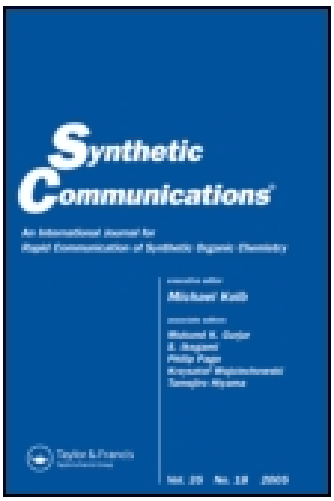

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Convenient Preparations of 2,3-Dihydro-4H-pyran-4-ones from D-Glucal Triacetate : Selective Oxidations of Alyllic Acetates and Allylic Silyl Ethers Using N-Bromosuccinimide

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Convenient Preparations of 2,3-dihydro-4H-pyran-4-ones from D-glucal triacetate : Selective Oxidations of Alyllic Acetates and Allylic Silyl Ethers using N-Bromosuccinimide[1].

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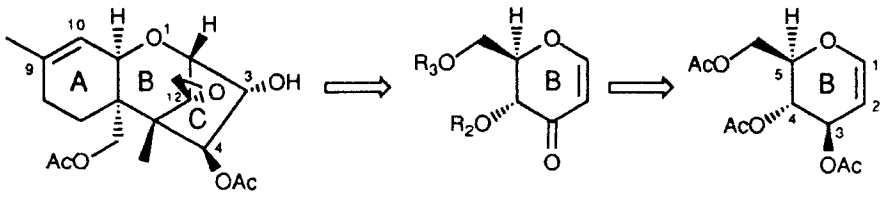
Abstract : N-Bromosuccinimide (1.1 eq) in the presence of potassium carbonate (2 eq) and a catalytic amount of dibenzoyl peroxide converts the allylic acetates and the allylic silyl ethers (O-TBDMS or O-$SiEt_3$) of secondary allylic alcohols, derived from D-glucal **3a** *into corresponding dihydro γ-pyrones* **2**.

During our investigation on the chiral synthesis of the B/C ring system of anguidine **1** [2],we became interested in developing methods of efficient syntheses of 2,3-dihydro-4H-pyranone derivatives **2** from D-glucal triacetate **3b** (scheme 1).

A few total syntheses of 2-alkyl-2,3-dihydro-4H-pyran-4-ones have been previously reported[3]. In contrast, the selective oxidation of the D-glucal allylic alcohol to the corresponding γ-pyrones **2** has received attention and numerous

* to whom correspondence should be addressed.

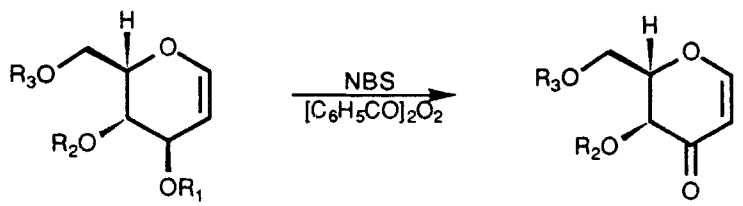


1 : Anguidine 2 3b

Scheme 1

reagents are available to achieve this transformation[4-7]. We now report the direct and selective radical-induced oxidation of D-glucal allylic acetates and allylic trialkylsilylethers to γ-pyrones **2** without deprotection.

Our interest in the preparation of γ-pyrones **2** prompted us to investigate the mode of formation of α,β-unsaturated ketones from D-glucal **3a**, with suitable protected primary and secondary alcohol groups, such as **3 (b,c,d,g,h)** (scheme 2).



