# Organotin Nucleophiles. 6.[1] Palladium-Catalyzed Allylic Etherification with Tin Alkoxides

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Tin alkoxides, although mildly nucleophilic, were found to be highly reactive nucleophiles toward π-allyl palladium intermediates. Providing a chemoselective approach to allylic etherification, these organotin reagents substitute allylic acetates in the presence of other electrophilic functional groups such as primary halides. With respect to the two termini of the allylic system, the regioselectivity of nucleophilic attack by tin alkoxides was found to follow the characteristic behavior of stabilized carbanions and amines, namely, preferred attack at the less sterically hindered position and/or at the position remote from an electron-withdrawing substituent. The stereochemical course of the allylic etherification was examined by using an indicator substrate **22b** and following the reaction by $^1H$ NMR. Tin phenoxide was found to substitute 10 times faster than epimerization of either starting material or product in a mildly stereospecific manner, the major product retaining the configuration of the starting material. This method has been applied to protect hydroxyl groups of carbohydrates and for selective glycosidation of allylic aglycons. This approach complements the more common Koenigs–Knorr method, providing the α-stereoisomer as the major product. Dialkyloxydialkyltin reagents were found to be as reactive nucleophiles as the monoalkoxide varieties providing a short and useful synthetic approach for obtaining macrocyclic unsaturated polyethers.

Organotin alkoxides exhibit special properties that make them attractive synthetic reagents.[3] On the one hand, like other metal alkoxides, organotin varieties are basic molecules; on the other hand, they are covalent compounds, of greater stability and lower reactivity than the common alkoxides of group 1 or 2[28] metals. They generally are liquids or low-melting solids and are conveniently soluble in organic solvents.

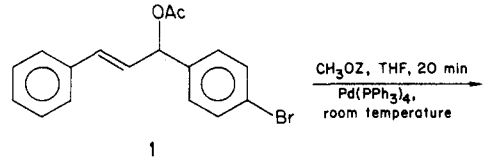
Due to the fine modulation of the nucleophilicity of the oxygen atom by the tin moiety, organotin alkoxides react with unique selectivity with a variety of electrophilic species. Their utility in organic synthesis has been recognized for about 20 years.[3]

The diminished reactivity of organotin alkoxides in nucleophilic substitutions and additions is readily appreciated by the fact that rapid reaction rates are only attained with highly reactive electrophiles, such as activated alkyl halides (e.g., methyl iodide, allyl bromide, methoxymethyl chloride), and reactive electron acceptors (e.g., acyl halides, tosyl chloride, cyanogen chloride, etc.).[3]

In the course of our search for new nucleophilic reagents for controlled reactions with π-allylpalladium electrophiles under mild conditions, we were attracted by the poor nucleophilicity of organotin alkoxides, a property which can lead to new varieities of chemoselective reactions. In fact, alkoxides in general have been seldom used as nucleophiles in π-allylpalladium chemistry. Their synthetic potential was appreciated only recently, and they were elegantly employed in controlled syntheses of spirocyclic ethers[4a] and optically active tetrahydrofurans.[4b]

## Results and Discussion

**Chemoselectivity.** In order to evaluate the effectiveness of tin alkoxides, we compared three representative nucleophiles (methanol, sodium methoxide, and tributyltin methoxide) in a palladium-catalyzed allylic etherification reaction (eq 1).

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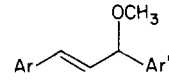


(1)

**2a**, Ar = $C_6H_5$; Ar' = $C_6H_4Br$
**b**, Ar = $C_6H_4Br$; Ar' = $C_6H_5$

| | |
|---|---|
| Z = H | 0% (30% after 24 h) |
| Z = Na | 6% (+85% of the corresponding allylic alcohol) |
| Z = $SnBu_3$ | 90% |
| Z = $SnBu_3$ [without Pd(0)] | 0% |

Apparently, the mild nucleophilic character of trialkyltin alkoxides, which allows them to withstand various electrophilic functional groups, does not impair their reactivity toward π-allylpalladium intermediates. Thus, methanolysis, which is faster than etherification when using sodium methoxide, is negligibly slow with tributyltin methoxide. This chemoselectivity is further exemplified by the inertness of primary alkyl chlorides and even alkyl bromides toward the reaction conditions. When chloro acetate **3** or bromo acetate **6** were allowed to react with phenoxytributyltin in the presence of a Pd(0) catalyst at room temperature, no substitution of the chloride or bromide by phenoxide took place (eq 2 and 3). Even at a higher temperature (refluxing THF), where the palladium-catalyzed elimination[5] of the elements of phenol occurred, no halide substitution was observed and the ω-bromo 1,4-

(1) Paper 5 in this series: Keinan, E.; Perets, M. *J. Org. Chem.* **1983**, *48* 5302.

(2) Teva Pharmaceutical Industries, Ltd., Petah Tikva, Israel.

(3) (a) Pommier, J. C.; Pereyre, M. *Adv. Chem. Ser.* **1976**, *157*, 82. (b) Davies, A. G.; Smith, P. J. In "Comprehensive Organometallic Chemistry" Pergamon Press: Oxford, 1982; Vol. 2, Chapter 11, pp 519–627. (c) Davies, A. G. *Synthesis* **1969**, 56. (d) Pommier, J. C.; Pereyre, M. *J. Organomet. Chem. Libr.* **1976**, *1*, 161. (e) Bloodworth, A. J.; Davies, A. G. In "Organotin Compounds", Sawyer, A. K., Ed.; Marcel Dekker: New York, 1971; Vol. 1, p 153.

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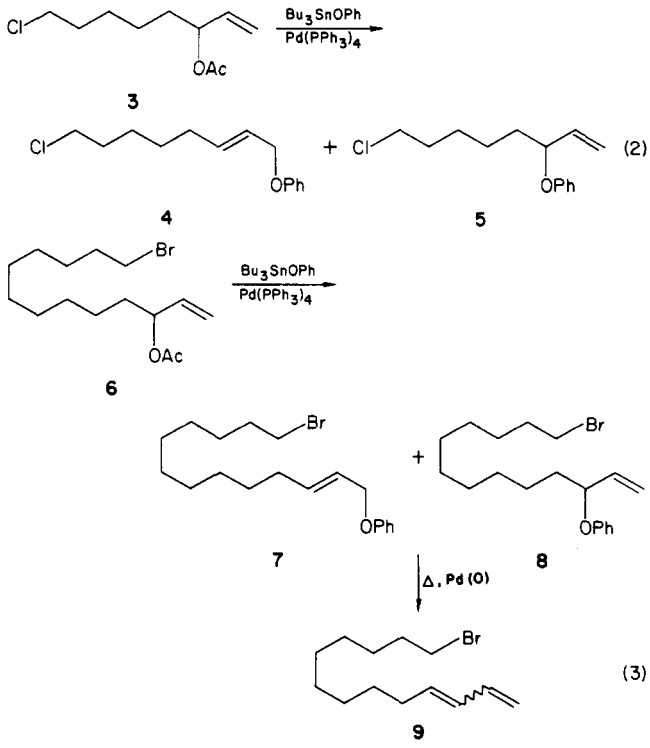


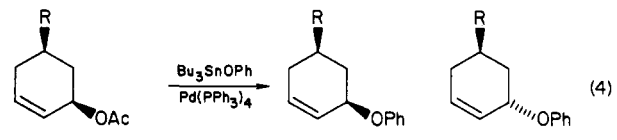

diene **9** was obtained as the sole product (eq 3).

**Regiocontrol and Stereocontrol.** The regiocontrol and stereocontrol of the reaction of a given nucleophile with electrophilic palladium complexes are important, not only for practical synthetic applications but also for gaining some insight into the mechanism by which it reacts.

The two distinct mechanistic pathways proposed for this reaction[6,7] involve either a direct attack at the allylic ligand or an initial attack at the palladium atom, followed by reductive elimination. These two modes of nucleophilic attack are reflected in two complementary stereospecificities and may also be associated with characteristic regioselectivities.

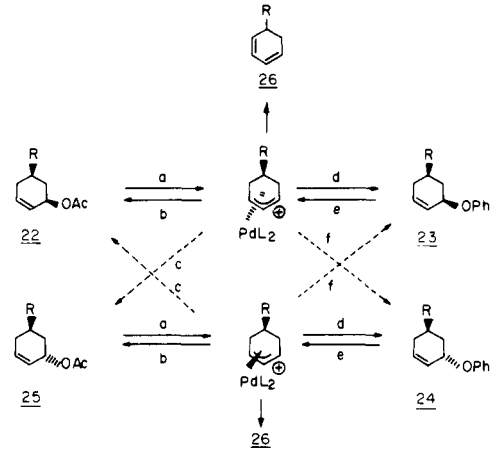
With respect to the two termini of the allylic system, the regioselectivity of the palladium-catalyzed allylic etherification was found to follow the characteristic behavior of stabilized carbanions and amines (Table I),[6-8] namely, preferred attack at the less sterically hindered position and/or at the position remote from an electron-withdrawing substituent.

