Regioselectivity of Tributyltin Ether Mediated Alkylations. A ^{119}Sn and ^{13}C NMR Study

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The ^{119}Sn and ^{13}C NMR spectra of the stannylated species resulting from the treatment of conformationally rigid polyhydroxylated compounds with bis(tributyltin) oxide have been determined and the effect of *N*-methylimidazole, added as catalyst in tributyltin ether mediated regioselective alkylations, has been investigated. The observed signal intensity changes, upfield shifts, signal broadenings, and the results of variable temperature experiments have been interpreted as indicative of the selective formation of pentacoordinated tin species, involving conveniently disposed adjacent hydroxyl groups, on addition of the catalyst. On these bases, a mechanistic hypothesis for the observed regioselectivity of *N*-methylimidazole-catalyzed tributyltin ether mediated benzylations is proposed.

The regioselective alkylation and acylation of alcohols using organotin derivatives is being extensively utilized in synthetic organic chemistry[1,2] and an understanding of the selective enhancement of the nucleophilicity of hydroxyl groups in the reaction conditions may be important in designing synthesis strategies. Tributyltin ether mediated alkylations are catalyzed by quaternary ammonium halides.[3] We have recently reported on a systematic study of the tributyltin ether mediated selective benzylation of the complete series of 1,6-anhydro-β-D-hexopyranoses, used as conformationally rigid model polyhydroxylated compounds, in the presence of various catalysts.[4] Our results indicated that, as previously reported,[5] *N*-methylimidazole (NMI), which has been found to alter the regioselectivity of tin-mediated acylations,[6] efficiently catalyzes benzylations. On the basis of the experimental data the preferential pentacoordination of stannylated species bearing a free, cis-disposed hydroxyl group adjacent to a stannylated hydroxyl group on addition of the catalyst was proposed.[3,4] We now have carried out a ^{119}Sn and ^{13}C NMR study in order to provide an insight into the course of these catalyzed tributyltin ether mediated regioselective alkylations.

Results and Discussion

Compounds **1**, **3**, **7**, **11**, **15**, **19**, **23**, **27**, and **30** (Chart I) were treated with different amounts of bis(tributyltin) oxide in refluxing toluene and the ^{119}Sn NMR spectra of the resulting stannylation mixtures were then recorded. Compounds having more than one free hydroxyl group gave different mixtures of stannylated derivatives depending on the molar ratio of bis(tributyltin) oxide. The assignment of the ^{119}Sn NMR signals to the various stannylated species was performed from the relative intensity of signals in the spectra of samples prepared by using different molar ratios of reagent and with the help of the corresponding ^{13}C NMR spectra.[2] Table I shows the ^{119}Sn chemical shift values for the stannylated compounds and includes those observed after addition of 1 molar equiv of NMI. The corresponding ^{13}C NMR data are given in Table II and the $^{2}J_{C,Sn}$ and $^{3}J_{C,Sn}$ values are summarized in Table III. Addition of NMI resulted in signal intensity changes, upfield shifts and, in some cases, signal broadening in the ^{119}Sn NMR spectra. Thus, the stannylation of **3** with 0.3 molar equiv of bis(tributyltin) oxide gave an equilibrium mixture of **4**, **5**, and **6** in the ratio 3:1:1.5, respectively, which, upon addition of 1 molar equiv of NMI, became a 3:2:1 mixture. Similarly, treatment of **11** with 0.5 molar equiv of bis(tributyltin) oxide gave a 4.5:1:4.5 mixture of **12**, **13**, and **14**, respectively, which was converted into a 1.5:1.5:1 mixture on addition of 1 molar equiv of NMI. The observed upfield shifts on addition of the catalyst were the highest for signals assigned to equatorially orientated tributyltin ethers having a free adjacent cis-orientated hydroxyl group (compounds **10** and **26**) and remarkable shifts were also observed for those attributed to axially orientated tributyltin ethers having a free adjacent cis-orientated hydroxyl group (compounds **9** and **25**). Signals assigned to equatorially orientated tributyltin ethers having a trans-disposed hydroxyl group (compounds **13**, **14**, **17**, and **18**) were also upfield shifted although to a lesser extent. A similarly small shift was observed for the tributyltin ether **29**. NMI-induced signal broadenings were observed for those corresponding to tributyltin ethers having a free, adjacent, cis-disposed hydroxyl group (compounds **9**, **10**, **25**, and **26**). These broadenings were also observed in the ^{13}C NMR spectra.