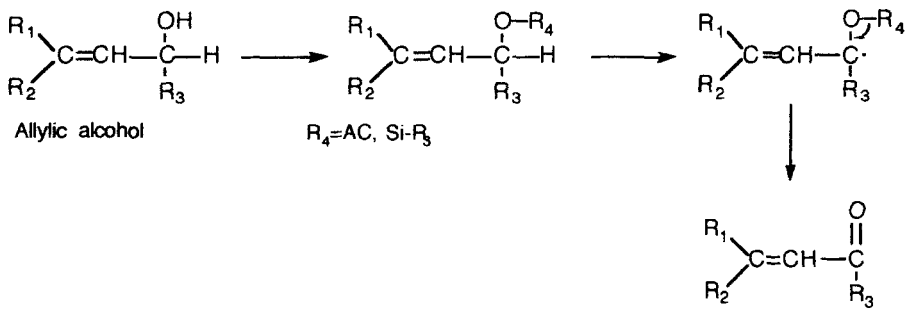
3 **2**

a : $R_1 = R_2 = R_3 = H$
b : $R_1 = R_2 = R_3 = Ac$
c : $R_1 = R_2 = Ac$, $R_3 = tBuSiMe_2$
d : $R_1 = R_2 = Ac$, $R_3 = tBuSiPh_2$
e : $R_1 = R_2 = H$, $R_3 = tBuSiMe_2$
f : $R_1 = R_2 = H$, $R_3 = tBuSiPh_2$
g : $R_1 = R_3 = tBuSiMe_2$, $R_2 = Ac$
h : $R_1 = SiEt_3$, $R_3 = tBuSiMe_2$, $R_2 = Ac$
i : $R_1 = SiEt_3$, $R_2 = H$, $R_3 = t\ BuSiMe_2$
j : $R_1 = R_3 = t\ BuSiMe_2$, $R_2 = H$

a : $R_2 = R_3 = H$
b : $R_2 = R_3 = Ac$
c : $R_2 = Ac$, $R_3 = tBuSiMe_2$
d : $R_2 = Ac$, $R_3 = tBuSiPh_2$

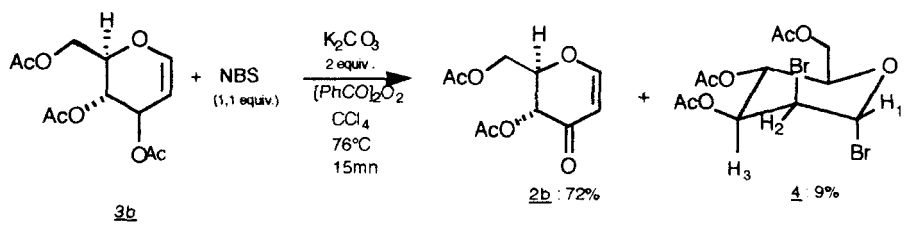
Scheme 2

Since the hydrogens on a carbon atom attached to substituents that possess π or n electrons, are easily removed, leading to a free radical[8], we reasoned that conversion of an allylic alcohol into unsymmetrical acetate or silyl ether[8c] and treatment with N-bromosuccinimide (NBS) would effect the desired oxidation (scheme 3).



Scheme 3

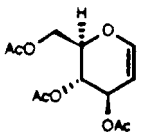
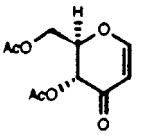
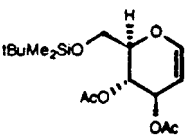
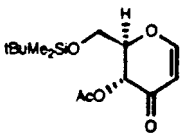
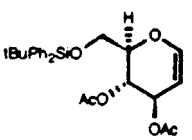
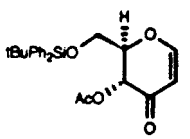
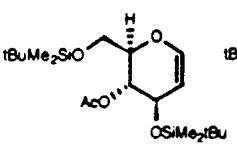
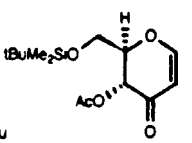
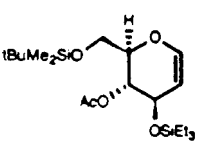
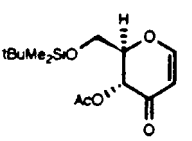
In fact, oxidation of tri-O-acetyl-D-glucal **3b** with 1.1 equimolar amount of N-bromosuccinimide (NBS) and 2 equivalents of potassium carbonate (as Br_2 scavenger) in the presence of a catalytic quantity of benzoyl peroxide (radical initiator), in boiling CCl_4, took place selectively at C-3 position, giving **2b** (72 %), together with some 1,2-dibromo-D-glucal triacetate **4** (9 %) (scheme 4).



