(1.5 M in hexane, 0.73 mL, 1.09 mmol) was injected dropwise into a stirred and cooled (-78 °C) solution of bromide **6** (348 mg, 1.09 mmol) in ether (8 mL). The mixture was stirred for an additional 20 min, and aldehyde **7** (176 mg, 1.0 mmol) in ether (3 mL + 1 mL rinse) was then added at -78 °C over ca. 3 min. The reaction mixture was allowed to warm to 0 °C over 2 h. Saturated aqueous ammonium chloride (10 mL) was added, and the mixture was extracted with ether (2 × 15 mL). The combined organic extracts were washed with brine and dried ($MgSO_4$). Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 15 cm) with 1% ethyl acetate–dichloromethane gave alcohols **9** (371 mg, 89%): IR (neat) 3540, 2240, 1585 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.22 (m, 1 H), 2.55–2.92 (m, 2 H), 3.15 (m, 1 H), 3.33 (2s, 1:2, 3 H), 3.95 (m, 7 H), 5.32 (m, 1 H), 6.45 (d, J = 8 Hz, 1 H), 6.68–6.90 (m, 3 H), 7.05 (t, J = 7.5 Hz, 1 H), 7.34 (m, 5 H); exact mass, m/z 414.1827 (calcd for $C_{27}H_{26}O_4$, 414.1824). Anal. Calcd for $C_{27}H_{26}O_4$: C, 78.22; H, 6.32. Found: C, 78.06; H, 6.38.

1-[3,6-Dimethoxy-2-(phenylethynyl)benzoyl]-2,3-dihydro-7-methoxy-1*H*-indene (10). Alcohols **9** (371 mg, 0.896 mmol) in dichloromethane (5 mL + 1 mL rinse) were added at room temperature to a stirred mixture of pyridinium chlorochromate (772 mg, 3.58 mmol) and 3-Å molecular sieves (1.79 g, 8–12 mesh) in dichloromethane (15 mL). Stirring was continued for 4 h, ether (50 mL) was added, and the brown suspension was filtered through a pad of Celite (3 × 6 cm) which was washed well with 1:1 ether–dichloromethane. The combined filtrates were evaporated, and flash chromatography of the residue over silica gel (2 × 15 cm) with dichloromethane gave ketone **10** (280 mg, 75%): IR (neat) 1690, 1580 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.10–2.33 (m, 1 H), 2.60–2.92 (m, 2 H), 3.05–3.35 (m, 1 H), 3.45 (s, 3 H), 3.64 (s, 3 H), 3.82 (s, 3H), 4.8 (dd, J = 8, 2 Hz, 1 H), 6.51 (d, J = 8 Hz, 1 H), 6.8 (d, J = 8 Hz, 1 H), 6.89 (s, 2 H), 7.10 (t, J = 7.5 Hz, 1 H), 7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 204.0, 156.3, 154.2, 150.2, 147.0, 135.6, 131.6, 128.8, 128.7, 128.0, 127.9, 123.2, 116.8, 112.1, 112.0, 111.1, 107.7, 97.0, 83.1, 56.7, 56.3, 55.6, 54.7, 32.3, 29.1; exact mass, m/z 412.1682 (calcd for $C_{27}H_{24}O_4$, 412.1668). Anal. Calcd for $C_{27}H_{24}O_4$: C, 78.60; H, 5.86. Found: C, 78.68; H, 5.88.

1-[3,6-Dimethoxy-2-(phenylethynyl)benzoyl]-2,3-dihydro-7-methoxy-1-(phenylseleno)-1*H*-indene (11). Ketone **10** (390 mg, 0.94 mmol) in THF (3 mL + 1 mL rinse) was added over 5 min to a cold (-78 °C) solution of LDA [from diisopropylamine (0.26 mL, 1.88 mmol) and n-butyllithium (1.5 M in hexane, 1.06 mL, 1.59 mmol)] in THF (8 mL). The yellow mixture was stirred at -78 °C for 1 h, and phenylselenenyl chloride (574 mg, 2.82 mmol) in THF (3 mL + 1 mL rinse) was added over 2 min. The mixture was stirred at -78 °C for 1 h and then warmed to -20 °C over 30 min. Saturated aqueous ammonium chloride (10 mL) was added followed by water (5 mL). The mixture was extracted with ether (2 × 20 mL), and the combined extracts were washed with brine and dried ($MgSO_4$). Evaporation of the solvent and flash chromatography of the residue over silica gel (3 × 15 cm) with 30% ethyl acetate–hexane gave selenide **11** (434 mg, 83%): IR ($CHCl_3$) 2300, 1670, 1585, 1460 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.45–3.05 (m, 4 H), 3.28 (s, 3 H), 3.43 (s, 3 H), 3.90 (s, 3 H), 6.40 (d, J = 8 Hz, 1 H), 6.55 (d, J = 7.5 Hz, 1 H), 6.67 (d, J = 7.5 Hz, 1 H), 6.80 (d, J = 8 Hz, 1 H), 7.00–7.71 (m, 11 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 202.7, 156.2, 154.7, 150.1, 146.9, 137.7, 134.6, 131.9, 130.4, 129.4, 128.0, 123.9, 116.4, 112.8, 111.1, 108.2, 97.2, 84.4, 66.9, 60.2, 57.2, 55.4, 54.4, 39.0, 31.3, 20.8, 14.1; mass spectrum, m/z 568 (M), 411 (M - PhSe).

