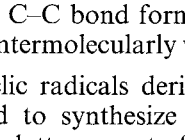
Addition of an Apiosyl Radical to Activated Olefins – Synthesis of *C*-Apiosyl Compounds

Martina Drescher, Friedrich Hammerschmidt*
Institut für Organische Chemie der Universität Wien, Währingerstraße 38, A-1090 Wien, Austria
Received 28 February, 1996; revised 3 June 1996

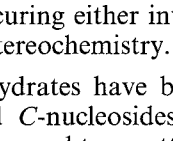
3′-*O*-Benzoyl-2,3-*O*-isopropylidene-D-apio-β-D-furanosyl bromide (**8**), prepared in two steps from 2,3-*O*-isopropylidene-D-apio-β-D-furanose (**6**), was reacted with tris(trimethylsilyl)silane/AIBN in the presence of an excess of a variety of activated olefins such as dimethyl maleate, methyl acrylate, acrylonitrile, methyl vinyl ketone, crotonaldehyde, cyclopent-2-enone, and cyclohex-2-enone to afford the corresponding *C*-apiosides **10** having β-configuration.

Free radical reactions have become popular in synthetic organic chemistry. Their ease of generation from many precursors by the use of tributyltin hydride[1] (TBTH) or more recently tris(trimethylsilyl)silane[2] [TTMS, $(TMSi)_3SiH$] in combination with AIBN, the high selectivity and tolerance of functional groups have contributed to the success and acceptance of radical chemistry. Its major applications are the reductive displacement of X (X = halogen, RS-C(S)-O, isonitrile etc.) by hydrogen and C–C bond forming processes occuring either intra- or intermolecularly with predictable stereochemistry.[1–5]

Cyclic radicals derived from carbohydrates have been used to synthesize *C*-glycosides and *C*-nucleosides.[6,7] This latter aspect of radical chemistry caught our attention, when we were looking for a method to prepare analog **2** of D-(+)-showdomycin[8] (**1**), which is a natural product with antibiotic and antitumor activity.



1
D-(+)-Showdomycin

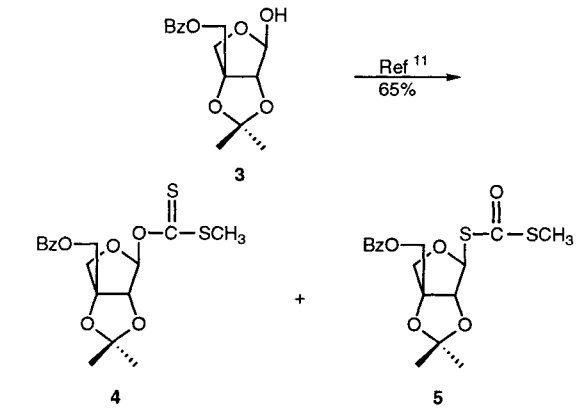


2

This work is a continuation[9] of our studies in the field of D-apio-β-D-furanosyl nucleosides as analogs of D-ribofuranosyl nucleosides. The chemistry of D-apio-D-furanose is distinctly different from the chemistry of D-ribofuranose, which extends to their respective radicals as well. We report here on the generation of D-apio-D-furanosyl radicals and their C–C bond forming capabilities with activated olefins.

3′-*O*-Benzoyl-2,3-*O*-isopropylidene-D-apio-β-D-furanose[10] (**3**) was used as starting material to prepare by a literature procedure[11] the (methylthio)thiocarbonyl derivative **4** as a radical source (Scheme 1).

Phase transfer catalysis afforded compounds **4** and **5** in 65 % yield as an inseparable mixture (**4**/**5** 1 : 0.22), which was used directly. When 2.2 equiv. of TBTH or TTMS were added slowly to a refluxing solution of **4** and **5**, 20 equiv. of dimethyl maleate and a catalytic amount of AIBN in dry benzene under argon, **4** was transformed