Scheme 4

The oxidation was complete in 15 minutes. When **3b** (not admixed with potassium carbonate), reacted with NBS in the presence of a catalytic amount of peroxide it yielded a variety of products, including the γ-pyrone **2b** (15 %) and the dibromoacetate **4** (20 %). The structure **4** (scheme 4) was established by ^1H NMR (J_{H1-H2} = 1 Hz, J_{H2-H3} = 3 Hz).

TABLE 1

Entry	Reactant	Product	Yields (a)	Starting material
1	 3b	 2b	72%(b) (15 mn)	0%
2	 3c	 2c	50% (1 h)	35%
3	 3d	 2d	55% (1 h)	30%
4	 3e	 2c	24% (2 h)	71%
5	 3f	 2c	60% (1 h)	38%

a) Yields non optimized are for isolated, pure materials, and are based on the starting material.

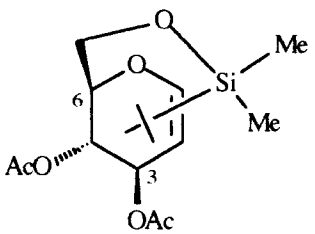
b) A by-product (9%) is the 1,2-dibromo-D-Glucal-triacetate 4

The high selectivity of the **3b** allylic acetate in the NBS reaction was remarkable and we decided to extend this oxidation procedure to more complex substrates, in particular, to trialkylsilylethers **3 (c,d,g,h)**.

The t-butyldimethylsilyl (TBDMS) and the t-butyldiphenylsilyl (TBDPS) ethers are among the most useful primary hydroxyl protective groups[9]. Because of the steric bulk of the TBDMS or TBDPS ethers, they are relatively stable under mild oxidizing conditions[9a]. Thus, from D-glucal **3a** (scheme 2), compounds **3 (c,d,g,h)** easily prepared by silylation of the primary 6-O-position, and further silylating attack at the 3-O-position, followed by acetylation, were subjected to the standard NBS-peroxide oxidizing conditions.

The results are summarized in table 1. With TBDMS (or TBDPS) as protecting group at C-6, oxidation of allylic acetates or silyl ethers at C-3, required longer reaction times than the triacetate compound **3b** and no 1,2-dibromo by-product formation, such as **4** was observed.

Therefore, it seems that a bulky group at C-6 prevents 1,2 bromination by free bromine (Scheme 5). And apparently, the yield of this reaction depends on the nature and size of the protecting group at C-3.



Scheme 5

Thus, D-glucal **3a** with three protected hydroxylic groups was selectively oxidized with NBS-peroxide conditions at the allylic C-3 position (acetate or silyl ether), giving chiral 2,3-dihydro-4H-pyran-4-ones **2** in good yield.

EXPERIMENTAL SECTION

General Methods

Carbon tetrachloride (CCl_4) was dried by distillation from calcium hydride. Melting points were determined on a REICHERT apparatus and are uncorrected.

Infrared spectra were recorded on a PERKIN-ELMER spectrometer 399 as solutions in CCl_4. ^1H and ^{13}C NMR spectra were recorded on a BRUKER WP.200 instrument as solutions in $CDCl_3$. Optical rotations were measured with a PERKIN-ELMER 241 polarimeter. All reactions were monitored by TLC carried out on Merck silica gel plates ($60F_{254}$; 0.2 mm), using U.V. light and 1/1 : v/v aqueous sulfuric acid and heat as developing agent. Flash chromatography was performed on 40-63 mm Merck silica gel 60.