2,3-Dihydro-7-methoxy-1*H*-indene-1-spiro-2′-(3′-benzylidene-4′,7′-dimethoxy-2*H*-inden-1′-one) (14). Triphenyltin hydride (456 mg, 1.30 mmol) in benzene (3 mL + 1 mL rinse) was added in one portion to a refluxing solution of selenide **11** (425 mg, 0.765 mmol) and AIBN (12 mg, 0.073 mmol) in benzene (15 mL). Refluxing was continued for 12 h, and the solvent was evaporated. Flash chromatography of the residue over silica gel (3 × 15 cm) with 40% ethyl acetate–hexane gave **14** (252 mg, 79%): IR ($CHCl_3$) 1700, 1585 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.05–2.50 (m, 3 H), 4.0 (m, 1 H), 3.49 (s, 3 H), 3.91 (s, 3 H), 3.99 (s, 3 H), 6.40–7.25 (m, 10 H), 8.09 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 205.0, 155.6, 151.9, 150.9, 148.1, 142.7, 139.6, 137.3, 134.4, 129.0, 128.6, 127.3, 126.1, 124.2, 118.3, 117.3, 110.9, 108.3, 63.8, 56.2, 55.9, 55.8, 36.3, 32.0; exact mass, m/z 412.1666 (calcd for $C_{27}H_{24}O_4$, 412.1668). Anal. Calcd for $C_{27}H_{24}O_4$: C, 78.60; H, 5.86. Found: C, 78.22; H, 5.71.

2,3-Dihydro-7-methoxy-1*H*-indene-1-spiro-2′-(4′,7′-dimethoxy-2*H*-inden-1′,3′-dione) (15). An ozone–oxygen stream was bubbled through a solution of olefin **14** (200 mg, 0.485 mmol) in dry methanol (7 mL) at -78 °C until the starting material had just disappeared [2.5 min, TLC (silica gel, 40% ethyl acetate–hexane)]. Argon was passed through the solution for 5 min to remove the excess of ozone, and trimethyl phosphite (0.17 mL, 1.45 mmol) was injected. The cold bath was removed, and the solution was stirred overnight. Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 15 cm) with 40% ethyl acetate–hexane gave diketone **15** (100 mg, 61%): IR ($CHCl_3$) 1740, 1705, 1590 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.43 (t, J = 7.5 Hz, 2 H), 3.22 (t, J = 7.5 Hz, 2 H), 3.51 (s, 3 H), 4.03 (s, 6 H), 6.65 (d, J = 8 Hz, 1 H), 6.92 (d, J = 8 Hz, 1 H), 7.20 (t, J = 8 Hz, 1 H), 7.32 (s, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 200.4, 155.1, 151.0, 148.4, 129.9, 129.6, 128.2, 119.9, 117.2, 108.3, 65.3, 56.6, 55.2, 35.3, 32.3; exact mass, m/z 338.1148 (calcd for $C_{20}H_{18}O_5$, 338.1149). Anal. Calcd for $C_{20}H_{18}O_5$: C, 70.98; H, 5.36. Found: C, 70.65; H, 5.53.

