal. Calcd for $C_{18}H_{31}FO$: C, 76.53; H, 11.08. Found: C, 76.70; H, 10.95] and 475 mg (27%) of the 14β-fluoro ketone **6**: IR (thin film) 2970, 1738, 1478, 1393, 1005 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80 (s, 3), 0.83 (s, 3), 0.87 (d, 3, J = 6.0 Hz), 1.01 (d, 3, J = 2.7 Hz), 1.04–1.90 (m, 16), 2.15–2.45 (m, 2), 2.56 (m, 1); ^{13}C NMR ($CDCl_3$) δ 16.0, 16.2, 19.4, 21.8, 22.5, 22.7, 24.5, 25.5, 25.6, 27.9, 28.7, 29.1, 34.2, 34.3, 36.9, 38.2, 39.3, 49.3, 51.7, 52.1, 103.6, 107.5, 207.2, 207.7; ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ −166.4 (s); MS m/z (relative intensity) 282 (6, M^+), 95 (100).

(7*E*)-9-Hydroxyvitamin D_3 (10). Under an argon atmosphere, at −78 °C, were added 0.84 g (1.85 mmol) of the A-ring phosphine oxide **9**,[7] 18.5 mL of dry THF, and 1.26 mL (1.94 mmol, 1.05 equiv) of *n*-butyllithium (1.54 M solution in hexanes). An orange solution was obtained and stirred at −78 °C for 0.5 h. Compound **4** (0.54 g, 1.91 mmol) in 9.2 mL of dry THF was added. The solution was stirred at −78 °C for 1 h and warmed to room temperature, slowly. The solvent was removed on a rotary evaporator. The residue was dissolved in ether and subjected to a standard aqueous workup. The solvent was removed on a rotary evaporator and the residue purified by flash chromatography (10% ethyl acetate/hexanes) to yield 0.23 g (24%) of the C-3 silylated product as a colorless oil: IR (thin film) 3350, 2965, 1470, 1257, 1090, 871, 835, 772 cm^{-1}; UV (hex) λ_{max} 261 nm (ϵ = 12000); ^1H NMR ($CDCl_3$) δ 0.05 (s, 3), 0.06 (s, 3), 0.60 (s, 3), 0.83 (s, 3), 0.87 (s, 12), 0.92 (d, 3, J = 6.0 Hz), 1.10–2.64 (m, 24), 3.74 (septet, 1, J = 4.1 Hz), 4.08 (s, 1), 4.75 (s, 1), 5.02 (s, 1), 6.25 (d, 1, J = 11.3 Hz), 6.39 (d, 1, J = 11.4); ^{13}C NMR (C_6D_6) δ −4.4, 12.1, 18.3, 19.4, 22.8, 23.1, 24.4, 26.1, 26.5, 28.4, 28.9, 30.7, 32.9, 35.1, 36.4, 36.6, 36.7, 39.9, 46.7, 47.6, 50.4, 55.1, 70.8, 76.0, 113.2, 122.8, 124.8, 139.8, 142.2, 145.3; MS m/z (relative intensity) 515 (5, M^+), 75 (100). Anal. Calcd for $C_{33}H_{58}O_2Si$: C, 76.95; H. 11.37. Found: C, 76.79; H, 11.36.

Under an argon atmosphere 176 mg (0.34 mmol) of the above silylated material was added to 1.7 mL of dry THF and 0.85 mL (0.85 mmol) of tetrabutylammonium fluoride (1 M solution in THF). The solution was stirred for 3 h. The solvent was removed on a rotary evaporator and the residue purified by flash chromatography (1:1 ethyl acetate/hexanes) and by HPLC (1:1 ethyl acetate/hexanes) to yield 73 mg (53%) of a white crystalline solid: mp 105 °C dec; $[\alpha]_D$ = 133° (CH_2Cl_2, c 0.27); UV (MeOH) λ_{max} 260 nm (ϵ = 17500); IR ($CHCl_3$) 3620, 2965, 1255, 896 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 0.63 (s, 3), 0.86 (d, 3, J = 0.6 Hz), 0.88 (d, 3, J = 0.6 Hz), 0.95 (d, 3, J = 6.0 Hz), 1.05–2.67 (m, 26), 3.68 (septet, 1, J = 4.0 Hz), 4.05 (s, 1), 4.79 (s, 1), 5.07 (s, 1), 6.32 (d, 1, J = 11.0 Hz), 6.38 (d, 1, J = 11.0 Hz); ^{13}C NMR (CD_2Cl_2) δ 11.9, 19.2, 22.7, 23.0, 24.2, 26.5, 28.4, 28.7, 30.5, 33.0, 35.1, 36.2, 36.5, 36.6, 39.8, 46.7, 50.4, 54.3, 55.2, 70.1, 76.1, 113.6, 122.7, 124.9, 139.5, 141.9, 144.7; MS m/z (relative intensity) 401 (8, M^+), 382 (100). Anal. Calcd for $C_{27}H_{44}O_2$: C, 80.93; H, 11.09. Found: C, 80.62; H, 11.01.

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Registry No. **1**, 66251-18-1; **2**, 133447-45-7; **3**, 93895-18-2; **4**, 138313-13-0; **5**, 138313-14-1; **6**, 138313-15-2; **7**, 75197-02-3; **8**, 93922-90-8; **9**, 100858-27-3; **10**, 133447-44-6; **10** C-3 silylated derivative, 133447-43-5; **11**, 138313-16-3; **12**, 138313-17-4; [5*S*-(1*Z*)]-2-(5-(*tert*-butyldimethylsiloxy)-2-methylenecyclohexylidene)ethanol, 96685-53-9; [5*S*-(1*Z*)]-2-(5-(*tert*-butyldimethylsiloxy)-2-methylenecyclohexylidene)-1-chloroethane–triphenylphosphine, 138313-18-5; [5*S*-(1*Z*)]-[2-(5-(*tert*-butyldimethylsiloxy)-2-methylenecyclohexylidene)ethyl]triphenylphosphonium iodide, 138313-19-6; triethyl phosphonoacetate, 867-13-0; diethyl [5*S*-(1*Z*)]-2-(5-(*tert*-butyldimethylsiloxy)-2-methylenecyclohexylidene)ethylphosphonate, 138313-20-9; methyltriphenylphosphonium bromide, 1779-49-3; vitamin D_3, 67-97-0; *N*-fluoropyridinium triflate, 107263-95-6.

Supplementary Material Available: The graphical results of the NOESY experiment and experimental procedures for compounds **9**, **11**, and **12** and some materials used in related studies and complete spectroscopic characterization of **7** and **8** (5 pages). Ordering information is given on any current masthead page.

(14) For spectral properties of this compound see the supplementary material.

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(16) This material is available in the USA from Onoda U.S.A., Inc., San Mateo, CA 94404. For the synthesis of the compound, see: Umemoto, T.; Tomita, K.; Kawada, K. *Org. Synth.* *69*, 129.

A New Positive Halogen Reagent. Oxidation of Secondary Alcohols to Ketones by Bis(quinuclidine)bromine(I) Bromide in the Presence of Pyridinium Catalyst

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The search for new and improved methods to oxidize alcohols to corresponding carbonyl compounds endures as a major pursuit in chemical synthesis.[1] Currently popular

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