The stereochemical course of the allylic etherification was examined initially by using the indicator substrate **22a**, which has been extensively employed for characterization of nucleophiles.[6,7] The reaction between **22a** and phenoxytributyltin in THF in the presence of Pd(0) catalyst was completed within 30 min at room temperature, giving rise to a 2:1 mixture of cis and trans products **23a** and **24a**, respectively (eq 4).




There is, however, the basic question of whether the measured distribution of isomeric products indeed reflects

**Scheme I**



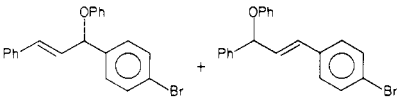
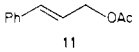
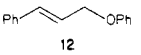
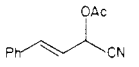
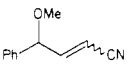
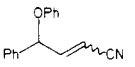
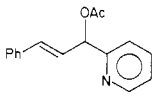
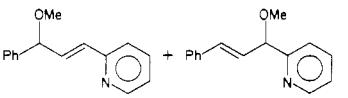
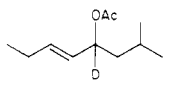
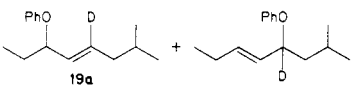
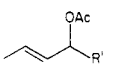
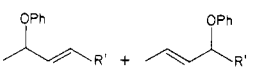

the relative importance of the two competing modes of nucleophilic attack.[7] For example, the steric integrity of the starting compound **22a** (having a relative cis stereochemistry) is jeopardized by the presence of basic alkoxides that may catalyze epimerization at the $\alpha$-position to the carbomethoxy group, leading to an equilibrium mixture of stereoisomers. However, after this difficulty was overcome by using a second model compound, **22b**, devoid of an easily epimerizable center, we still obtained the same 2:1 mixture of isomeric products **23b** and **24b**.

The poor stereospecificity observed in both cases may arise from the intrinsic nature of the acetate group which, in addition to its serving as a leaving group, is also a nucleophile. It has been shown that a stereochemically defined allylic acetate such as **22a** can epimerize rather efficiently in the presence of palladium(0) catalyst,[9] presumably via paths a and c in Scheme I. Therefore, it is necessary to compare the relative rate of epimerization vs. that of substitution by alkoxides. If the rate of substitution is slower or even similar to the rate of epimerization, then the ratio between the two isomeric products **23** and **24** is not indicative of the mechanistic pathway of substitution. Similarly, there is uncertainity concerning the stereochemical stability of the product. It is conceivable that an allylic phenoxy group, being a good leaving group in $\pi$-allylpalladium chemistry,[10] can undergo a palladium-catalyzed epimerization, similar to that observed for allylic acetates via paths e and f in Scheme I.

To check this possibility, both processes, epimerization and substitution, of **22b** were followed by 270-MHz proton NMR at 32 °C in benzene-$d_6$. As shown in Figure 1, isomerization is a rather fast process, which is practically complete within 25 min, in accordance with previous findings.[9] However, substitution with tin alkoxides under the same conditions is much faster, with the reaction going to completion in less than 3 min. Because precise measurement of substitution rates, at 32 °C, could not be efficiently achieved by NMR spectroscopy, it was necessary to recheck the rate differential at a lower temperature. As may be concluded from Figure 2, epimerization at 6 °C takes more than 4 h to reach equilibrium. Substitution, on the other hand, was completed within 25 min (see Figure 3), again about one order of magnitude faster than epimerization. It is also evident from Figure 3 that product epimerization does occur but is much slower than substitution. Isomeric products **23b** and **24b** were initially

(6) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385 and references cited therein.
(7) Keinan E.; Roth, Z. *J. Org. Chem.* **1983**, *48*, 1769.
(8) Keinan E.; Sahai, M. *J. Chem. Soc., Chem. Commun.* **1984**, 648.
(9) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730.
(10) Takahashi, K.; Miyake, A.; Hata, G. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 230.

Table I. Palladium-Catalyzed Allylic Etherification with $Bu_3SnOR$[a]

| starting material | R | products and ratios | yield, % |
|---|---|---|---|
|  1 | Ph |  10a + 10b 50:50 | 71 |
|  11 | Ph |  12 | 92 |
|  13 | Me |  14 | 55 |
| 13 | Ph |  15 | 89 |
|  16 | Me |  17a + 17b 85:15 | 98 |
|  18 | Ph |  19a + 19b 88:12 | 79 |
|  20 | Ph |  21a + 21b | 82 |
| $R'=n\text{-}C_3H_7$ | | 81:19 | 80 |
| $R'=n\text{-}C_4H_9$ | | 80:20 | 85 |
| $R'=i\text{-}C_4H_9$ | | 91: 9 | 88 |
| $R'=i\text{-}C_5H_{11}$ | | 77:23 | 72 |
| $R'=i\text{-}C_3H_7$ | | 92: 8 | 85 |
| $R'=CD_3$ | | 50:50 | 85 |

[a] All reactions were carried out in THF at room temperature using 1.5-2 equiv of $Bu_3SnOR$ and 5-10% $Pd(PPh_3)_4$. Yields are of isolated products.

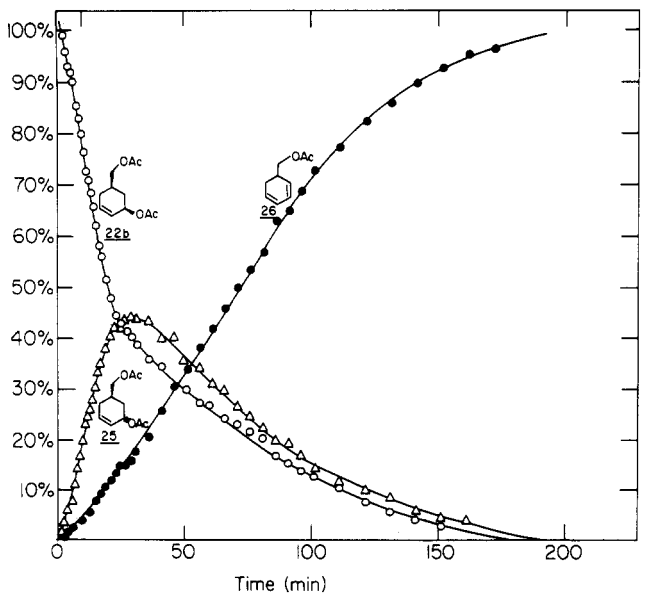



**Figure 1.** Palladium-catalyzed isomerization of **22b** at 32 °C. Compound **22b** was dissolved in $C_6D_6$ together with 18.4% $Pd(PPh_3)_4$ and the reaction was followed by $^1H$ NMR.

formed in a 3:1 ratio. This original ratio slowly changed until an equilibrium was reached.

A notorious side reaction associated with the utilization of $\pi$-allylpalladium intermediates in organic synthesis is a competing $\beta$-hydride elimination reaction of the elements

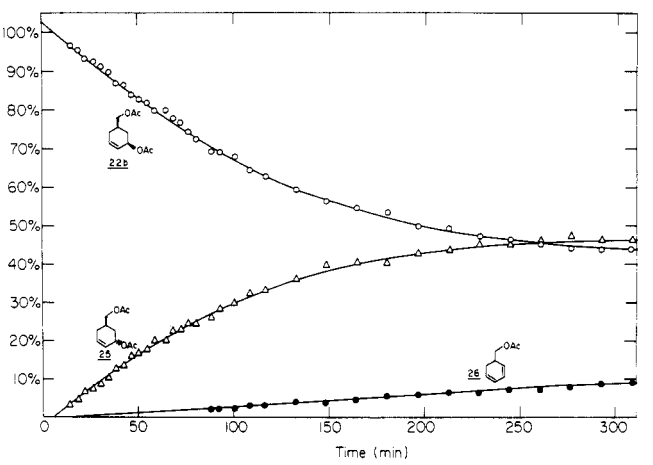



**Figure 2.** Palladium-catalyzed isomerization of **22b** at 6 °C. The experiment was carried out as described in Figure 1, except the temperature was kept at 6 °C.

of either acetic acid or phenol, leading to the formation of a conjugated diene[5,9] **26**. To our delight, this reaction was found to be even more temperature-sensitive than either epimerization or substitution, allowing an efficient suppression of this undesirable process by carrying out the reaction at 6 °C.