2,3-Dihydro-7-methoxy-1*H*-indene-1-spiro-2′-(4′,7′-dihydroxy-2*H*-inden-1′,3′-dione) (16). Boron tribromide (1 M in dichloromethane, 0.61 mL, 0.61 mmol) was injected over a period of 5 min to a cold (-78 °C) solution of diketone **15** (23 mg, 0.068 mmol) in dichloromethane (2 mL). The cold bath was removed, and stirring was continued overnight. Water (10 mL) was added, and the mixture was extracted with dichloromethane (2 × 5 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1 × 10 cm) with dichloromethane gave **16** (17.3 mg, 85%): IR (CH_2Cl_2) 1720, 1671, 1595, 1483 cm^{-1}; ^1H NMR (acetone-d_6, 400 MHz) δ 2.44 (t, J = 8 Hz, 2 H), 3.17 (t, J = 8 Hz, 2 H), 6.59 (d, J = 8 Hz, 1 H), 6.80 (d, J = 8 Hz, 1 H), 7.08 (t, J = 8 Hz, 1 H), 7.23 (s, 2 H); ^{13}C NMR (acetone-d_6, 100.6 MHz) δ 204.1, 153.5, 149.7, 149.1, 130.5, 128.2, 126.5, 124.6, 116.5, 113.3, 78.8, 35.1, 32.7; exact mass, m/z 296.0693 (calcd for $C_{17}H_{12}O_5$, 296.0681). Anal. Calcd for $C_{17}H_{12}O_5$: C, 68.90; H, 4.08. Found: C, 68.56; H, 4.02.

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Acid- and Base-Catalyzed Ring-Opening Reactions of a Sterically Hindered Epoxide

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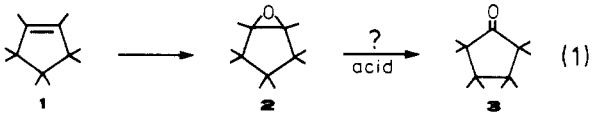
Epoxides are known to rearrange to carbonyl compounds under acidic conditions.[1] When we tried to employ this reaction for the synthesis of octamethylcyclopentanone (**3**)[2] via the sequence shown in eq 1, unexpected rearrangements took place, which we report in this paper.



(1)

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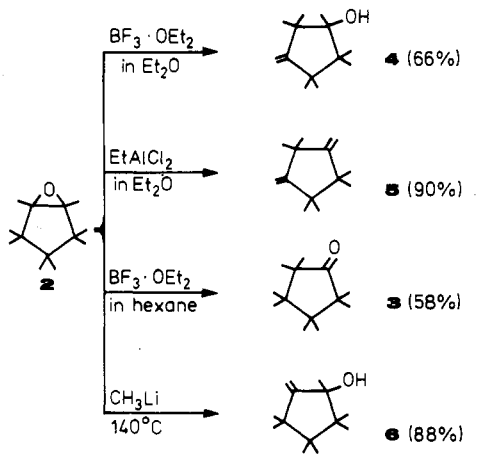
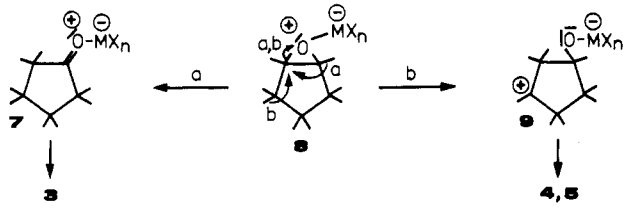
0022-3263/87/1952-1342$01.50/0

Scheme I



Scheme II



Octamethylcyclopentene (**1**)[3,4] was smoothly converted into epoxide **2** with either *m*-chloroperbenzoic acid or magnesium monoperoxyphthalate.[5]

Treatment of **2** with BF_3·OEt_2 in diethyl ether at −20 °C yielded 66% of the homoallylic alcohol **4** along with 12% of the diene **5** (Scheme I). These two compounds were formed in a 1:1 ratio with small amounts of unidentified products when gaseous BF_3 was bubbled through a solution of **2** in hexane at 0 °C. Various mixtures of **4**, **5**, and unknown compounds were also obtained when **2** was treated with BCl_3, $TiCl_4$, H_2SO_4, HSO_3F, and trityl tetrafluoroborate under a variety of conditions. While **2** was inert toward diethylaluminum chloride in diethyl ether at 20 °C, it was almost quantitatively converted into diene **5** by ethylaluminum dichloride under the same conditions. Octamethylcyclopentanone (**3**) was finally produced when **2** was stirred in the heterogeneous mixture BF_3·OEt_2/hexane at 20 °C. Though **3** is thermodynamically more stable than **4**, attempts to convert **4** or **5** into **3** by treatment with aqueous proton acids have not been successful.