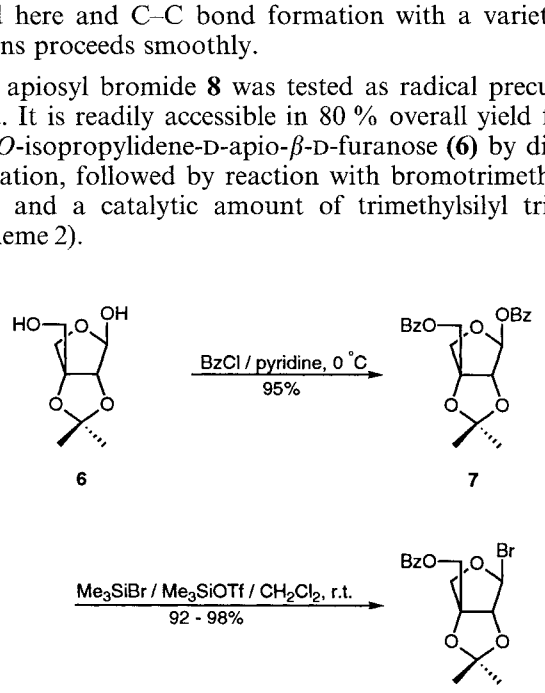


3 **4** **5**

Scheme 1

into **5**, which could be isolated in yields of 71 % and 59 %, respectively. Products indicating an addition of the radical formed to the activated olefin could not be obtained. 5-*O*-Benzoyl-2,3-*O*-isopropylidene-1-*O*-(methylthio)thiocarbonyl-β-D-ribofuranose which is isomeric to **4** is an ideal radical source[12] under the conditions used here and C–C bond formation with a variety of olefins proceeds smoothly.

The apiosyl bromide **8** was tested as radical precursor next. It is readily accessible in 80 % overall yield from 2,3-*O*-isopropylidene-D-apio-β-D-furanose (**6**) by dibenzoylation, followed by reaction with bromotrimethylsilane and a catalytic amount of trimethylsilyl triflate (Scheme 2).



6 **7** **8**

Scheme 2

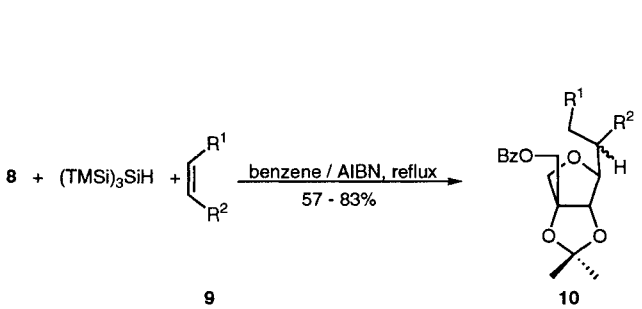
Contrary to the corresponding ribofuranosyl bromide, the apiosyl bromide **8** is stable enough to be handled at ambient temperature and normally the crude product was used immediately after isolation. It was allowed to react with a large excess of dimethyl maleate (**9a**) under the same conditions as the (methylthio)thiocarbonyl derivative **4** with either TBTH or TTMS and AIBN (Scheme 3, Table 1).

Downloaded by: York University libraries. Copyrighted material.

Table 1. Reaction Products **10** and **11** of Radical Generated from **8** with Olefins

Entry	Olefin (equiv.)	Time (h)	Product	Yield[a] (%)	R_f[b] (TLC)	mp[c] (°C)	$[\alpha]_D^{20}$ (c)[d]	IR (neat) ν (cm^{-1})[e]
1	**9a** (20)	1	**10a**	83	0.28[f]	67–69	+3.55 (1.2)	1731, 1270, 1097
					0.25[f]	64–66	−34.79 (0.7)	1730, 1269, 1109
2	**9b** (2)	1	**10b**	62	0.40	46–48	−16.10 (1.1)	1730, 1270, 1097
3	**9b** (5)	1	**10b**	64				
4	**9c** (5)	20	**10c**	58	0.26	87–88	−16.70 (2.2)	1712, 1208, 1180
5	**9d** (5)	3.5	**10d**	57	0.25	58–61	−16.50 (0.9)	1718, 1270, 1110
6	**9e** (5)	1	**10e**	64	0.25		−2.73 (1.2)	1724, 1270, 1109
			11	19	0.37			
7	**9f** (5)	1	**10f**	63	0.21		−13.03 (1.0)	1741, 1270, 1109
			11	24				
8	**9g** (5)	1.75	**10g**	44	0.24			
9	**9g** (10)	1	**10g**	67	0.24		−12.17 (0.9)	1722, 1270, 1109
10	**9h** (5)	2	**11**	87	0.37		+10.92 (1.0)	1724, 1272, 1107

[a] Satisfactory microanalyses obtained: C ± 0.30 (except **10g**), H ± 0.29, N ± 0.14.
[b] Solvent system: PE/EA, 4 : 1.
[c] Crystallization from Et_2O/PE.
[d] In $CHCl_3$; concentration rounded to the nearest tenth.
[e] **10e** in Nujol.
[f] Ratio of compound with R_f 0.28: compound R_f 0.25 = 60 : 40. Diastereomers of **10a** could be separated by flash chromatography.