On the basis of the above, we believe that the initial ratio (3:1) between isomeric products fairly represents the kinetic rates of the two alternative mechanistic pathways, d and f in Scheme I. It also implies that there is only a

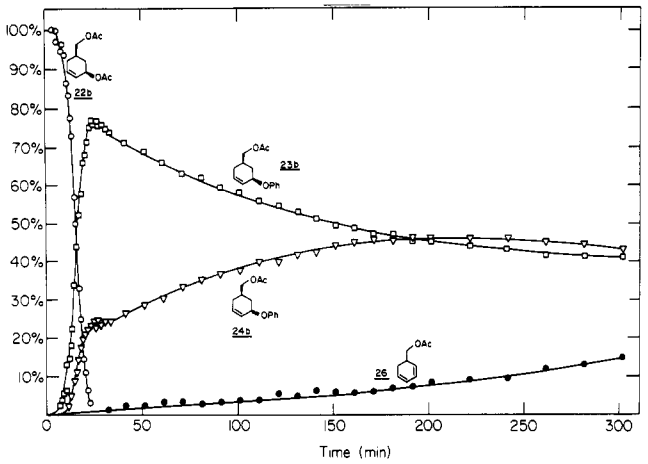
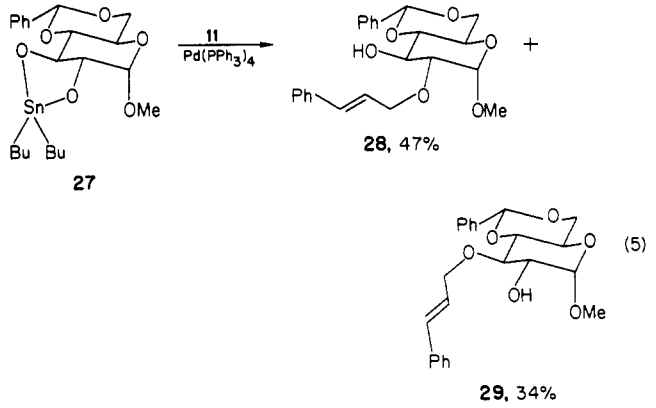



**Figure 3.** Palladium-catalyzed allylic substitution by phenoxide at 6 °C. Compound **22b** was mixed with $Bu_3SnOPh$ (2.1 equiv) and 18.4% $Pd(PPh_3)_4$ in $C_6D_6$ at 6 °C and the reaction was followed by $^1H$ NMR.

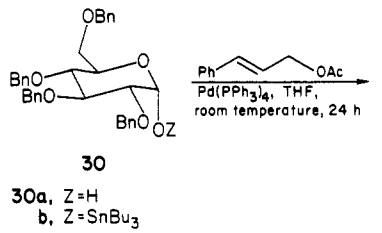
small difference in activation energy of the two pathways. In fact, somewhat higher values (5:1 and 20:1 in favor of the product resulting from ligand attack) were recently reported for intramolecular attack of alkoxides on $\pi$-allylpalladium intermediates.[4a] Similarly, ratios of up to 10:1 were reported for attack by methoxide ion, which is generated during palladium-catalyzed decarboxylation of allylic carbonates.[11] This range of ratios may well result from minor differences in the reactants and alkoxides used in the various studies. The ambident behavior of alkoxides seems to be more general and is also shared by other heteroatom nucleophiles such as amines[12] and acetates.[9,12c,d]

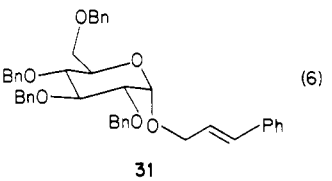
**Synthetic Applications. A. Carbohydrates.** Novel etherification procedures may obviously find immediate application in carbohydrate chemistry, where improved methods for glycosidation and for protecting hydroxyl groups are in great demand.

Stannylated sugar derivatives can be conveniently prepared,[13] but their etherification with allyl halides requires rather harsh conditions (i.e., elevated temperatures and prolonged reaction time)[14] even with the assistance of a stannophilic catalyst, such as a tetraalkylammonium halide.[15] However, palladium-catalyzed allylation offers a greater degree of chemoselectivity since it employs allylic acetates, which are much less reactive than the corresponding allylic bromides, and the reaction occurs at ambient temperatures. For example, the reaction between glucopyranoside **27**[13d] and cinnamyl acetate with a catalytic amount of $Pd(PPh_3)_4$ proceeded smoothly at room temperature to give the two monoallylated derivatives **28** and **29** (eq 5).




The use of sugars stannylated at the anomeric oxygen may provide an efficient method for glycosidation of allylic aglycons. The importance of stannylation of the anomeric oxygen for subsequent, efficient O-allylation is evident from a comparison between the palladium-catalyzed allylation of the free 1-OH derivative **30a** and the corresponding O-stannylated derivative **30b** of 2,3,4,6-tetra-*O*-benzyl-$\alpha$-glucopyranose (eq 6). In the former case less




than 10% of glucoside **31** was formed within 24 h at room temperature, whereas in the latter reaction, the yield exceeded 60%, in agreement with the observations mentioned in eq 1.

An important application of this method for glycosidation is the possibility of producing a 1-*O*-stannyl derivative in situ from the corresponding 1-OH sugar and then, without further purification, reacting it with an organopalladium electrophile. Glycosidation methods that employ sugars with a free anomeric hydroxyl group are rather few,[16,17] although this approach is desirable for reasons of convenient synthesis. This method is also useful for conserving the stereochemistry at the anomeric position, since the nucleophilic role played by the anomeric oxygen of the sugar moiety is characterized by retention of configuration. The resulting $\alpha$-stereochemistry is complementary to the $\beta$-stereochemistry produced by the well-known Koenigs–Knorr glycosidation, in which the sugar plays the role of the electrophilic partner. For example, reaction between $\alpha$-bromoglucuronate **32** and cinnamyl alcohol under typical Koenigs–Knorr conditions gave rise to $\beta$-cinnamylglucuronide **33** (eq 7), whereas using the glucuronate moiety as the nucleophilic partner in the palladium-catalyzed allylation with cinnamyl acetate led to the formation of the $\alpha$-epimer **36** as the major product (eq 8). We have

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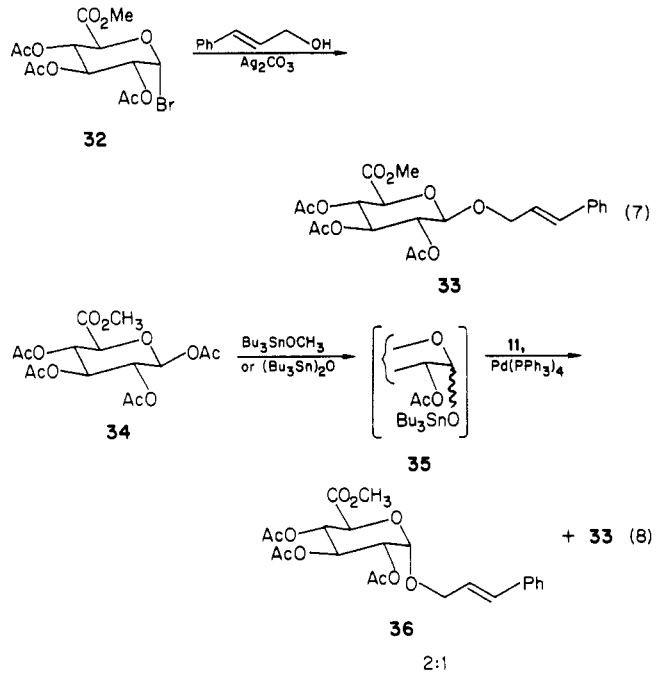
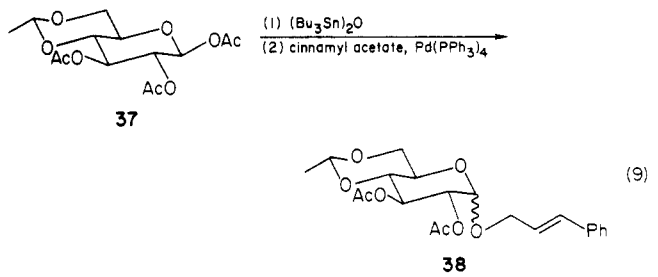
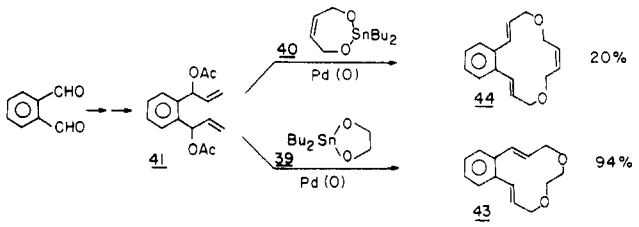



recently found that organotin alkoxides can be employed efficiently for selective deacetylation of an anomeric acetate in polyacetylated sugars.[18] The formation of a postulated 1-*O*-stannyl intermediate, **35**, implies that 1-*O*-acetate sugar derivatives may also be used as starting materials for palladium-catalyzed allylation (eq 8). The general applicability of this allylation method for both glucuronidation and glycosidation reactions is further exemplified by the transformation shown in eq 9.