The reactivity of **2** toward organometallic compounds is also controlled by steric effects, and we have not been able to carry out a methylating ring-opening reaction of **2**. While **2** was inert toward neat methyllithium up to 120 °C, deprotonation of a methyl group with formation of the allylic alcohol **6** took place at 140 °C.[6]

The transformation of **2** into **3**–**5** under acidic conditions is rationalized in Scheme II. When a carbon–oxygen bond in the complex **8** is breaking, two different methyl migrations are feasible. Methyl shift a yields the cyclopentanone complex **7**, which is thermodynamically favored over the 1,5-dipole **9**, the precursor of **4** and **5**. In spite of that, path b is observed under the majority of conditions. This behavior may be attributed to an early transition state, which does not reflect the relative stabilities of **7** and **9** but the different release of steric strain. Path b may then be favored since in the early stage of this migration a perfectly eclipsed interaction between two CC bonds is abandoned. We do not understand, however, the relationship between reaction conditions and reaction products.

Experimental Section

General. Infrared spectra were recorded on a Beckmann Acculab 1 and a Shimadzu 435 IR spectrophotometer. NMR spectra were taken on a JEOL JNM-PS-100, a Varian EM 390, or a Varian XL 200 spectrometer. Chemical shifts (δ) were recorded relative to $(CH_3)_4Si$ as an internal standard. Mass spectra were recorded on a Varian MAT CH 4 spectrometer.

1,2,2,3,3,4,4,5-Octamethyl-6-oxabicyclo[3.1.0]hexane (2). A solution of octamethylcyclopentene (**1**) (6.60 g, 36.6 mmol) in 30 mL of isopropyl alcohol was added dropwise to a vigorously stirred solution of magnesium monoperoxyphthalate hexahydrate (17.8 g, 36.0 mmol ≃ 2 equiv) in 200 mL of isopropyl alcohol/water (v/v = 1/1) at ambient temperature. The mixture was stirred for 15 h, 500 mL of aqueous K_2CO_3 solution (3%) was added, and the product was extracted with ether (2 × 100 mL). The ether solutions were washed with $NaHSO_3$ solution, dried over Na_2CO_3, and evaporated. Distillation [68 °C (6 mbar)] yielded 5.60 g (78%) of **2**, which solidified at room temperature. Low-temperature recrystallization from pentane gave colorless prisms with mp 43–46 °C: IR (neat): 2950, 2860, 1480, 1450, 1380, 1370, 1115, 1090, 855 cm^{-1}; ^1H NMR (CCl_4) δ 0.68 (s, 3 H), 0.90, 0.92 (2 s, 15 H), 1.17 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 12.19 (q, 1,5-CH_3), 20.26, 24.72 (2 q, 2,4-CH_3), 22.02, 27.21 (2 q, 3-CH_3), 43.89 (s, C-3), 44.96 (s, C-2,4), 73.78 (s, C-1,5); mass spectrum (96 eV), *m/z* (relative intensity) 196 (0.9, M^+), 125 (12), 111 (100). Anal. Calcd for $C_{13}H_{24}O$ (196.3): C, 79.53; H, 12.32. Found: C, 79,54; H, 12.39.

2 was obtained in 80% yield from **1** and *m*-chloroperbenzoic acid according to a standard procedure.[7]

1,2,2,3,3,5,5-Heptamethyl-4-methylenecyclopentan-1-ol (4). Epoxide **2** (2.94 g, 15.0 mmol) and BF_3·OEt_2 (8 mL, 64 mmol) were allowed to react in 150 mL of anhydrous ether at −20 °C for 5 days. The orange solution was poured onto 400 mL of aqueous $NaHCO_3$ solution. The ether phase was dried with $CaCl_2$ and evaporated to give a mixture of **4** and **5** (≈5:1 by ^1H NMR), which was separated by column chromatography (silica gel 60 (70–230 mesh), Merck, *l* = 20 cm, i.d. = 2.5 cm). Elution with 150 mL of hexane/ether (v/v = 99/1) yielded 0.32 g (12%) of **5**. Successive elution with 150 mL of hexane/dichloromethane (v/v = 1/2) gave 1.94 g (66%) of **4**. Colorless plates with mp 43–45 °C (from hexane) were obtained: IR (Nujol) 3600, 1640, 920, 880 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.82 (s, 3 H), 0.92 (s, 3 H), 0.97 (s, 3 H), 1.04 (s, 1 H), 1.11 (s, 3 H), 1.12 (s, 3 H), 1.13 (s, 3 H), 1.21 (s, 3 H), 4.83 (s, 1 H), 4.85 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 17.66 (q), 21.57 (q), 24.26 (q), 24.80 (q), 27.75 (q), 30.07 (q), 30.68 (q), 47.46 (s), 47.79 (s), 49.08 (s), 84.59 (s), 103.23 (t), 171.98 (s); mass spectrum (96 eV); *m/z* (relative intensity) 196 (11, M^+), 181 (14), 178 (5), 163 (14), 153 (12), 111 (100), 110 (67), 95 (65). Anal. Calcd for $C_{13}H_{24}O$ (196.3): C, 79.53; C, 12.32. Found: C, 79.61; H, 12.36.