Preparation of 3f : 6-O-TBDPS-D-glucal

To a magnetically stirred solution of 3.6 g (24.5 mmol) of D-glucal [4b] **3a** in 10 ml of anhydrous dimethylformamide and 50 ml of dry dichloromethane was added successively with imidazole (2.5 g, 36.75 mmol) and tert-butyldiphenylsilyl chloride (6.17 g; 26.95 mmol). The reaction mixture was stirred at 20°C for 12 h, diluted with dichloromethane (50 ml) and washed with water (2 x 50 ml). The combined aqueous layers were reextracted with dichloromethane (50 ml) and the total organic solution was dried and concentrated. The resulting oil was purified by silica gel chromatography (20 % ethylacetate in petroleum ether) to give 9.1 g (96 %) of 6-O-TBDPS-D-glucal **3f** as a clear colorless oil homogeneous by TLC analysis : IR (CCl_4 cm^{-1}) 3429, 3085, 3070, 1645, 710 ; ^1H NMR (200 MHz, $CDCl_3$) δ 7.65 (m, 4H), 7.35 (m, 6H), 6.30 (dd, J 6.1, 1.5 Hz, 1H), 4.72 (dd, J 6.1, 2 Hz, 1H), 4.28 (m, 1H), 3.95 (dd, J 4, 1 Hz, 2H), 3.85 (m, 2H), 2.85 (m, 1H), 2.25 (m, 1H), 1.05 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) 144.43, 135.78, 135.70, 133.2, 130.01, 127.91, 127.01, 102.55, 77.35, 71.82, 69.84, 64, 27, 19.41.

Anal. calcd for $C_{22}H_{28}O_4Si$: C, 68.75 ; H, 7.28 ; Found : C, 69.05 ; H, 7 40.

3,4-di-O-acetyl-6-O-TBDPS-D-glucal 3d

To a magnetically strirred solution of 3.84 g (10 mmol) of **3f** in 5 ml of anhydrous dichloromethane was added successively pyridine (2.6 ml, 30 mmol) and acetic anhydride (2 ml, 20 mmol) and the mixture was left overnight. After disappearance of the diol **3f** followed by TLC (petroleum ether-AcOEt : 4-1), the solution was evaporated and treated with toluene (3 x 20 ml, vide supra). The residue was then dissolved in CH_2Cl_2 (50 ml) and washed with 5 % $NaHSO_4$ aqueous solution (50 ml) in order to eliminate any remaining traces of pyridine.

Drying over anhydrous $MgSO_4$, filtration and evaporation afforded a colorless oil that was purified by flash chromatography (petroleum ether-ACOEt : 9-1) ; **3d** : 4.45 g (95 %) : IR (CCl_4, cm^{-1}) 3085, 3070, 1750, 1650, 710 ; ^1H NMR (200 MHz, $CDCl_3$) δ 7.65 (m, 4H), 7.45 (m, 6H), 6.43 (dd, J 6.1, 1.5 Hz, 1H), 5.39 (t, J 7 Hz, 1H), 5.20 (m, 1H), 4.78 (dd, J 6.1, 3 Hz), 4.15 (m, 1H), 3.83 (d, J 6 Hz, 2H), 2 (s, 3H), 1.97 (s, 3H), 1.056 (s, 9H) ; ^{13}C NMR (50 MHz, $CDCl_3$) 170.36, 169.30, 146.01, 135.60, 133.15, 129.76, 127.70, 98.23, 76.47, 67.44, 61.64, 26.72, 20.97, 20.79, 19.20.

The same procedure was used to prepare **3c** from 6-O-TBDMS-D-glucal **3e** [4b] and **3g** from **3j** [4b,10].

3,4-di-O-acetyl-6-O-TBDMS-D-glucal 3c

Colorless oil ; IR (CCl_4, cm^{-1}) 3070, 1745, 1645, 710 ; ^1H NMR (200 MHz, $CDCl_3$) δ 6.45 (dd, J 6.1, 1.5 Hz, 1H), 5.30 (m, 1H), 5.22 (t, J 7 Hz, 1H), 4.76 (ddd, J, 6.1, 3, 0.5 Hz), 4.17 (m, 1H), 3.78 (d, J 6 Hz, 2H), 2.04 (s, 3H), 2.01 (s, 3H), 0.86 (s, 9H), 0.32 (s, 6H) ; ^{13}C NMR (50MHz, $CDCl_3$) 170.42, 169.33, 145.99, 98.37, 76.74, 67.62, 61.24, 25.82, 21.04, 20.86, 18.25, - 5.41.