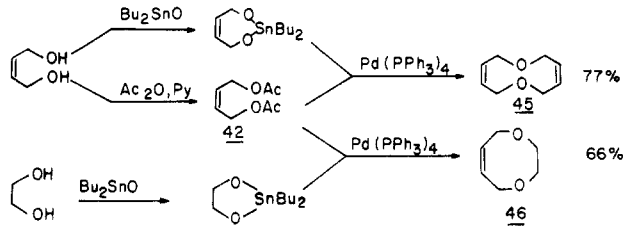



**B. Macrocyclic Ethers.** The above-mentioned stannylene **27** is an interesting example of the dialkoxydialkylstannanes, a family of organotin nucleophiles that can be easily prepared from dialkyltin oxide and the corresponding alcohol or diol.[19] Of special interest are the cyclic dialkoxides which may react as either monobasic or dibasic nucleophiles with variety of electrophiles.[20,21] The ease with which these compounds react with $\pi$-allylpalladium intermediates provides a convenient entry to macrocyclic unsaturated polyethers. For example, the palladium-catalyzed reaction between a cyclic dialkoxide having dibasic character such as **39** or **40** (derived from ethylene glycol and *cis*-1,4-dihydroxybutene, respectively) and a readily available bis-allylic acetate such as **41** or **42** (derived from *o*-phthalaldehyde and *cis*-1,4-dihydroxybutene, respectively) gave rise to macrocyclic ethers such as **43–46** (Schemes II and III).[21]

**Scheme II**




**Scheme III**




## Experimental Section

**General Methods.** Melting points (uncorrected) were determined on a Büchi apparatus. Elemental analyses were performed by the microanalytical laboratory of the Weizmann Institute of Science. Infrared spectra were recorded on a Perkin-Elmer 467 grating spectrometer or on a Nicolet MX-1 FT spectrometer and are given in units of $cm^{-1}$. Proton NMR spectra were measured in deuterated chloroform (unless otherwise cited) on a Varian FT-80A or Bruker WH-270 NMR spectrometer. All chemical shifts are reported in $\delta$ units downfield from $Me_4Si$, and $J$ values are given in hertz. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broadened. Mass spectra were recorded on a Varian Mat 731 spectrometer or on a Finnigan 4500 GC–MS. Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60, F-254, Art. 5549). Column chromatographic separations were performed on silica gel (Merck, Kieselgel 60, 230–400 mesh, Art. 9385) under a pressure of 1 atm (flash chromatography). Preparative TLC was performed on glass plates precoated with silica gel (Merck, Kieselgel 60 F-254 Art. 5717). Distillations of products were performed in a Kugelrohr apparatus; the temperatures given are pot temperatures. GLC analyses were performed on a Hewlett-Packard 7260 (FI detector) equipped with a 0.125 in. × 6 ft column packed with 10% Carbowax 20 on Chromosorb w or with 10% SE-30 on Chromosorb w; peak areas were measured by the cut and weigh method. Preparative GLC separations were performed on a Varian Aerograph 90P (TC detector) equipped with a $^1/_2$ in. × 12 ft column packed with 10% Carbowax 20M on Chromosorb w or a $^3/_8$ in. × 12 ft column packed with 10% SE-30 on Chromosorb W. All reactions were carried out under anhydrous conditions, in flame-dried flasks under a nitrogen atmosphere, and in dry, freshly distilled solvents.

**1,3-Diaryl-3-methoxy-1-propene (2). A. Reaction with Methoxytributyltin.** Methoxytributyltin (240 mg, 0.75 mmol) was added dropwise to a stirred solution of 1-phenyl-3-(4-bromophenyl)-3-acetoxy-1-propene (**1**)[1] (165 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (80 mg, 0.07 mmol) in 4 mL of THF. The mixture was stirred at room temperature for 20 min, after which no starting material could be detected by TLC. The solvent was removed by an $N_2$ stream, and the residue was purified by flash chromatography (97:3 hexane–ethyl acetate), affording 135 mg (90%) of a 1:1 mixture of 1-phenyl-3-(4-bromophenyl)-3-methoxy-1-propene (**2a**) and 3-phenyl-1-(4-bromophenyl)-3-methoxy-1-propene (**2b**): NMR ($CDCl_3$) 7.45–7.07 (m, 9 H), 6.52 (d, $J$ = 15.8 Hz) and 6.46 (d, $J$ = 15.8 Hz) [at 1:1 ratio, together 1H], 6.17 (dd, $J$ = 15.8, 7 Hz) and 6.11 (dd, $J$ = 15.8, 7 Hz) [at 1:1 ratio, together 1 H], 4.69 (d, $J$ = 7 Hz) and 4.65 (d, $J$ = 7 Hz) [at 1:1 ratio, together 1 H], 3.25 (s, 3 H); IR ($CCl_4$) 3020, 2920, 2840, 2820, 1485,

(18) Herzig, J.; Nudelman, A.; Fischer, B.; Keinan, E., *J. Org. Chem.*, submitted for publication.
(19) (a) Considine, W. J. *J. Organomet. Chem.* **1966**, *5*, 263. (b) Mehrotra, R. C.; Gupta, V. D. *J. Organomet. Chem.* **1965**, *4*, 145. (c) Pommier, J. C.; Valade, J. *J. Organomet. Chem.* **1968**, *12*, 433. (d) Smith, P. J.; White, R. F. M.; Smith, L. *J. Organomet. Chem.* **1972**, *40*, 341.
(20) Shanzer, A.; Libman, J. *J. Organomet. Chem.* **1982**, *239*, 301 and references cited therein.
(21) Keinan, E.; Sahai, M., submitted for publication.

1460, 1445, 1395, 1290, 1180, 1080, 1060, 955, 687; MS, *m/e* (relative intensity) 304, 302 ($M^+$, 3.5, 3.6), 272 (10), 223 (7), 192 (23), 191 (42), 178 (2), 165 (6), 131 (1), 115 (10), 105 (10), 95 (8), 85 (29), 71 (46), 57 (100). Anal. Calcd for $C_{16}H_{15}BrO$: C, 63.38; H, 4.99. Found: C, 63.21; H, 5.20.

**B. Reaction with Methoxytributyltin without Pd Catalyst.** Methoxytributyltin (144 mg, 0.45 mmol) was added dropwise to a stirred solution of **1** (100 mg, 0.3 mmol) in 3 mL of THF. The mixture was stirred at room temperature and followed by TLC. No reaction could be observed even after 24 h.

**C. Reaction with Methanol.** Methanol (14.4 mg, 0.45 mmol) was added to a stirred solution of **1** (120 mg, 0.36 mmol) and $Pd(PPh_3)_4$ (30 mg, 0.026 mmol) in 3 mL of THF. The mixture was stirred at room temperature and followed by TLC. No reaction was apparent after 1 h. After 24 h, 30% conversion of **1** to **2** was observed.

**D. Reaction with Sodium Methoxide.** Freshly prepared sodium methoxide (24 mg, 0.44 mmol) was added to a stirred solution of **1** (120 mg, 0.36 mmol) and $Pd(PPh_3)_4$ (50 mg, 0.04 mmol) in 3 mL of THF. The mixture was stirred at room temperature, and the reaction was followed by TLC. Complete conversion of **1** was observed within 20 min. The mixture was subjected to flash chromatography (9:1 ethyl acetate–hexane), affording 7 mg (6%) of **2a** and **2b** and 88 mg (85%) of 1-phenyl-3-(4-bromophenyl)-3-hydroxy-1-propene.

**Reaction of 1 with Phenoxytributyltin.** Phenoxytributyltin (176 mg, 0.46 mmol) was added to a stirred solution of **1** (100 mg, 0.3 mmol) and $Pd(PPh_3)_4$ (50 mg, 0.043 mol) in 4 mL of THF. The mixture was stirred at room temperature and followed by TLC. After complete conversion (15 min), the solvent was removed by an $N_2$ stream, and the residue was subjected to flash chromatography (97:3 hexane–ethyl acetate), affording 80 mg (71%) of **10** as a 1:1 mixture of two isomers, 1-phenyl-3-(4-bromophenyl)-3-phenoxy-1-propene (**10a**) and 3-phenyl-1-(4-bromophenyl)-3-phenoxy-1-propene (**10b**): NMR ($CDCl_3$) 7.5–7.1 (m, 12 H), 6.88 (m, 2 H), 6.57 (d, $J$ = 15.5 Hz) and 6.52 (d, $J$ = 15.5 Hz) [at 1:1 ratio, together 1 H], 6.35 (dd, $J$ = 15.5, 6.5 Hz) and 6.29 (dd, $J$ = 15.5, 6.5 Hz) [at 1:1 ratio, together 1 H], 5.72 (d, $J$ = 6.5 Hz) and 5.70 (d, $J$ = 6.5 Hz) [at 1:1 ratio, together 1 H]; IR ($CCl_4$) 3025, 2920, 2850, 1585, 1480, 1445, 1395, 1297, 1215, 1180, 1070, 1027, 960, 878, 685; MS *m/e* (relative intensity): 366, 364 ($M^+$, 72, 59), 285 ($M^+$ – Br, 100), 272 (39), 270 (43), 247 (2), 245 (3), 208 (26), 207 (45), 195 (40), 191 (39), 181 (75), 178 (22), 167 (21), 91 (15). Anal. Calcd for $C_{21}H_{17}BrO$: C, 69.05; H, 4.69. Found: C, 69.33; H, 5.00.