1,1,2,2,4,4-Hexamethyl-3,5-bis(methylene)cyclopentane (5). A 50% solution of $C_2H_5AlCl_2$ in hexane (15 mL, ≈60 mmol) was added to a solution of **2** (1.96 g, 10.0 mmol) in 200 mL of anhydrous ether (ambient temperature, N_2 atmosphere). The mixture, which turned yellow, was stored at room temperature for 60 h and was then slowly poured onto 200 mL of water. After separation of the layers, the aqueous layer was extracted with 100 mL of ether. The organic fractions were dried with $CaCl_2$, and the solvent was evaporated to yield crude **5**. According to ^1H NMR the product was contaminated by ≈5% of **3**, which was removed by filtration of the mixture over silica gel (eluent hexane/ether = 99/1). Distillation [30–35 °C (bath) (0.1 mbar)] yielded 1.60 g (90%) of **5** as a colorless liquid, which solidified in the freezer

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(-20 °C): IR (neat) 3080, 2970, 2870, 1640, 1460, 1450, 1420, 1380, 1365, 1180, 1140, 880, 780, 680 cm^{-1}; ^1H NMR (CCl_4) δ 0.91 (s, 12 H), 1.20 (s, 6 H), 4.77 (s, 2 H), 4.82 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.21 (q, 1,2-CH_3), 32.94 (q, 4-CH_3), 43.80 (s, C-4), 47.66 (s, C-1,2), 102.71 (t), 169.60 (s); mass spectrum (70 eV), m/z (relative intensity) 178 (11, M^+), 163 (100), 135 (38), 122 (45), 121 (60). Anal. Calcd for $C_{13}H_{22}$ (178.3): C, 87.56; H, 12.44. Found: C, 87.36; H, 12.64.

Octamethylcyclopentanone (3). A solution of **2** (1.96 g, 10.0 mmol) in 100 mL of hexane was added dropwise (≈60 min) to a rapidly stirred mixture of 10 mL of BF_3·OEt_2 (80 mmol) in 300 mL of hexane at ambient temperature. The mixture was stirred for another 30 min and then hydrolyzed with 400 mL of aqueous $NaHCO_3$ solution (5%). The organic layer was dried with $CaCl_2$ and evaporated to give **3** contaminated by traces of **5**, which were removed by column chromatography: **5** was washed from a column of silica gel 60 (l = 15 cm, i.d. = 2.5 cm) with 100 mL of hexane/ether (v/v = 99/1). **3** (1.13 g, 58%) was then eluted with 150 mL of CH_2Cl_2. Analytical data of **3** is given in ref 2.

1,2,2,3,3,4,4-Heptamethyl-5-methylenecyclopentan-1-ol (6). Compound **2** (0.98 g, 5.0 mmol) was added to 10 mL of a 1.6 M solution of CH_3Li in ether. The ether was distilled off, and the residue was heated at 140 °C for 2 h to give a brownish mixture, which was cooled and treated with 5 mL of the CH_3Li solution as before. After the mixture was cooled, 10 mL of ether was added, and the solution was hydrolyzed with 10 mL of concentrated aqueous NH_4Cl solution. The organic layer was dried with $CaCl_2$ and evaporated to give a mixture of **6** and some nonidentified byproducts. The mixture was separated by column chromatography (silica gel 60, l = 15 cm, i.d. = 2.5 cm). After elution of the byproducts with 100 mL of hexane/ether (v/v = 99/1), pure **6** (0.86 g, 88%) was washed from the column with hexane/ether (v/v = 92/8). Colorless plates with mp 40–45 °C (from pentane) were obtained: IR (neat) 3330, 2950, 1450, 1380, 1075, 910, 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.82 (s, 3 H), 0.84 (s, 3 H), 0.93 (s, 3 H), 1.07 (s, 3 H), 1.09 (s, 3 H), 1.11 (s, 3 H), 1.17 (s, 1 H), 1.27 (s, 3 H), 4.95 (s, 1 H), 5.18 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.67 (q), 22.54 (q), 23.73 (q), 23.97 (q), 25.60 (q), 29.96 (q), 30.53 (q), 45.00 (s), 46.17 (s), 48.79 (s), 82.27 (s), 105.84 (t), 169.77 (s). Anal. Calcd for $C_{13}H_{24}O$ (196.3): C, 79.52; H, 12.32. Found: C, 78.77; H, 12.15.