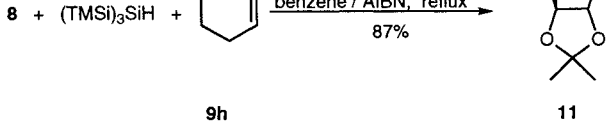


9, 10	R^1	R^2
a	CO_2Me	CO_2Me
b	CO_2Me	H
c	CN	H
d	$COCH_3$	H
e	CHO	CH_3 (*E*)
f	$CO(CH_2)_2$	
g	$CO(CH_2)_3$	

Scheme 3

As the latter reducing agent gave a cleaner reaction and the yield of the desired product was better, it was used throughout this work. Removal of dimethyl maleate by bulb-to-bulb distillation and flash chromatography of the residue furnished a mixture of two addition products **10a** (60 : 40 for the faster moving compound), which could be separated by flash chromatography using petroleum ether/acetone (6:1). On the basis of extensive NOE experiments both compounds were assigned β-configuration [$J_{1,2}$ = 1.5 Hz for the faster moving diastereomer on TLC (petroleum ether/acetone 4:1) and 3.5 Hz for the slower moving one] in agreement with the experiment in the ribofuranose series[12] reported in the literature. It was not possible to assign the configuration at the newly generated asymmetrically substituted carbon atom.

Dimethyl maleate could be replaced by other activated olefins such as methyl acrylate **(9b)**, acrylonitrile **(9c)**, methyl vinyl ketone **(9d)**, crotonaldehyde **(9e)**, cyclopent-2-enone **(9f)**, and cyclohex-2-enone **(9g)** to afford *C*-apiosides **10b–g** regioselectively which were assigned by analogy to compound **10a**'s β-configuration (Table 1). The mixtures **10e–g** of *C*-glycosides with diastereomeric ratios of 55:45 for **9e** and **9f** and 52:48 for **9g** could not be separated. In the case of methyl acrylate and methyl vinyl ketone side products were formed in about 20 % yield, possibly arising from addition of two molecules of olefin. Additionally, the reduction product **11** was isolated in quantities of 19 % and 24 %, when crotonaldehyde and cyclopent-2-enone, respectively, were used as olefins (see Table 1, entries 6 and 7). Only the reduction product **11** was isolated in 87 % yield, when cyclohexene **(9h)** was used as olefin (Scheme 4). Maleimide and maleic anhydride did not add to the apiosyl radical.



Scheme 4

These experiments demonstrate the utility of apiosyl bromide **8** as source for a radical that easily adds to a variety of olefins activated by electron-withdrawing substituents.

Alkenes were obtained from commercial suppliers and were distilled prior to use. ^{1}H- and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as internal standard on a Bruker AM 400 WB at 400.13 and 100.61 MHz, respectively. Melting points were taken on a Kofler apparatus and are uncorrected. IR spectra were run on a Perkin Elmer 1600 FT-IR spectrometer as films on a silicon plate.[13] Optical rotations were measured at 20 °C on a Perkin-Elmer 241 polarimeter in $CHCl_3$ solution in a 1 dm cell. TLC was carried out on 0.25 mm thick Merck plates, silica gel 60 F_{254}. Flash chromatography was performed with Merck silica gel 60 (230–400 mesh). Spots were visualized by UV light and/or spraying with 2 % $Ce(SO_4)_2 \cdot 4\,H_2O$

Downloaded by: York University libraries. Copyrighted material.