**8-Chloro-1-phenoxy-2(*E*)-octene (4) and 8-Chloro-3-phenoxy-1-octene (5).** Phenoxytributyltin (0.4 mL, 1.1 mmol) was added to a stirred solution of 8-chloro-3-acetoxy-1-octene (**3**, prepared from addition of vinylmagnesium bromide to 6-chlorohexanal, followed by acetylation with $Ac_2O$/Py) (102 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (62 mg, 0.054 mmol) in 4 mL of THF. The mixture was stirred at room temperature for 30 min and then subjected to preparative TLC (9:1 hexane–ethyl acetate, $R_f$ 0.63) affording 92 mg (77%) of a 3:2 mixture of **4** and **5**: NMR ($CDCl_3$) (**4**) 7.25 (m, 2 H), 6.92 (m, 3 H), 5.83 (dt, $J$ = 15.9, 5.5 Hz, 1 H), 5.70 (dt, $J$ = 15.9, 5.6 Hz, 1 H), 4.40 (d, $J$ = 5.5 Hz, 2 H), 3.52 (t, $J$ = 6.9 Hz, 2 H), 2.11 (q, $J$ = 6 Hz, 2 H), 1.77 (quintet, $J$ = 7 Hz, 2 H), 1.44 (br s, 4 H), (**5**) 7.25 (m, 2 H), 6.92 (m, 3 H), 5.86 (m, 1 H), 5.25 (d, $J$ = 18 Hz, 1 H), 5.19 (d, $J$ = 11 Hz, 1 H), 4.56 (q, $J$ = 6 Hz, 1 H), 3.52 (t, $J$ = 6.9 Hz, 2 H), 1.77 (quintet, $J$ = 7 Hz, 2 H), 1.44 (br s, 6 H); MS, *m/e* (relative intensity) 238 (1.5), 240 (0.6), 144 (15), 146 (6), 109 (10), 105 (3), 94 (100), 81 (15), 77 (10), 67 (39), 55 (38).

**Reaction of 3-Acetoxy-13-bromo-1-tridecene (6) with Phenoxytributyltin.** Phenoxytributyltin (1.2 mL, 3.2 mmol) was added to a stirred solution of 3-acetoxy-13-bromo-1-tridecene (**6**, prepared from 11-bromoundecanol which was first oxidized to 11-bromoundecanal by PCC and then condensed with vinylmagnesium bromide and the resulting alcohol acetylated with $Ac_2O$/Py) (306 mg, 0.96 mmol) and $Pd(PPh_3)_4$ (115 mg, 0.1 mmol) in 6 mL of THF. The mixture was stirred at room temperature. TLC indicated complete disappearance of **6** within 30 min. One-half of the reaction mixture was withdrawn and separated by preparative TLC to give 97 mg (60%) of 13-bromo-1-phenoxy-2(*E*)-tridecene (**7**) and 13-bromo-3-phenoxy-1-tridecene (**8**) in a 2:1 ratio: NMR ($CDCl_3$) (**7**) 7.25 (m, 2 H), 6.97 (m, 3 H), 5.84 (dt, $J$ = 15.4, 5.9 Hz, 1 H), 5.69 (dt, $J$ = 15.4, 6.4 Hz, 1 H), 4.47 (d, $J$ = 5.9 Hz, 2 H), 3.40 (t, $J$ = 7 Hz, 2 H), 2.08 (q, $J$ = 7 Hz, 2 H), 1.85 (quintet, $J$ = 7 Hz, 2 H), 1.28 (br s, 14 H) (**8**) 7.25 (m, 2 H), 6.97 (m, 3 H), 5.85 (m, 1 H); 5.24 (d, $J$ = 16.8 Hz, 1 H), 5.18 (d, $J$ = 10 Hz, 1 H), 4.58 (br q, $J$ = 5 Hz, 1 H), 3.40 (t, $J$ = 7 Hz, 2 H), 1.85 (quintet, $J$ = 7 Hz, 2 H), 1.28 (br s, 16 H).

The rest of the reaction mixture was refluxed for 2 h, followed by removal of the solvent under reduced pressure and flash chromatography to give 13-bromotrideca-1,3-diene (**9**) as a 2:1 mixture of the 3*E* and 3*Z* isomers (56 mg, 45%): NMR ($CDCl_3$) [(*E*)-**9**] 6.29 (dt, $J$ = 16.8, 10.1 Hz, H-2, 1 H), 6.04 (dd, $J$ = 15.5, 10.1 Hz, H-3, 1 H), 5.69 (dt, $J$ = 15.5, 7.2 Hz, H-4, 1 H), 5.09 (d, $J$ = 16.8 Hz, H-1 trans, 1 H), 4.94 (d, $J$ = 10.1 Hz, H-1 cis, 1 H), 3.41 (t, $J$ = 7 Hz, 2 H), 2.06 (q, $J$ = 7 Hz, 2 H), 1.85 (quintet, $J$ = 7 Hz, 2 H), 1.3 (br s, 12 H); [(*Z*)-**9**] 6.64 (br dt, $J$ = 16.8, 10.5 Hz, H-2, 1 H), 5.99 (t, $J$ = 10.5 Hz, 1 H), 5.46 (br q, $J$ = 8.7 Hz, H-4, 1 H), 5.18 (d, $J$ = 16.8 Hz, H-1 trans, 1 H), 5.07 (d, $J$ = 10.5 Hz, H-1 cis, 1 H), 3.41 (t, $J$ = 7 Hz, 2 H), 2.17 (q, $J$ = 7 Hz, 2 H), 1.85 (quintet, $J$ = 7 Hz, 2 H), 1.3 (br s, 12 H).

**Cinnamyl Phenyl Ether (12).** Phenoxytributyltin (770 mg, 1.6 mmol) was added to a stirred solution of cinnamyl acetate (**11**) (173 mg, 1 mmol) and $Pd(PPh_3)_4$ (116 mg, 0.1 mmol) in 4 mL of THF. The mixture was stirred at room temperature for 30 min. The solvent was removed by a stream of $N_2$ and the residue separated by flash chromatography to give 194 mg (92%) of **12**: mp 68–69 °C (Lit.[22] mp 65–66 °C); NMR ($CDCl_3$) 7.25 (m, 8 H), 6.97 (m, 2 H), 6.66 (d, $J$ = 15.8 Hz, 1 H), 6.30 (dt, $J$ = 15.8, 5.6 Hz, 1 H), 4.60 (d, $J$ = 5.6 Hz, 2 H).

**1-Cyano-3-methoxy-3-phenyl-1-propene (14).** Methoxytributyltin (0.43 mL, 1.3 mmol) was added over 30 min (via a syringe pump) to a stirred solution of 3-acetoxy-3-cyano-1-phenyl-1-propene (**13**[1,7]) (505 mg, 1.02 mmol) and $Pd(PPh_3)_4$ (107 mg, 0.09 mmol) in 5 mL of THF. The mixture was stirred at room temperature for an additional 1.5 h. The solvent was removed by a stream of $N_2$ and the residue subjected to flash chromatography (8:1 hexane–ethyl acetate), affording 97 mg (55%) of **14** as a 4:1 mixture of *E* and *Z* isomers. Two other side products were identified, cinnamaldehyde and its cyanohydrin derivative. IR (neat) 3040, 2930, 2820, 2220, 1670, 1625, 1450, 1190, 1100, 965, 755, 700; NMR ($CDCl_3$) [(*E*)-**14**] 7.3 (m, 5 H), 6.66 (dd, $J$ = 16.2, 4.4 Hz, 1 H), 5.64 (dd, $J$ = 16.2, 1.8 Hz, 1 H), 4.71 (dd, $J$ = 4.4, 1.8 Hz, 1 H), 3.27 (s, 3 H), [(*Z*)-**14**] 7.3 (m, 5 H), 6.51 (dd, $J$ = 11.1, 8.5 Hz, 1 H), 5.37 (dd, $J$ = 11.1, 0.9 Hz, 1 H), 5.14 (dd, $J$ = 8.5, 0.9 Hz, 1 H), 3.35 (s, 3 H); MS, [(*E*)-**14**] *m/e* (relative intensity) 173 (41), 159 (3), 158 (25), 143 (26), 142 (35), 140 (24), 121 (33), 115 (72), 105 (39), 103 (26), 96 (9), 91 (24), 80 (30), 77 (97), 63 (28), 52 (36), 51 (100), [(*Z*)-**14**] 173 (60), 158 (35), 143 (34), 142 (47), 141 (29), 140 (29), 121 (52), 116 (29), 115 (99), 103 (29), 96 (10), 91 (29), 80 (33), 77 (100), 63 (34), 52 (36), 51 (98).

**1-Cyano-3-phenoxy-3-phenyl-1-propene (15).** Phenoxytributyltin (0.50 mL, 1.30 mmol) was added dropwise over 10 min to a stirred solution of **13** (222 mg, 1.1 mmol) and $Pd(PPh_3)_4$ (107 mg, 0.09 mmol) in 5 mL of THF. The mixture was stirred for 1 h at room temperature and then treated as described in the previous experiment, affording 231 mg (89%) of **15** as a 7:1 mixture of *E* and *Z* isomers: IR (neat) 3050, 2900, 2220, 1770, 1580, 1480, 1445, 1225, 1175, 1155, 1070, 1025, 960, 745, 685; NMR ($CDCl_3$) [(*E*)-**15**] 7.4 (m, 10 H), 6.85 (dd, $J$ = 16.1, 4.1 Hz, 1 H), 5.77 (dd, $J$ = 16.1, 1.8 Hz, 1 H), 5.71 (dd, $J$ = 4.1, 1.8 Hz, 1 H), [(*Z*)-**15**] 7.4 (m, 10 H), 6.65 (dd, $J$ = 11.1, 8.5 Hz, 1 H), 6.12 (dd, $J$ = 8.5, 0.9 Hz, 1 H), 5.42 (dd, $J$ = 11.1, 0.9 Hz, 1 H); MS, *m/e* (relative intensity) 235 (11), 195 (7), 142 (32), 140 (10), 116 (12), 115 (56), 105 (55), 102 (16), 95 (7), 94 (100), 77 (25), 76 (9), 65 (9), 63 (9), 51 (40).