The variable-temperature ^{119}Sn NMR spectra of compounds **2**, **9**, **10**, **28**, and **29** were recorded between −80 °C and 100 °C before and after addition of 1 molar equiv of NMI. As a general rule a small downfield shift of the signals was observed at low temperature but addition of NMI in these conditions resulted in remarkable upfield shifts. The variable-temperature ^{119}Sn NMR results are summarized in Table IV. In a typical experiment, treatment of **7** with 1 molar equiv of bis(tributyltin) oxide gave a stannylation mixture whose ^{119}Sn NMR spectrum at room temperature showed signals for the 3,4-di-*O*-tributylstannyl (**8**) and the 3-*O*- (**9**) and the 4-*O*-tributylstannyl (**10**) ethers, which upon addition of NMI undergo upfield shifts of 1.0 and 0.6 ppm (signals corresponding to **8**), 21 ppm (signal corresponding to **9**), and 35 ppm (signal corresponding to **10**) with a noticeable broadening of the signals assigned to **9** and **10**. Addition of more **7** of the original stannylation mixture gave a mixture whose ^{119}Sn-NMR spectrum at room temperature showed signals only for the monostannylated derivatives **9** and **10**. The variable-temperature (−60 °C to 100 °C) ^{119}Sn NMR spectra of this mixture showed no appreciable changes in the absence of NMI. However, when the catalyst was added, the signals appearing at 76.0 (compound **9**) and 58.7 (compound **10**) in the spectrum at 35 °C became a very

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Table I. ^{119}Sn NMR Chemical Shift Values of the Stannylated Derivatives at the Indicated Position before and after Addition of 1 Molar Equiv of NMI in C_6D_6

	δ (^{119}Sn)			δ (^{119}Sn) after addition NMI			Δδ		
compd	O-2	O-3	O-4	O-2	O-3	O-4	O-2	O-3	O-4
2	104.7			98.4			6.3		
4	75.9		100.1	75.2		93.1	0.7		7.0
5	82.9			78.1			4.8		
6			105.3			95.4			9.9
8		73.9[a]	101.6[a]		72.8	100.4		1.1	1.2
9		113.5			96.7[c]			16.8	
10			119.4			94.1[c]			25.3
12	78.5	90.4		78.1	90.3		0.4	0.1	
13	90.0			75.5			15.5		
14		102.5			94.3			8.2	
16	91.3[a]	90.1[a]		90.7	89.3		0.6	0.8	
17	102.7[b]			91.8[b]			10.9[b]		
18		102.2[b]			94.2[b]			8.0[b]	
20	93.7[a]	83.5[a]		88.6[a]	82.6[a]		0.6	0.8	
21	105.9			98.2			7.7		
22		99.3			94.8			5.5	
24	95.0[a]	60.2[a]	104.9[a]	93.7	59.7	104.2	1.3	0.3	0.7
25	91.9[a]	105.9[a]		90.5	91.0[a]		1.4	13.0	
26	100.1		114.3	96.8		90.7[c]	3.2		24.0
28	94.7			93.2			1.5		
29	106.4			98.4			8		
31	90.8			90.6			0.2		

[a] Assignation of the signals may be reversed. [b] The assignation of compounds 17 and 18 may be reversed. [c] Broad signals.