4-O-acetyl-3,6-di-O-TBDMS-D-glucal 3g from 3j [4b,10]

Colorless oil ; IR (CCl_4, cm^{-1}) 3070, 1745, 1645, 710 ; ^1H NMR (200 MHz, $CDCl_3$) δ 6.32 (dd; J 6.5, 0.81 Hz, 1H), 4.88 (td, J 6.5, 0.5 Hz, 1H), 4.7 (ddd, J 6.5, 3.5, 0.5 Hz, 1H), 4.12 (m, 1H), 4.08 (m, 1H), 3.85 (dd, J 14, 6.5 Hz, 1H), 3.71 (dd, J 14, 3.25 Hz, 1H), 2.014 (s, 3H), 0.89 (s, 9H), 0.55 (s, 3H), 0.30 (s, 3H) ; ^{13}C NMR (50 MHz, $CDCl_3$) 169.54, 143.36, 102.26, 77.41, 70.97, 64.92, 62.07, 25.95, 25.69, 21.06, 18.41, 17.94, - 5.27, - 4.86, - 4.57.

3-O-TES-6-O-TBDMS-D-glucal 3i

To a cold (- 5°C) magnetically stirred solution of **3e** [4b] (606 mg, 2.33 mmol) in 20 ml of anhydrous CH_2Cl_2 was added imidazole (158.62 mg, 2.33 mmol). After 10 min, triethylsilylchloride (168.05 mg, 1.165 mmol) in 10 ml of

anhydrous CH_2Cl_2 was slowly added dropwise. The reaction mixture was stirred for 1 h at - 5°C, and was warmed to 20°C. After disappearance of triethylsilylchloride followed by TLC, the mixture was treated slowly with water (10 ml) and extracted with CH_2Cl_2 (2 x 25 ml). Following drying and solvent evaporation, the residue was purified by chromatography (silica gel, elution with 5 % ethyl acetate in petroleum ether) to give 426.5 mg of **3i** (50 %, 98 % based on recovered **3e**, 300 mg) as a clear colorless oil homogeneous by TLC analysis : IR (CCl_4, cm^{-1}) 3620, 3490, 3070, 1645, 710 ; ^1H NMR (200 MHz, $CDCl_3$) δ 6.27 (dd, J 6.3, 1.3 Hz, 1H), 4.62 (dd, J 6.3, 3.5 Hz, 1H), 4.24 (m, 1H), 4.03 → 3.70 (m, 4H), 2.70 (m, 1H), 0.97 (t, 9H), 0.89 (s, 9H), 0.63 (q, 6H), 0.07 (s, 6H) ; ^{13}C NMR (50 MHz, $CDCl_3$) 143.48, 103.52, 78.04, 70.93, 69.92, 63.11, 25.96, 18.43, 6.84, 5.06, - 5.28, - 5.33, $[\alpha]_D^{25}$ + 8° (C1, $CHCl_3$).

Anal.calcd for $C_{18}H_{38}O_4Si_2$: C, 58.75 ; H, 10.16 ; Found : C, 59.08, H, 10.30.

3-O-TES-4-O-acetyl-6-O-TBDMS-D-glucal 3h

To a cold (-10°C) magnetically stirred solution of **3i** (420 mg, 1.122 mmol) in 1 ml af anhydrous pyridine, was added acetic anhydride (0.110 ml, 1.2 mmol). The reaction mixture was stirred for 4 h at - 10°C and was warmed to 20°C, treated with methanol (0.1 ml) and extracted two times with ether (2 x 20 ml). The combined organic layers were washed with water (2 x 20 ml) drying over anhydrous $MgSO_4$, filtration and evaporation affording **3h** (444 mg) as a colorless oil. IR (CCl_4, cm^{-1}) 3080, 1748, 1640, 710 ; ^1H NMR (200 MHz, $CDCl_3$) 6.30 (dd, J 6, 0.5 Hz, 1H), 4.95 (t, J 6 Hz, 1H), 4.63 (dd, J 6, 4 Hz), 4.15 (m, 1H), 4.03 (m, 1H), 3.95 →3.65 (m, 2H), 2.03 (s, 3H), 0.91 (t, 9H), 0.85 (s, 9H), 0.58 (q, 6H), 0.03 (s, 6H) ; ^{13}C NMR (50 MHz, $CDCl_3$) 169.40, 143.15, 102.07, 77.15, 70.75, 64.43, 61.71, 25.66, 20.81, 18.13, 6.48, 4.60, - 5.57.