**3-Phenyl-3-methoxy-1-(2-pyridyl)-1-propene (17a) and 1-phenyl-3-methoxy-3-(2-pyridyl)-1-propene (17b).** Methoxytributyltin (341 mg, 1.06 mmol) was added slowly over 20 min to a stirred solution of 1-phenyl-3-acetoxy-3-(2-pyridyl)-1-propene (**16**, prepared from addition of 2-pyridylmagnesium bromide to cinnamaldehyde, followed by acetylation with $Ac_2O$/Py) (215 mg, 0.85 mmol), and $Pd(PPh_3)_4$ (156 mg, 0.13 mmol) in 5 mL of THF. The mixture was stirred for an additional 3 h and worked up as described above. Flash chromatography (3:1 hexane–ethyl acetate)

(22) Claisen, L. Z. *Angew. Chem.* **1923**, *36*, 478; *Chem. Abstr.* **1924**, *18*, 234.

afforded 158 mg (82%) of **17a** (first eluted) and 30 mg (16%) of **17b** (second eluted): NMR ($CDCl_3$) (**17a**) 8.52 (d, $J$ = 4.7 Hz, 1 H), 7.58 (br t, $J$ = 8 Hz, 1 H), 7.4–7.2 (m, 6 H), 7.1 (br t, $J$ = 6 Hz, 1 H), 6.79 (dd, $J$ = 16, 4.7 Hz, 1 H), 6.72 (d, $J$ = 16 Hz, 1 H), 4.85 (d, $J$ = 4.7 Hz, 1 H), 3.39 (s, 3 H), (**17b**) 8.58 (d, $J$ = 4.7 Hz, 1 H), 7.7 (m, 1 H), 7.5–7.15 (m, 7 H), 6.74 (d, $J$ = 15.8 Hz, 1 H), 6.32 (dd, $J$ = 15.8, 7.3 Hz, 1 H), 4.94 (d, $J$ = 7.3 Hz, 1 H), 3.44 (s, 3 H); IR (neat) (**17a**) 3400, 3015, 2915, 2805, 1720, 1570, 1550, 1455, 1420, 1300, 1180, 1140, 1075, 960, 745, 690, (**17b**) 3400, 3010, 2895, 2800, 1730, 1575, 1485, 1460, 1425, 1320, 1180, 1075, 960, 740, 690; MS, $m/e$ (relative intensity) 225 (20), 210 (63), 195 (28), 194 (89), 182 (48), 167 (33), 148 (10), 117 (26), 115 (26), 105 (61), 104 (25), 97 (32), 91 (36), 84 (28), 78 (66), 77 (100), 65 (29), 63 (25), 52 (30), 51 (96).

**Reaction of 5-Acetoxy-5-deuterio-7-methyloct-3-ene (18) with Phenoxytributyltin.** Compound **18** was prepared from 4-methylpentan-2-one which was condensed with propanal to give 7-methyloct-3-ene-5-one. $NaBD_4$ reduction followed by acetylation gave **18** (for more details, see ref 8). Phenoxytributyltin (1 mL, 2.5 mmol) was added to a stirred solution of **18** (148 mg, 0.8 mmol) and $Pd(PPh_3)_4$ (101 mg, 0.09 mmol) in 4 mL of THF. The mixture was stirred at room temperature under $N_2$ for 1 h and then subjected to preparative TLC (9:1 hexane–ethyl acetate, $R_f$ 0.54), affording 140 mg (79%) of 5-deuterio-3-phenoxy-7-methyloct-4-ene (**19a**) and 5-deuterio-5-phenoxy-7-methyloct-3-ene (**19b**) at an 88:12 ratio (based on $^2H$ NMR): $^2H$ NMR ($CHCl_3$) 5.71 ($w_{1/2}$ = 7.1 Hz), 4.64 ($w_{1/2}$ = 6.5 Hz) [at a ratio of 88:12]; $^1H$ NMR ($CDCl_3$) (**19a**) 7.8 (m, 3 H), 7.4 (m, 2 H), 5.80 (d, $J$ = 7.5 Hz, 1 H), 4.71 (q, $J$ = 7.5 Hz, 1 H), 1.4–1.8 (m, 5 H), 0.76 (d, $J$ = 7 Hz, 6 H), 0.63 (t, $J$ = 7.5 Hz, 3 H), (**19b**) 7.8 (m, 3 H), 7.4 (m, 2 H), 6.13 (m, 1 H), 5.8 (d, $J$ = 16.7 Hz, 1 H), 1.4–1.8 (m, 5 H), 0.76 (d, $J$ = 7 Hz, 6 H), 0.63 (t, $J$ = 7.5 Hz, 3 H) [the ratio between **19a** and **19b**, based on the $^1H$ NMR, was found to be 82:18, respectively]; IR 2950, 2925, 2860, 1600, 1585, 1490, 1240, 965, 750, 690. MS, $m/e$ (relative intensity) 219 (0.5, $M^+$), 134 (2), 125 (33), 110 (6), 96 (14), 94 (14), 84 (15), 83 (17), 82 (15), 77 (6), 70 (95), 69 (100), 68 (26), 55 (24).

**Reaction of 20 with Phenoxytributyltin.** All starting materials **20** were prepared from crotonaldehyde and the appropriate alkylmagnesium bromide, followed by acetylation of the resulting alcohol (for more details, see ref 8). Phenoxytributyltin (2 mmol) was added to a stirred solution of **20** (1 mmol) and $Pd(PPh_3)_4$ (115 mg, 0.1 mmol) in 4 mL of THF. The mixture was stirred at room temperature under $N_2$ for 30 min, the solvent was removed by a stream of $N_2$, and the residue was purified by flash chromatography (5:1 hexane–ethyl acetate). Yields and ratios between isomeric products **21a** and **21b** (based on $^1H$ NMR and GC–MS analyses) are given in Table I. For more details, see ref 8.

**Reaction of 22a with Phenoxytributyltin.** Phenoxytributyltin (0.53 mL, 1.38 mmol) was added to a stirred solution of **22a**[9] (218 mg, 1.1 mmol) and $Pd(PPh_3)_4$ (100 mg, 0.09 mmol) in 5 mL of THF. The mixture was stirred at room temperature under $N_2$ for 30 min and then subjected to flash chromatography (8:1 hexane–ethyl acetate), affording 205 mg (80%) of a 2:1 mixture of **23a** and **24a**: IR (neat) 3020, 2940, 1770, 1725, 1585, 1485, 1430, 1385, 1225, 1030, 950, 880, 810, 750, 685; MS, $m/e$ (relative intensity) 232 (0.2, $M^+$), 201 (0.7), 173 (0.2), 140 (2.5), 139 (29), 138 (3), 107 (8), 95 (5), 94 (14), 81 (4), 80 (12), 79 (100), 78 (25), 77 (25), 65 (14), 59 (13), 51 (13); NMR ($CHCl_3$): 7.3 (m, 2 H), 6.9 (m, 3 H), 5.99 (m) and 5.86 (br s) [at a 2:1 ratio, together 2 H], 4.94 (m, $W_{1/2}$ = 20 Hz) and 4.82 (m, $W_{1/2}$ = 10 Hz) [at a 2:1 ratio, together 1 H], 3.68 (s, 3 H), 2.94 (m), and 2.74 (m) [at a 1:2 ratio, together 1 H], 2.2–2.5 (m, 3 H), 1.9 (m, 1 H).

**3-Acetoxy-5-(acetoxymethyl)cyclohexene (22b).** 7-Oxabicyclo[3.2.1]oct-2-en-6-one[23] was treated with excess $LiAlH_4$ in THF, followed by acetylation with acetic anhydride–pyridine in $CH_2Cl_2$ in the presence of a catalytic amount of 4-(dimethylamino)pyridine. NMR ($CDCl_3$) 5.86 (m, $J$ = 9 Hz, 1 H), 5.63 (br d, $J$ = 9 Hz, 1 H); 5.40 (m, $W_{1/2}$ = 20 Hz, 1 H), 4.00 (dd, $J$ = 6.4, 2.2 Hz, 2 H), 2.12 (m, 3 H); 2.07 (s, 6 H); 1.83 (m, 1 H), 1.37 (br q, $J$ = 11.5 Hz, 1 H); IR (neat) 2940, 1735, 1425, 1365, 1235, 1020, 960, 925, 740, 690; MS, $m/e$ (relative intensity) 152 (11, $M^+ - 60$), 127 (13), 110 (100), 109 (18), 95 (57), 93 (35), 92 (84), 91 (51), 82 (13), 81 (19), 79 (36), 77 (27), 69 (14), 68 (35), 67 (21), 55 (16).