Table II. ^{13}C NMR Chemical Shift Values (δ) for Compounds 1–31 in C_6D_6 Solution

compd	C-1	C-2	C-3	C-4	C-5	C-6	other resonances
1	101.82	70.90	76.81	72.57	69.59	63.34	
2	104.21	75.28	80.02	72.45	70.26	63.04	107.80
3	98.64	70.89	82.75	70.61	78.41	69.45	56.58
4	99.63	74.42	86.20	74.95	79.89	69.53	56.23
5	99.44	73.77	84.30	71.47	77.81	69.01	56.29
6	97.22	71.82	83.44	74.58	79.79	69.72	56.29
7	100.46	78.78	69.07	65.01	74.95	63.43	71.91
8	101.43	83.81	74.75	71.78	77.12	63.93	72.21
9	100.13	81.63	72.54	65.98	75.40	63.62	71.77
10	100.84	79.61	70.41	68.02	75.89	63.53	72.22
12[a]	103.79	79.17	75.75	85.35	63.12	69.80	103.37 55.19
13[a]	102.08	76.68	73.06	82.54	63.00	69.46	102.75 54.96
14[a]	101.08	75.76	74.49	84.33	63.50	69.41	102.81 55.13
15	105.70	75.72	74.38	82.01	67.08	69.25	101.50 57.03
16	107.36	80.87	79.53	84.28	66.66	69.38	102.88 56.58
17	106.46	78.47	76.26	81.39	66.93	69.15	101.78 56.63
18	105.08	77.35	77.11	83.47	67.09	69.15	102.65 56.63
19	102.25	72.17	70.33	72.51	72.83	71.33	64.22
20	104.60	79.80	77.56	76.43	72.61	71.88	64.34
21	104.38	76.20	72.89	72.77	73.10	71.30	64.10
22	102.71	75.85	74.68	75.46	72.81[b]	72.05[b]	64.31
23	103.15	73.06	72.16	65.19	75.53	63.86	
24	104.81	80.00	79.78	71.93	77.22	63.91	
25	104.15	78.73	76.99	65.80	75.88	63.64	
26	104.63	76.35	75.62	68.41	76.23	63.50	
27	76.75	76.75					
28	82.99	82.99					
29	80.79	78.21					
31	65.8	77.3					

[a] Assignation related to 11.[12] [b] Tentative assignation.

broad signal centered at −62 ppm in the spectrum at −60 °C and a sharp signal at 100.3 ppm in the spectrum recorded at 100 °C. These temperature-induced spectral changes were also observed in the spectrum of **2**, which showed a band at 130.0 ppm shifting to 90 ppm with simultaneous broadening in the presence of NMI at 35 °C. This band appeared at −50.9 ppm in the spectrum recorded at −80 °C and 96.4 ppm in that at 90 °C. It is interesting to note that the signals corresponding to the methyl group and to C-5 of NMI in the ^{13}C NMR spectrum of the stannylation mixture of **7**, after addition of NMI, that appeared at 31.6 and 119.3 ppm, respectively, in the spectrum at 40 °C appeared splitted into two bands each at 32.0 and 31.9 and 120.2 and 120.0, respectively, in the spectrum at −60 °C.

The effect of the amount of NMI added on the ^{119}Sn NMR spectra was also investigated. Addition of increasing amounts (1–3 molar equiv) of NMI to the mixture of **24**, **25**, and **26**, obtained by stannylation of compound **23**, resulted in noticeable upfield shifts of the signals assigned to the equatorially substituted derivative **26** and the axially stannylated **25**, but these shifts (Δδ) were smaller on each new addition (23.6, 20.9, and 13.8 ppm for **26** and 14.9, 11.5, and 7.2 ppm for **25**, after addition of 1, 2, and 3 molar equiv of NMI, respectively). These results are summarized in Table V.

Table III. $^2J_{C,Sn}$ and $^3J_{C,Sn}$ Values (Hz) of Stannylated Derivatives

	$^2J_{C,Sn}$			$^3J_{C,Sn}$					
compd	C_2–Sn_2	C_3–Sn_3	C_4–Sn_4	C_1–Sn_2	C_2–Sn_3	C_3–Sn_2	C_3–Sn_4	C_4–Sn_3	C_5–Sn_4
2	26			15		12			
4	31		23	10		27	10		19
5	30			*a*		27			
6			23				10		17
9		26			*a*			15	
10			22				10		10
12	29	29		18	22	*a*		*a*	
13	28			*a*		*a*			
14		26			15			9	
16	27	29		*a*	18	16		*a*	
17	27			14		10			
18		28			13			12	
20	27	31		16	22	11		*a*	
21	24			14		11			
22		32			19			14	
24	31	32	22	17	26	12[b]	19[b]	*a*	5
25	31	25		11	*a*	18		17	
26	26		24	15		12[b]	9[b]		11
28	26			26					
29	24			23					
31	25			11					

[a] Not observable. [b] These values may be reversed.