Table 2. NMR Data of Compounds **10** and **11**

Product	^{1}H NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ, J (Hz)
10a		
R_f 0.28	1.43, 1.54 [2s, 3H each, $C(CH_3)_2$], 2.74 (m, 2H, CH_2COOCH_3), 3.10 (ddd, 1H, J = 5.4, 7.9, 10.0, $CHCOOCH_3$), 3.68, 3.71 (2s, 3H each, $COOCH_3$), 3.92 (AB system, J = 10.8, 4-H), 4.19 (dd, 1H, J = 1.5, 10.0, 1-H), 4.51 (AB system, J = 11.8, 3′-H), 4.69 (d, 1H, J = 1.5, 2-H), 7.43–8.12 (m, $5H_{arom}$)	27.72, 27.78 [$C(CH_3)_2$], 33.28 (CH_2COOCH_3), 42.40 ($CHCOOCH_3$), 51.87, 52.32 ($COOCH_3$), 65.18 (C-3′), 74.13 (C-4), 85.27, 85.78 (C-1, C-2), 90.66 (C-3), 114.50 [$C(CH_3)_2$], 128.48, 129.44, 129.73, 133.30 (C_{arom}), 166.11 (CO), 171.91, 172.27 ($COOCH_3$)
R_f 0.25	1.42, 1.54 [2s, 3H each, $C(CH_3)_2$], 2.52 (dd, 1H, J = 4.4, 17.2, CH_2COOCH_3), 2.90 (dd, 1H, J = 10.3, 17.2, CH_2COOCH_3), 3.15 (ddd, 1H, J = 4.4, 8.4, 10.3, $CHCOOCH_3$), 3.65, 3.73 (2s, 3H each, $COOCH_3$), 3.99 (AB system, J = 10.3, 4-H), 4.12 (dd, 1H, J = 2.5, 8.4, 1-H), 4.50 (AB system, J = 11.8, 3′-H), 4.58 (d, 1H, J = 2.5, 2-H), 7.44–8.10 (m, $5H_{arom}$)	27.81, 28.07 [$C(CH_3)_2$], 33.14 (CH_2COOCH_3), 43.44 ($CHCOOCH_3$), 51.95, 52.21 ($COOCH_3$), 65.33 (C-3′), 74.87 (C-4), 85.49, 85.95 (C-1, C-2), 90.83 (C-3), 115.26 [$C(CH_3)_2$], 128.51, 129.46, 129.71, 133.30 (C_{arom}), 166.14 (CO), 171.46, 172.29 ($COOCH_3$)
10b	1.35, 1.47 [2s, 3H each, $C(CH_3)_2$], 1.79, 2.37 (2m, 2H each, $CH_2CH_2COOCH_3$), 3.59 (s, 3H, $COOCH_3$), 3.86 (AB system, J = 10.3, 4-H), 4.03 (ddd, 1H, J = 1.5, 4.9, 9.8, 1-H), 4.31 (d, 1H, J = 1.5, 2-H), 4.44 (AB system, J = 11.8, 3′-H), 7.36–8.02 (m, $5H_{arom}$)	26.63 ($CH_2CH_2COOCH_3$), 27.95, 28.17 [$C(CH_3)_2$], 30.65 (CH_2COOCH_3), 51.95 ($COOCH_3$), 65.94 (C-3′), 74.07 (C-4), 84.88, 87.57 (C-1, C-2), 91.18 (C-3), 114.65 [$C(CH_3)_2$], 128.80, 129.80, 130.01, 133.61 (C_{arom}), 166.47 (CO), 173.62 ($COOCH_3$)
10c	1.42, 1.55 [2s, 3H each, $C(CH_3)_2$], 1.88, 2.47 (2m, 2H each, CH_2CH_2CN), 3.94 (AB system, J = 10.3, 4-H), 4.14 (ddd, 1H, J = 2.0, 5.9, 8.4, 1-H), 4.37 (d, 1H, J = 2.0, 2-H), 4.51 (AB system, J = 11.8, 3′-H), 7.44–8.07 (m, $5H_{arom}$)	13.94, 27.43 (CH_2CH_2CN), 27.68, 27.99 [$C(CH_3)_2$], 65.37 (C-3′), 74.07 (C-4), 83.51, 86.90 (C-1, C-2), 90.79 (C-3), 114.96 [$C(CH_3)_2$], 118.95 (CN), 128.63, 129.40, 129.67, 133.51 (C_{arom}), 166.16 (CO)
10d	1.41, 1.53 [2s, 3H each, $C(CH_3)_2$], 1.80 (m, 2H, $CH_2CH_2COCH_3$), 2.14 (s, 3H, $COCH_3$), 2.55 (m, 2H, CH_2COCH_3), 3.90 (AB system, J = 10.3, 4-H), 4.05 (ddd, 1H, J = 1.5, 4.9, 6.4, 1-H), 4.37 (d, 1H, J = 1.5, 2-H), 4.50 (AB system, J = 11.8, 3′-H), 7.43–8.09 (m, $5H_{arom}$)	24.99 ($CH_2CH_2COCH_3$), 27.63, 27.86 [$C(CH_3)_2$], 30.05 ($COCH_3$), 39.50 (CH_2COCH_3), 65.63 (C-3′), 73.70 (C-4), 84.70, 87.30 (C-1, C-2), 90.87 (C-3), 114.29 [$C(CH_3)_2$], 128.50, 129.49, 129.70, 133.30 (C_{arom}), 166.16 (CO), 207.53 ($COCH_3$)