**Palladium-Catalyzed Isomerization of 22b. A.** 3-Acetoxy-5-(acetoxymethyl)cyclohexene (**22b**) (25 mg, 0.117 mmol) was dissolved in 0.25 mL of $C_6D_6$ in a 5-mm NMR tube. A solution of $Pd(PPh_3)_4$ (25 mg, 0.021 mmol, 18.4%) in 0.25 mL of $C_6D_6$ was added. The tube was placed in the NMR probe (Bruker, 270-MHz spectrometer) at 32 °C and $^1H$ spectra were taken every 30 s. The concentration of starting material **22b**, as well as its isomer **25**, and diene **26** were followed by measuring the integrals of the following absorptions: 5.40 (**22b**); 5.27 (**25**); 3.93 (**26**). The results are given in Figure 1. Flash chromatography separation of the reaction mixture (8:1 hexane–ethyl acetate) afforded a 1:1 mixture of **22b** and **25**. **25**: NMR ($CDCl_3$) 5.99 (dm, $J$ = 9 Hz, 1 H), 5.81 (dm, $J$ = 9 Hz, 1 H), 5.25 (m, $W_{1/2}$ = 10 Hz, 1 H), 3.98 (d, $J$ = 6 Hz, 2 H), 2.12–2.25 (m, 3 H), 2.05 (s, 6 H), 1.86 (m, 1 H), 1.55 (m, 1 H).

**B.** The same experiment was repeated as for A with the same quantities except the temperature, which was kept at 6 °C. Spectra were recorded every 60 s. The result are given in Figure 2.

**3-Phenoxy-5-(acetoxymethyl)cyclohexene (23b, 24b). A.** Phenoxytributyltin (0.44 mL, 1.15 mmol) was added to a stirred solution of **22b** (195 mg, 0.92 mmol) and $Pd(PPh_3)_4$ (180 mg, 0.15 mmol) in 5 mL of THF. The mixture was stirred at room temperature for 20 min, after which no starting material **22b** could be detected by TLC. The solvent was removed by a stream of $N_2$ and the residue purified by flash chromatography (8:1 hexane–ethyl acetate), affording 190 mg (83%) of a 2:1 mixture of **23b** and **24b**: IR (neat) 3043, 2960, 1710, 1603, 1592, 1493, 1473, 1365, 1265, 1235, 1068, 1028, 888, 815, 755, 693; NMR (**23b**, cis isomer) 7.3 (m, 2 H), 6.9 (m, 3 H), 5.86 (br s, 2 H), 4.93 (m, $W_{1/2}$ = 20 Hz, 1 H), 4.00 (d, $J$ = 6 Hz, 2 H), 2.1–2.3 (m, 3 H), 2.05 (s, 3 H), 1.85 (m, 1 H), 1.55 (br q, $J$ = 11.5 Hz, 1 H), (**24b**, trans isomer) 7.3 (m, 2 H), 6.9 (m, 3 H) 5.99 (dm, $J$ = 10 Hz, 1 H), 5.90 (dm, $J$ = 10 Hz, 1 H), 4.81 (m, $W_{1/2}$ = 8 Hz, 1 H), 3.98 (d, $J$ = 6 Hz, 2 H), 2.1–2.3 (m, 3 H) 2.05 (s, 3 H), 1.85 (m, 1 H), 1.60 (m, 1 H).

**B.** The allylic acetate **22b** (25 mg, 0.117 mmol) and phenoxytributyltin (0.25 mmol) were dissolved in 0.25 mL of $C_6D_6$ in a 5-mm NMR tube. The solution was cooled to 6 °C and then mixed with cold (6 °C) solution of $Pd(PPh_3)_4$ (25 mg, 0.021 mmol, 18.4%) in 0.25 mL of $C_6D_6$. The tube was immediately placed in the cold (6 °C) NMR probe (Bruker 270-MHz spectrometer), and the first spectrum was taken 1 min after mixing. Spectra were taken every 30 s, and the reaction was followed by measuring the integrals of the following absorptions: 5.40 (**22b**): 4.93 (**23b**); 4.81 (**24b**); 3.93 (**26**). Absorptions related to isomeric allylic acetate **25** could not be detected in any of the spectra. The results are given in Figure 3.

**C.** The same experiment was carried out as in B except the probe temperature was kept at 32 °C. It was evident from the first five spectra that the substitution reaction was complete within 2.5 min (complete conversion of **22b** to **23b** and **24b**).

**Methyl 4,6-*O*-Benzylidene-2-*O*-cinnamyl-α-D-glucopyranoside (28) and Methyl 4,6-*O*-Benzylidene-3-*O*-cinnamyl-α-D-glucopyranoside (29).** Methyl-4,6-*O*-benzylidene-2,3-*O*-(dibutylstannylene)-α-D-glucopyranoside (**27**)[13d,24] (256 mg, 0.5 mmol) was added to a stirred solution of cinnamyl acetate (158 mg, 0.9 mmol) and $Pd(PPh_3)_4$ (138 mg, 0.12 mmol) in 3 mL of THF. The mixture was stirred at room temperature for 4 h. The solvent was removed by a stream of $N_2$ and the residue subjected to flash chromatography (7:3 hexane–ethyl acetate), affording two products in the form of white fluffy solids, which were recrystallized from hexane: **28** (93 mg, 47%), mp 115 °C; **29** (68 mg, 34%), mp 148 °C (**28** is less polar than **29**). **28**: NMR ($CDCl_3$) 7.51–7.21 (m, 10 H), 6.62 (br d, $J$ = 15.9 Hz, 1 H), 6.31 (dt, $J$ = 15.9, 6.0 Hz, 1 H), 5.53 (s, 1 H), 4.86 (d, $J$ = 3.5 Hz, 1 H), 4.38 (br t, $J$ = 5.9 Hz, 2 H), 4.27 (dd, $J$ = 9.7, 4.4 Hz, 1 H), 4.14 (t, $J$ = 9.2 Hz, 1 H), 3.81 (dt, $J$ = 9.3, 4.4 Hz, 1 H), 3.72 (t, $J$ = 9.7 Hz, 1 H), 3.52 (t, $J$ = 9.3 Hz, 1 H), 3.50 (dd, $J$ = 9.3, 3.5 Hz, 1 H), 3.44 (s, 3 H); MS, $m/e$ (relative intensity) 396 ($M^+ - 2$, 0.3), 373 (0.2), 270 (0.5), 149 (1.4), 131 (79), 117 (7), 105 (100), 103 (7), 91 (37), 77 (31). Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.33; H, 6.58. Found: C, 69.55; H, 6.59. **29**: NMR ($CDCl_3$) 7.50–7.20 (m, 10 H), 6.59 (br d, $J$ = 15.9 Hz, 1 H), 6.31 (dt, $J$ = 15.9, 6.1 Hz, 1 H), 5.55 (s, 1 H), 4.80 (d, $J$ = 3.6 Hz, 1 H), 4.55 (dd, $J$ = 12.9,

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6.1 Hz, 1 H), 4.44 (dd, $J$ = 12.9, 6.1 Hz, 1 H), 4.28 (dd, $J$ = 9.4, 3.6 Hz, 1 H), 3.86–3.66 (m, 4 H), 3.58 (t, $J$ = 9 Hz, 1 H), 3.44 (s, 3 H); MS, $m/e$ (relative intensity) 398 ($M^+$, 2.7), 335 (21), 285 (25), 221 (12), 201 (15), 149 (10), 133 (21), 117 (100), 107 (30), 105 (30), 91 (48), 87 (20), 77 (16). Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.33; H, 6.58. Found: C, 69.50; H, 6.44.

**Cinnamyl 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranoside (31).** **A.** Methoxytributyltin (1.69 g, 5.25 mmol) was added to a solution of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (**30a**) (2.69 g, 5 mmol) in dry benzene (30 mL). The clear solution was refluxed for 10 min, and then the solvent was removed by distillation. Removal of the last traces of solvent under reduced pressure afforded *O*-(tributylstannyl)-2,3,4,6-tetra-*O*-benzylglucopyranoside (**30b**) in the form of a white amorphous solid. This crude product was used without any further purification.

**B.** Tributylstannyl glucopyranoside **30b** (375 mg, 0.45 mmol) was added to a stirred solution of cinnamyl acetate (158 mg, 0.9 mmol) and $Pd(PPh_3)_4$ (139 mg, 0.12 mmol) in 5 mL of THF. The mixture was stirred at room temperature for 5 h and the residue subjected to flash chromatography (75:25 hexane–ethyl acetate), affording 150 mg (51%) of **31** in the form of colorless needles: NMR ($CDCl_3$) 7.42–7.06 (m, 25 H), 6.62 (br d, $J$ = 16.1 Hz, 1 H), 6.37 (dt, $J$ = 16.1, 5.7 Hz, 1 H), 5.23 (d, $J$ = 3.2 Hz, 1 H), 4.97–4.46 (m, 8 H), 4.33 (dd, $J$ = 5.7, 1.3 Hz, 2 H), 4.03 (br d, $J$ = 9.5 Hz, 1 H), 3.97 (t, $J$ = 9.5 Hz, 1 H), 3.74–3.50 (m, 3 H), 3.54 (dd, $J$ = 9.5, 3.2 Hz, 1 H).