Table IV. ^{119}Sn NMR Chemical Shift Values of Compounds 2, 9, 10, 28, and 29 before and after Addition of 1 Molar Equiv of NMI in Toluene. Variable-Temperature Experiments

temp, °C	**2**[a]		**9** + **10**[a]		**28**[a]		**29**[a]	
100		96.4	109.7 (**9**)	100.3 (**9** + **10**)				
60		94.3	114.6 (**10**)	85.4 (**9**), 83.5 (**10**)				99.7
40	103.0	90.0	112.0 (**9**), 118.0 (**10**)	76.1 (**9**), 58.7 (**10**)	94.7	93.2	106.4	98.4
0	105.9	57.9						89.9
−20		28[b]	111.2 (**9**),[b] 118.5 (**10**)[b]	−23.3 (**9** + **10**)[b]				
−40		−2.8[b]		−45.6 (**9** + **10**)[b]		72.3[b]	113.7[b]	66.2[b]
−60		−31.7[b]		−62.0 (**9** + **10**)[b]		63.3[b]	115.4[b]	46.2[b]
−80		−50.9[b]				30.0[b]		

[a] First and second columns before and after addition of NMI, respectively. [b] Broad to very broad signals.

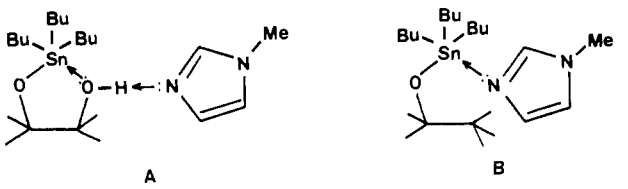
Table V. ^{119}Sn NMR Chemical Shift Values of the Mixture of Compounds 24–26 upon Addition of 1–3 Molar Equiv of NMI in C_6D_6

			molar equiv of NMI			
compd	Sn position	δ(^{119}Sn)	1	2	3	Δδ (total)
24	O-4	104.9	104.2	102.8	101.5	3.4
	O-2	95.0	93.7	91.9	90.3	4.7
	O-3	60.2	59.7	59.2	58.7	1.5
25	O-3	105.9	91.0[a]	79.5	72.3	33.6
	O-2	91.9	90.5[a]	88.7	87.2	4.7
26	O-4	114.3	90.7[b]	69.8[b]	56.0[b]	58.3
	O-2	100.1	96.8	93.5	91.1	9.0

[a] These assignments may be reversed. [b] Broad signals.

The above results indicate that these tributyltin ether mediated alkylations of polyols catalyzed by NMI follow a complex course and that, as previously postulated,[3,4] pentacoordination of tin plays an important role. Treatment of a polyol with bis(tributyltin) oxide affords an equilibrium mixture among various stannylated species and the starting material. Some selectivity is observed in the stannylation conditions but most of the expected stannylation species can be detected in the spectra. Addition of the catalyst seems to selectively alter the composition of this equilibrium by specifically interacting with some of the stannylated species. In contrast to dialkylstannylene derivatives[8-11] and as previously reported,[12]

Scheme I



these tributylstannyl ethers exist as monomers containing a tetrahedral tin atom geometry in toluene or benzene solution, as can be readily deduced from the ^{119}Sn NMR spectra. The observed signal intensity changes, upfield shifts, and signal broadenings, and the variable-temperature experiments are consistent with a preferential coordination of some stannylated species. On the basis of these

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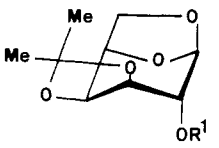
Chart I



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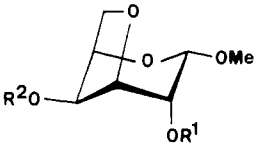
2 $R^1 = SnBu_3$