10e	1.02, 1.04 (2d, J = 6.4, 3H each, CH_3CH), 1.42, 1.43 [2s, 3H each $C(CH_3)_2$], 1.54, 1.55 [2s, 3H each, $C(CH_3)_2$], 2.21–2.44 (m, 2 × 2H, CH_2CHO), 2.57, 2.69 (2m, 1H each, CH_3CH), 3.71 (dd, 1H, J = 2.5, 10.3, 1-H), 3.83 (dd, 1H, J = 3.5, 6.9, 1-H), 3.93 (2 × AB system, J = 9.9, 4-H), 4.40 (d, 1H, J = 3.5, 2-H), 4.45 (d, 1H, J = 2.5, 2-H), 4.50, 4.51 (2 × AB system, J = 11.8, 3′-H), 7.44–8.10 (m, 2 × $5H_{arom}$)	15.86, 16.53 (CH_3), 27.71, 27.79, 27.97, 28.35 [$C(CH_3)_2$], 29.69, 30.16 (CH_3CH), 46.98, 47.73 (CH_2CHO), 65.31, 65.47 (C-3′), 74.02, 74.57 (C-4), 84.61, 85.84, 88.84, 89.75 (C-1, C-2), 90.62, 90.89 (C-3), 114.69, 115.47 [$C(CH_3)_2$], 128.50, 128.52, 129.49, 129.56, 129.70, 133.32, 133.35 (C_{arom}), 166.18, 166.20 (CO), 200.87, 201.28 (CHO)
10f	1.43, 1.44 [2s, 2 × 3H, $C(CH_3)_2$], 1.55, 1.56 [2s, 2 × 3H, $C(CH_3)_2$], 1.75 (m, 2 × 1H, CH), 2.11 (m, 2 × 3H, CH_2), 2.35 (m, 2 × 3H, CH_2), 3.90–3.99 (m, 2 × 3H, 1-H, 4-H), 4.38 (d, 1H, J = 2.5, 2-H), 4.46 (d, 1H, J = 3.0, 2-H), 4.51, 4.54 (2 × AB system, J = 11.8, 3′-H), 7.43–8.08 (m, 2 × $5H_{arom}$)	25.50, 25.85 (CH_2), 27.59, 27.66, 28.07, 28.11 [$C(CH_3)_2$], 37.82, 37.83 (CH_2), 38.08, 38.09 (CH), 41.11, 41.72 (CH_2), 65.34 (C-3′), 74.37, 74.42 (C-4), 85.55, 85.88, 88.62, 88.94 (C-1, C-2), 90.79 (C-3), 115.02, 115.10 [$C(CH_3)_2$], 128.54, 129.44, 129.62, 133.43 (C_{arom}), 166.14 (CO), 217.34, 217.74 (CO)
10g	1.41, 1.43 [2s, 2 × 3H, $C(CH_3)_2$], 1.54, 1.55 [2s, 2 × 3H, $C(CH_3)_2$], 1.49 (m, 2 × 3H, CH_2, CH), 1.85–2.60 (m, 2 × 6H, CH_2), 3.79 (dd, 1H, J = 3.0, 8.8, 1-H), 3.83 (dd, 1H, J = 2.5, 7.9, 1-H), 3.90, 3.91 (2 × AB system, J = 10.4, 4-H), 4.43 (d, 1H, J = 3.0, 2-H), 4.45 (d, 1H, J = 2.5, 2-H), 4.452, 4.50 (2 × AB system, J = 11.8, 3′-H), 7.43–8.60 (m, 2 × $5H_{arom}$)	24.72, 24.78, 27.07, 27.61 (CH_2), 27.57, 27.68, 28.08, 28.12 [$C(CH_3)_2$], 39.96, 40.40 (C-1′), 41.18, 41.28, 43.70, 44.17 (CH_2), 65.22, 65.26 (C-3′), 74.24, 74.37 (C-4), 85.05, 85.47, 88.70, 88.75 (C-1, C-2), 90.47, 90.58 (C-3), 115.04, 115.15 [$C(CH_3)_2$], 128.52, 128.53, 129.42, 129.43, 129.63, 129.65, 133.35, 133.39 (C_{arom}), 166.09, 166.11 (CO), 209.95, 210.38 (CO)
11	1.43, 1.54 [2s, 3H each, $C(CH_3)_2$], 3.638 (d, 1H, J = 10.8, 1-H), 3.642 (dd, 1H, J = 3.4, 10.8, 1-H), 4.08 (t, 2H, J = 10.8, 4-H), 4.53 (AB system, J = 11.8, 3′-H), 4.70 (d, 1H, J = 3.4, 2-H), 7.43–8.06 (m, $5H_{arom}$)	27.31, 27.44 [$C(CH_3)_2$], 65.37 (C-3′), 74.19 (C-4), 75.66 (C-1), 83.74 (C-2), 90.60 (C-3), 113.55 [$C(CH_3)_2$], 128.50, 129.45, 129.64, 133.35 (C_{arom}), 166.06 (CO)