Typical procedure for NBS oxidation

NBS (320 mg, 2.2 mmol) was added in one batch to a stirred solution of allylic acetates or allylic silyl ethers **3** (2 mmol) in boiling CCl_4 in the presence of K_2CO_3 (4 mmol) and a catalytic quantity of benzoyl peroxide. The reaction times are listed in Table I. After completion, the mixture was filtered through a sintered-glass funnel. Following solvent evaporation, the residue was purified by flash chromatography (elution with 20-30 % ethyl acetate in petroleum ether).

(2R-trans)-2[(acetoxy)-methyl]-2,3-dihydro-3-acetoxy-4H-pyran-4 one 2b

Colorless oil ; $[\alpha]_D^{20}$ 253° (C 1.09, $CHCl_3$). Lit.[5] : $[\alpha]_D^{20}$ 255° (C 1 $CHCl_3$) ; IR (CCl_4, cm^{-1}) 1775, 1762, 1715, 1225 ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J 6.25 Hz, 1H), 5.55 (d, J 13, 4 Hz, 1H), 5.49 (d, J 6.25 Hz, 1H), 4.62 (td, J 4, 13.4 Hz, 1H), 4.49 (dd, J 4, 12.7 Hz, 1H), 4.41 (dd, J 2.5, 12.7 Hz, 1H), 2.20 (s, 3H), 2.12 (s, 3H) ; ^{13}C NMR (50 MHz, $CDCl_3$) 187.8, 170.25, 169.1, 162.5, 105.2, 78.1, 67.9, 61.3, 20.5, 20.3.

1α,2β-dibromo-D-glucal triacetate 4

Rf : 0.55 (ethylacetate-petroleum ether : 3/7), colorless oil ; IR (CCl_4 cm^{-1}) 1755, 600 ; ^1H NMR (200 MHz, $CDCl_3$) δ 6.61 (d, J 1 Hz, 1H), 5.60-5.40 (m, 2H), 4.83 (dd, J 1, 3 Hz, 1H), 4.34-4.05 (m, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H) ; ^{13}C NMR (50 MHz, $CDCl_3$) 170.53, 169.63, 169.29, 85.24, 73.65, 68.57, 65.16, 61.19, 51.73, 20.74, 20.68, 20.62.
Anal. calcd. for $C_{12}H_{16}O_7Br_2$: C, 33.36 ; H, 3.70 ; Br, 37.04 ; Found : C, 33.53 ; H, 3.85 ; Br, 37.45.

(2R-trans)-2[[[(tert-butyl)dimethylsilyl]oxy]-methyl]-2,3-dihydro-3-acetoxy-4H-pyran-4-one 2c [4b]

(2R-trans)-2[[[(tert-butyl)diphenylsilyl]oxy]-methyl]-2,3-dihydro-3-acetoxy-4H-pyran-4-one 2d

White crystals, m.p. 81-82°C (ether-pentane) ; $[\alpha]_D^{20}$ 270.5° (C 1, $CHCl_3$) ; IR (CCl_4, cm^{-1}) 3085, 3070, 1745, 1675, 1645, 710 ; ^1H NMR (200 MHz, $CDCl_3$) δ 7.65 (m, 4H), 7.40 (m, 7H), 5.18 (d, J 11 Hz, 1H), 5.42 (d, J 6.25 Hz, 1H), 4.45 (2m, J 11 Hz, 1H), 3.95 (dd, J 2.2, 11 Hz, 1H), 3.85 (dd, J 3.5, 11 Hz, 1H), 2.02 (s, 3H), 1.05 (s, 9H) ; ^{13}C NMR (50 MHz, $CDCl_3$), 188.78, 168.98, 162.77, 135.64, 132.80, 129.98, 127.85, 104.91, 81.05, 68.49, 61.92, 26.77, 20.48, 19.32.
Anal. calcd. for $C_{24}H_{28}O_5Si$: C, 67.94 ; H, 6.60 ; Found : C, 68.15 ; H, 6.75.

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REFERENCES AND NOTES

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