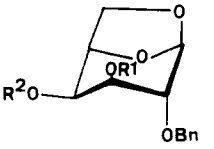


3 $R^1 = R^2 = H$

4 $R^1 = R^2 = SnBu_3$

5 $R^1 = SnBu_3$, $R^2 = H$

6 $R^1 = H$, $R^2 = SnBu_3$

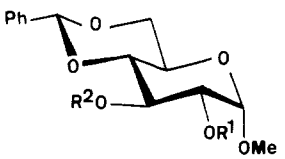


7 $R^1 = R^2 = H$

8 $R^1 = R^2 = SnBu_3$

9 $R^1 = SnBu_3$, $R^2 = H$

10 $R^1 = H$, $R^2 = SnBu_3$

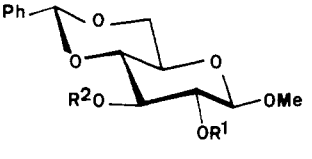


11 $R^1 = R^2 = H$

12 $R^1 = R^2 = SnBu_3$

13 $R^1 = SnBu_3$, $R^2 = H$

14 $R^1 = H$, $R^2 = SnBu_3$



15 $R^1 = R^2 = H$

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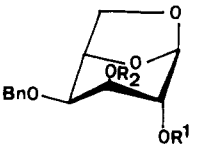
17 $R^1 = SnBu_3$, $R^2 = H$

18 $R^1 = H$, $R^2 = SnBu_3$

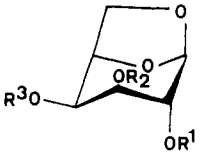


19 $R^1 = R^2 = H$

20 $R^1 = R^2 = SnBu_3$

21 $R^1 = SnBu_3$, $R^2 = H$

22 $R^1 = H$, $R^2 = SnBu_3$

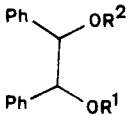


23 $R^1 = R^2 = R^3 = H$

24 $R^1 = R^2 = R^3 = SnBu_3$

25 $R^1 = R^2 = SnBu_3$, $R^3 = H$

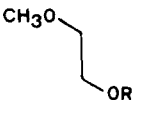
26 $R^1 = R^3 = SnBu_3$, $R^2 = H$



27 $R^1 = R^2 = H$

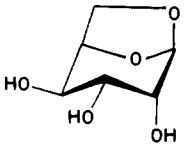
28 $R^1 = R^2 = SnBu_3$

29 $R^1 = SnBu_3$, $R^2 = H$

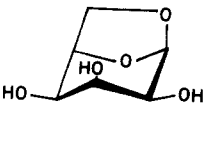


30 R = H

31 $R = SnBu_3$



32



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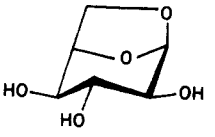

34

results, the hypothesis of a reversible preferential formation of anionic pentacoordinate tin species from species containing an equatorially orientated tributyltin ether having a free adjacent cis-disposed hydroxyl group on addition of the catalyst receives further support. The selective upfield shifts of ^{119}Sn NMR signals on addition of NMI can be interpreted as indicative of preferential pentacoordination of a conveniently orientated tin atom with a lone pair of the adjacent hydroxyl oxygen atom that could be activated through hydrogen bonding to the catalyst as shown in A (Scheme I). This situation favors the establishment of rapid thermodynamic equilibria of the mixture of tributyltin ethers and the observed temperature-induced splitting of the ^{13}C NMR signals of NMI mentioned above could be interpreted in this direction. The electrophilic attack of the alkylating agent is favored in these conditions, with consequent reduced reaction time and improved regioselectivity. When a trans-diaxially orientated hydroxyl group adjacent to the stannylated oxygen or an isolated hydroxyl group is present in the stannylated species, NMI may be directly involved in tin coordination as shown in B (Scheme I), although in competition with hydrogen-bond formation. In these conditions the alkylation time becomes longer and selectivity decreases. When a trans-diequatorially orientated hydroxyl group adjacent to the stannylated oxygen is present, in between situations may arise.