in 1M H_2SO_4 followed by heating on a hot plate. Abbreviations used: PE: petroleum ether (bp 60–95°C), EA: ethyl acetate.

1,3′-Di-*O*-benzoyl-2,3-*O*-isopropylidene-D-apio-β-D-furanose (7):
Under Ar at 0°C, benzoyl chloride (1.6 mL, 13.9 mmol) was added dropwise to a solution of **6**[9] [1.9 g, 6.3 mmol; purified by flash chromatography (PE/EA, 7:3) to remove α-anomer and crystallization from Et_2O/PE] in anhyd CH_2Cl_2 (24 mL) and anhyd pyridine (2.5 mL, 31.6 mmol). The reaction mixture was allowed to warm up to r. t. overnight, poured into water/ice and was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (PE/EA, 10:1) to afford **7** (2.38 g, 95 %); R_f 0.35 (PE/EA, 9:1); R_f 0.79 (PE/EA, 7:3); mp 67–68°C (Et_2O/PE).

IR: ν = 1726, 1602, 1585, 1492, 1270, 1070 cm^{-1}.

^{1}H NMR ($CDCl_3$/TMS): δ = 1.45, 1.55 [2 s, 3H each, $C(CH_3)_2$], 4.25 (AB system, J = 10.3 Hz, 4-H), 4.64 (AB system, J = 11.8 Hz, 3′-H), 4.80 (s, 1H, 2-H), 6.45 (s, 1H, 1-H), 7.40–8.10 (m, $5H_{arom}$).

^{13}C NMR ($CDCl_3$/TMS): δ = 27.60, 27.76 [$C(CH_3)_2$], 65.01 (C-3′), 75.81 (C-4), 87.01 (C-2), 90.00 (C-3), 102.40 (C-1), 114.65 [$C(CH_3)_2$], 128.48, 128.51, 129.34, 129.37, 129.74, 133.40, 133.44 (C_{arom}), 165.00, 166.08 (CO).

$C_{22}H_{22}O_7$ (398.3) calc. C 66.33 H 5.53 found C 66.53 H 5.57

3′-*O*-Benzoyl-2,3-*O*-isopropylidene-D-apio-β-D-furanosyl Bromide (8):
Compound **7** (0.215 g, 0.54 mmol) was coevaporated with anhyd toluene and then dissolved under Ar in anhyd CH_2Cl_2 (5 mL).

Downloaded by: York University libraries. Copyrighted material.