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2-Halogenated Purine Nucleosides: Synthesis and Reactivity[1]

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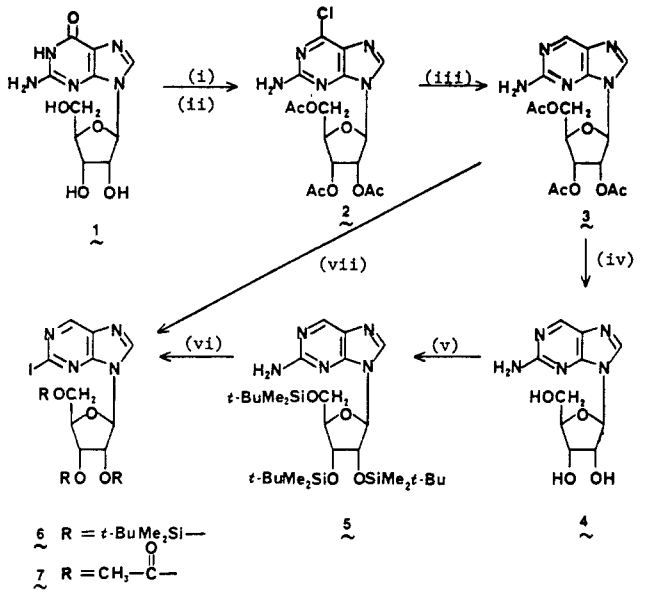
Although considerable attention has been devoted to the synthesis and reactions of 6-halogenated purine nucleosides,[3-7] the same cannot be said for the corresponding 2-halogenated compounds.[8,9] This is in part due to limitations in synthetic accessibility to this class of nucleosides. 2-Halogenated purines are potentially key synthetic intermediates to a variety of novel 2-substituted purine nucleosides. A logical approach to 2-halogenated purines may be via the corresponding 2-amino compound. 2-Amino-9-β-D-ribofuranosylpurine is an important biologically active nucleoside. It is a potent inhibitor of a number of purine metabolizing enzymes including adenosine deaminase,[10] purine nucleoside phosphorylase,[11] and adenosine kinase.[12] It is incorporated in *E. coli* and phage T4 DNA.[13,14] However, an efficient general method for the preparation of this compound is not currently available. Previous syntheses involved, as the key step, the hydrogenolysis of the corresponding 6-chloro compound (protected) using Pd/C and hydrogen, treatment of the protected 6-thio compound with Raney nickel in water, and coupling of a halogenated sugar with protected 2-aminopurine in the presence of mercuric chloride.[9,13,15,16] Photochemical methods are rarely used in nucleoside synthesis. We wish to report a high yielding and reproducible photochemical synthesis of 2-aminopurine nucleoside, its conversion to the corresponding novel 2-halogenated compound, and the synthetic utilization of the latter.

Scheme I[a]



[a] (i) Ac_2O, $(C_2H_5)_3N$, *N,N*-(dimethylamino)pyridine; (ii) $POCl_3$, *N,N*-diethylaniline, Δ; (iii) $(C_2H_5)_3N$, THF, $h\nu$; (iv) NH_3, C_2H_5OH; (v) *t*-Bu$(CH_3)_2SiCl$, imidazole, DMF, Δ; (vi) *n*-$C_5H_{11}ONO$, CH_2I_2, $(CH_3)_3SiI$, hexane, Δ; (vii) *n*-$C_5H_{11}ONO$, CH_2I_2, CH_3CN.

The starting material for the synthesis was guanosine (**1**) which was selectively acetylated in 93% yield by using acetic anhydride, triethylamine, and 4-(dimethylamino)-pyridine in acetonitrile.[17] Treatment of the triacetylated guanosine with phosphorus oxychloride and *N,N*-diethylaniline at 70 °C for 1 h gave the 6-chloro compound

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