These postulated mechanisms are in agreement with the experimental results previously reported by us on the tributyltin ether mediated benzylation of compounds **7** and **23**, which afforded the 4-*O*-benzyl derivatives in more than 90% yield after 1.5 h whilst that of compound **32** afforded the 3-*O*-benzyl derivative in 90% yield after 1.5 h, and compound **3** gave a mixture of the 2-*O*- and the 4-*O*-benzyl ethers in approximately 50% yield each after 24 h. In addition, compound **33** gave the 2,4-di-*O*-benzyl derivative in 95% yield after 2 h, in contrast to compound **34**, which afforded a mixture of 2-*O*-, 3-*O*-, 4-*O*-benzyl ethers after 4.5 h. The behavior of all other studied compounds may be rationalized on a similar basis.

Although this work has been accomplished by using NMI as benzylation catalyst, alkylammonium halides

commonly used in these alkylations may play a similar role as indicated by the ^{119}Sn spectra of derivatives **9** and **10** in which, upon addition of 1 molar equiv of tetrabutylammonium bromide, similar broadening and upfield shift of the signals could be observed. No further experiments with other catalysts were carried out.

Experimental Section

General. ^{119}Sn NMR spectra were recorded on a Bruker WP-80 spectrometer (29 MHz) at 40 °C, with proton-noise decoupling under gated NOE supression, for ~0.25 M solutions in C_6D_6, under an argon atmosphere. The equivalent amount of NMI (calculated from the starting material) was directly added to the NMR sample. ^{13}C NMR spectra were obtained on a Varian XL-300 (75 MHz) spectrometer under proton-noise decoupling for the same solutions. The NMR samples were prepared as described below and directly analyzed without any previous purification. Assignment of signals was done by selective proton irradiation.[13] Chemical shifts values are given in ppm from internal C_6D_6 (128.0 ppm, ^{13}C) and Me_4Sn as external standard (^{119}Sn). The variable-temperature experiments were carried out for toluene solutions with external DMSO-d_6 (high temperature) or acetone-d_6 (low temperature).

Preparation of NMR Samples. (a) Mono-*O*-tributylstannyl Ethers 2 and 31. Compounds **1** and **30** (1.2 mmol) were separately refluxed with bis(tributyltin) oxide (0.62 mL, 1.2 mmol) in toluene (15 mL) under argon overnight with azeotropic removal of water, then evaporated, dissolved in C_6D_6, and filtered.

(b) Di-*O*-tributylstannyl Ethers 4, 12, 16, and 28. Diols **3**, **11**, **15**, and **27** (0.6 mmol) were separately treated with bis(tributyltin) oxide (0.62 mL, 1.2 mmol) for 18 h as in (a).

(c) Di-*O*-tributylstannyl Ethers 8 and 20 were prepared from diols **7** and **19** (0.6 mmol), respectively, by treatment with bis(tributyltin) oxide (0.93 mL, 1.8 mmol) for 48 h as in (a).

(d) Tri-*O*-tributylstannyl Ether 24 was prepared from triol **23** (0.6 mmol) by treatment with bis(tributyltin) oxide (0.93 mL, 1.8 mmol) for 48 h as in (a).

(e) Mixture of Stannylated Derivatives from Diol 3. From **3** (0.317 g, 1.8 mmol) and bis(tributyltin) oxide (0.31 mL, 0.6 mmol) in the above conditions for 24 h, a mixture of **3**, **4**, **5**, and **6** was obtained from which most of unreacted **3** could be separated by filtration. The final solution contained a 3:1:1.5 mixture of **4**, **5**, and **6**, respectively.

(f) Mixture of Stannylated Derivatives from Diol 7. From **7** (0.160 g, 0.6 mmol) and bis(tributyltin) oxide (0.31 mL, 0.6 mmol) refluxed overnight as above, a 2:1:2.5 mixture of **8**, **9**, and **10** was obtained. This mixture was refluxed overnight with more **7** (0.160 g, 0.6 mmol) to afford a new 1:3 mixture of **9** and **10** and unreacted **7**. An identical result was obtained when **7** (0.320 g, 1.2 mmol) was treated overnight with bis(tributyltin) oxide (0.31 mL, 0.6 mmol).