Me_3SiBr (0.279 mL, 2.16 mmol) and Me_3SiOTf (0.029 mL, 0.16 mmol) were added and stirring was continued at r. t. for 16–20 h, the flask being covered with an aluminum foil. The mixture was poured into cold sat. aq $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (3 × 5 mL). After drying (Na_2SO_4), the combined organic layers were evaporated to give **8** as an oil (0.184 g, 95 %), which was used immediately thereafter without further purification. TLC (PE/EA, 4:1) showed only traces of impurities. Once the crude product was purified by flash chromatography (PE/EA, 15:1) to yield a colourless oil; R_f 0.75 (PE/EA, 4:1).

IR: ν = 1726, 1652, 1592, 1306, 1165, 1059, 955, 833 cm^{-1}.

^1H NMR ($CDCl_3$/TMS): δ = 1.35, 1.45 [2s, 3H each, $C(CH_3)_2$], 4.25 (AB system, J = 10.8 Hz, 4-H), 4.68 (AB system, J = 11.8 Hz, 3′-H), 5.10 (s, 1H, 2-H), 6.50 (s, 1H, 1-H), 7.35–8.10 (m, $5H_{arom}$).

Reaction of 8 with $(TMSi)_3SiH$ and Olefin 9; General Procedure:
Compound **8** (1 mmol) was coevaporated with anhyd toluene in a 3-necked flask. Last traces of toluene were removed in vacuo (0.01 Torr, 30 min). A reflux condenser, a dropping funnel and a septum cap were attached. A catalytic amount (2–4 mg) of AIBN was added and drying was continued for another 30 min. Anhyd benzene (10 mL) and olefin **9** (Table 1) were added under Ar. The mixture was refluxed and $(TMSi)_3SiH$ (0.68 mL, 2.2 mmol) in anhyd benzene (4 mL) was added dropwise. After completion (TLC, PE/EA, 4:1; Table 1), the cooled reaction mixture was concentrated and excess olefin, if necessary, was removed by bulb-to-bulb distillation. The residue was purified by flash chromatography (PE/EA, 20:1 to 10:1 to 5:1 for **10b**; 7:1 for **10c**; 10:1 to 7:1 to 5:1 to 3:1 for **10d**; 10:1 for **10e**; 10:1 to 5:1 for **10f** and **10g**; 20:1 to 10:1 for **11**). Only in case of **10a** could the two diastereomers be separated by flash chromatography (PE/acetone, 6:1).

We thank the Fonds zur Förderung der wissenschaftlichen Forschung (projects no. P10566-CHE and 6537C) for support of this work and Dipl. Ing. Mag. Biljana Peric for the first preparation of compounds **7** and **8**.

(1) Neumann, W.P. *Synthesis* **1987**, 665.
(2) Chatgilialoglu, C. *Acc. Chem. Res.* **1992,** *25*, 188.
(3) Hartwig, W. *Tetrahedron* **1983,** *39*, 2609.
(4) Giese, B. *Angew. Chem.* **1985,** *97*, 555; *Angew. Chem., Int. Ed. Engl.* **1995,** *24*, 553.
(5) Giese, B. *Angew. Chem.* **1989,** *101*, 993; *Angew. Chem., Int. Ed. Engl.* **1989,** *28*, 969.
(6) Giese, B. *Pure Appl. Chem.* **1988,** *60*, 1655.
(7) Postema, M.H.D. *Tetrahedron* **1992,** *48*, 8545.
(8) Buchanan, J.G. *Prog. Chem. Org. Nat. Prod. Chem.* **1983,** *44*, 243.
(9) Hammerschmidt, F.; Polsterer, J.-P.; Zbiral, E. *Synthesis* **1995**, 415.
Hammerschmidt, F.; Öhler, E.; Polsterer, J.-P.; Balzarini, J.; DeClercq, E. *Liebigs Ann. Chem.* **1995**, 559.
(10) Hammerschmidt, F.; Öhler, E.; Polsterer, J.-P.; Balzarini, J.; DeClercq, E. *Liebigs Ann. Chem.* **1995**, 551.
(11) Di Cesare, P.; Gross, B. *Synthesis* **1980**, 714.
(12) Araki, Y.; Endo, T.; Tanji, M.; Nagasawa, J.; Ishido, Y. *Tetrahedron Lett.* **1988,** *29*, 351.
(13) Mikenda, W. *Vib. Spectrosc.* **1992,** *3*, 327.

Downloaded by: York University libraries. Copyrighted material.