(g) Mixture of Stannylated Derivatives from Diol 11. From **11** (0.338 g, 1.2 mmol) and bis(tributyltin) oxide (0.31 mL, 0.6 mmol) refluxed overnight, a mixture of **11**, **12**, **13**, and **14** was obtained. Most of unreacted **11** could be separated by filtration to give a 4.5:1:4.5 mixture of **12**, **13**, and **14**.

(h) Mixture of Stannylated Derivatives from Diol 15. Treatment of **15** (0.338 g, 1.2 mmol) as in (g) gave a 2:1:1 mixture of **16**, **17**, and **18** and some unreacted **15**.

(i) Mixture of Stannylated Derivatives from Diol 19. Treatment of **19** (0.320 g, 1.2 mmol) as in (g) gave a 1:5:1 mixture of **20**, **21**, and **22** and some unreacted **19**.

(j) Mixture of Stannylated Derivatives from Triol 23. From **23** (0.194 g, 1.2 mmol) and bis(tributyltin) oxide (0.93 mL, 1.8 mmol) refluxed overnight, a 1:1:3 mixture of **24**, **25**, and **26** was obtained.

(k) Mixture of Stannylated Derivatives from Diol 27. Reaction of **27** (0.257 g, 1.2 mmol) with bis(tributyltin) oxide (0.31 mL, 0.6 mL) gave a 1:5 mixture of **28** and **29** and some starting **27**.

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Registry No. **1**, 52579-97-2; **2**, 117755-77-8; **3**, 5540-31-8; **4**, 117755-78-9; **5**, 117755-79-0; **6**, 117755-80-3; **7**, 55287-63-3; **8**, 117755-81-4; **9**, 117755-82-5; **10**, 117755-83-6; **11**, 57701-27-6; **12**, 77388-88-6; **13**, 77388-87-5; **14**, 77388-86-4; **15**, 71117-37-8; **16**, 117858-39-6; **17**, 117755-84-7; **18**, 117858-40-9; **19**, 116836-98-7; **20**, 117755-85-8; **21**, 117755-86-9; **22**, 117755-87-0; **23**, 644-76-8; **24**, 117755-88-1; **25**, 117755-89-2; **26**, 117755-90-5; **27**, 492-70-6; **28**, 117755-91-6; **29**, 109482-27-1; **30**, 109-86-4; **31**, 117755-92-7; NMI, 616-47-7; ^{119}Sn, 14314-35-3; $(Bu_3Sn)_2O$, 56-35-9.

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1,5-Stereocontrol via (η^6-Arene)tricarbonylchromium Complexes

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1,5-Stereocontrol is achieved by diastereoselective $Cr(CO)_3$ complexation of *o*-alkoxyphenyl derivatives possessing a benzylic acetal and an allylic alcohol on the side chain, chirality transfer of the allylic alcohol system, and subsequent stereoselective conversion of the acetal to an alkyl substituent. The stereocontrolled ligand exchange reaction of (naphthalene)$Cr(CO)_3$ with the arene compounds **8** gives predominantly the (arene)chromium complexes **9**. The allylic acetate complexes **21** and **23** are reacted with sodium malonate in the presence of Pd(0) to afford the complexes **22** and **24** with a C-5 chiral center, by the stereo- and regioselective S_N2 type substitution. *O*-Methyl glycolate chromium complexes **26** and **28** are converted into the chirality transferred chromium complexes **27** and **29** by the enolate Claisen rearrangement. The benzylic acetal function of these chromium complexes with the chiral center at the C-5 position can also be transformed to the stereoisomeric methyl substituted function by the two series of reaction sequences.

Introduction

One of the most exciting challenges in synthetic methodology is control of stereochemistry in conformationally nonrigid systems. In recent years a number of efforts have been devoted to the exploration of stereoselective reactions in acyclic precursors, and various excellent methods have been developed for the diastereoselection between adjacent carbon atoms (1,2-relationships).[1] However, general approaches to the construction of remote chiral relationships

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