**C.** 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranose (**30a**) (180 mg, 0.33 mmol) was added to a stirred solution of cinnamyl acetate (116 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (138 mg, 0.12 mmol) in 5 mL of THF. The mixture was stirred at room temperature and followed by TLC. No reaction was observed after 5 h. Less than 10% conversion of **30a** to **31** was detected after 24 h.

**Methyl 2,3,4-Tri-*O*-acetyl-β-*O*-cinnamylglucuronate (33).** Methyl 2,3,4-tri-*O*-acetyl-α-bromoglucuronate (**32**)[25] (423 mg, 1.1 mmol) was added to a stirred mixture of cinnamyl alcohol (152 mg, 1.13 mmol) and silver carbonate (200 mg, 0.72 mmol) in 5 mL of benzene. The mixture was stirred for 20 h at room temperature. The solid was removed by filtration and the solution washed with 2 N aqueous KOH and then with water and dried over $MgSO_4$. Removal of the solvent under reduced pressure afforded 200 mg of colorless oil, which was further purified by flash chromatography (65:35 hexane–ethyl acetate) to give 248 mg (50%) of **33**: NMR ($CDCl_3$) 7.40–7.22 (m, 5 H), 6.59 (br d, $J$ = 16 Hz, 1 H), 6.19 (dt, $J$ = 16, 6.0 Hz, 1 H), 5.25 (m, 2 H), 5.07 (m, 1 H), 4.66 (d, $J$ = 7.6 Hz, 1 H), 4.52 (dd, $J$ = 13.3, 6.0 Hz, 1 H), 4.28 (dd, $J$ = 13.3, 6.0 Hz, 1 H), 4.04 (m, 1 H), 3.75 (s, 3 H), 2.04 (s, 3 H), 2.01 (s, 6 H); IR (Nujol) 3020, 1755, 1735, 1460, 1450, 1375, 1245, 1210, 1155, 1070, 1037, 965, 910, 890, 860, 800; MS, $m/e$ (relative intensity) 333 (0.1), 317 (1.7), 257 (4.4), 215 (4.5), 197 (10), 155 (50), 139 (63), 133 (8.5), 117 (100).

**Methyl 2,3,4-Tri-*O*-acetyl-α-*O*-cinnamylglucuronate (36).** A solution of methyl 1,2,3,4-tetra-*O*-acetyl-β-glucuronate (**34**) (200 mg, 0.53 mmol) and $(Bu_3Sn)_2O$ (316 mg, 0.53 mmole in 3 mL of dichloroethane was refluxed for 3 h and then cooled to room temperature. Cinnamyl acetate (158 mg, 0.9 mmol) and $Pd(PPh_3)_4$ (90 mg, 0.08 mmol) were then added, and the solution was stirred at room temperature under $N_2$ for 20 h. The solvent was removed under reduced pressure, and the residue was subjected to flash chromatography (65:35 hexane–ethyl acetate), affording 52 mg (22%) of **36** and 26 mg (11%) of **33**: NMR ($CDCl_3$) (**36**) 7.42–7.28 (m, 5 H), 6.62 (br d, $J$ = 16 Hz, 1 H), 6.24 (dt, $J$ = 16, 6 Hz, 1 H), 5.55 (t, $J$ = 10 Hz, 1 H), 5.24 (d, $J$ = 3.5 Hz, 1 H), 5.18 (t, $J$ = 10 Hz, 1 H), 4.93 (dd, $J$ = 10, 3.5 Hz, 1 H), 4.40 (d, $J$ = 10 Hz, 1 H), 4.38 (dd, $J$ = 12, 6 Hz, 1 H), 4.22 (dd, $J$ = 12, 6 Hz, 1 H), 3.71 (s, 3 H), 2.04 (s, 3 H), 2.01 (s, 6 H); IR (Nujol) 3020, 1760–1730, 1460, 1440, 1370, 1250–1205, 1150, 1070–1020, 965, 910, 890, 860, 800; MS, $m/e$ (relative intensity) 333 (0.6), 317 (3), 257 (7), 215 (8), 197 (15), 155 (85), 139 (69), 133 (9), 117 (100).

**Cinnamyl 4,6-*O*-Ethylidene-2,3-di-*O*-acetylglucopyranoside (38).** A solution of 4,6-*O*-ethylidene-1,2,3-tri-*O*-acetyl-β-glucopyranose (**37**)[26] (160 mg, 0.48 mmol) and methoxytributyltin (202 mg, 0.63 mmol) in 5 mL of dichloroethane was refluxed for 3 h and then cooled to room temperature. Cinnamyl acetate (158 mg, 0.9 mmol) and $Pd(PPh_3)_4$ (130 mg, 0.11 mmol) were then added, and the solution was stirred at room temperature for 30 h. The solvent was removed under reduced pressure and the residue was subjected to flash chromatography (70:30 hexane–ethyl acetate), affording 75 mg (38%) of **38** as a 2:1 mixture of β and α anomers: NMR ($CDCl_3$) (β anomer) 7.4–7.19 (m, 5 H), 6.56 (br d, $J$ = 16 Hz, 1 H), 6.18 (dt, $J$ = 16, 6 Hz, 1 H), 5.19 (t, $J$ = 8.5 Hz, 1 H), 4.97 (t, $J$ = 8.5 Hz, 1 H), 4.69 (q, $J$ = 4.8 Hz, 1 H), 4.66 (d, $J$ = 8.5 Hz, 1 H), 4.47 (dd, $J$ = 13.3, 6 Hz, 1 H), 4.25 (dd, $J$ = 13.3, 6 Hz, 1 H), 4.18 (t, $J$ = 8.5 Hz, 1 H), 3.6–3.3 (m, 2 H), 3.37 (dd, $J$ = 10, 4.8 Hz, 1 H), 2.08 (s, 3 H), 2.06 (s, 3 H), 1.33 (d, $J$ = 4.8 Hz, 3 H), (α anomer) 7.4–7.19 (m, 5 H), 6.60 (br d, $J$ = 16 Hz, 1 H), 6.21 (dt, $J$ = 16, 6 Hz, 1 H), 5.52 (t, $J$ = 10 Hz, 1 H), 5.09 (d, $J$ = 4 Hz, 1 H), 4.84 (dd, $J$ = 10, 4 Hz, 1 H), 4.69 (q, $J$ = 4.8 Hz, 1 H), 4.34 (dd, $J$ = 12.3, 6 Hz, 1 H), 4.12 (dd, $J$ = 12.3, 6 Hz, 1 H), 4.14 (t, $J$ = 10 Hz, 1 H), 3.86 (dt, $J$ = 10, 4.8 Hz, 1 H). 3.6–3.3 (m, 2 H), 2.08 (s, 3 H), 2.06 (s, 3 H), 1.33 (d, $J$ = 4.8 Hz, 3 H); MS, $m/e$ nrelative intensity) 405 ($M^+ - 1$, 3), 317 (7), 287 (47), 273 (5), 213 (9), 169 (11), 155 (7), 139 (29), 133 (4), 127 (12), 117 (100), 109 (8), 97 (22).

**5,6-Benzo-1,10-dioxacyclododeca-3,7-diene (43).**[27] 1,1-Dibutyl-1-stanna-2,5-dioxacyclopentane (**39**)[19] (135 mg, 0.57 mmol) was added to a stirred solution of 1,2-bis(1-acetoxyprop-2-enyl)benzene (**41**) (155 mg, 0.57 mmol) (prepared from *o*-phthalaldehyde by reaction with vinylmagnesium bromide followed by acetylation with acetic anhydride–pyridine) and $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) in 5 mL of THF. The mixture was stirred at room temperature under $N_2$ atmosphere for 30 min, the solvent was then removed under reduced pressure, and the residue was subjected to preparative TLC (7:3 hexane–ethyl acetate), affording **43** ($R_f$ 0.2) as a colorless viscous oil (115 mg, 94%): NMR 7.43 (m, 4 H); 6.93 (dd, $J$ = 15.8, 1.8 Hz, 2 H), 6.11 (dt, $J$ = 15.8, 5.9 Hz, 2 H), 4.22 (dd, $J$ = 5.9, 1.8 Hz, 4 H), 3.78 (t, $J$ = 5.3, 2 H), 3.63 (t, $J$ = 4.7 Hz, 2 H); MS, $m/e$ (relative intensity) 216 ($M^+$, 11), 171 (3), 159 (5), 155 (30), 154 (48), 143 (25), 142 (57), 141 (78), 129 (57), 128 (100), 116 (17), 115 (45), 91 (15), 77 (15), 75 (49), 73 (58), 57 (11); IR (neat) 2900, 1600, 1430, 1350, 1070, 1060, 1020, 970, 885, 750, 720, 690.

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(27) More details concerning the preparation of compounds **44–46** will appear in ref 21.

(28) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

97372-94-6; **32**, 21085-72-3; **33**, 97337-66-1; **34**, 7355-18-2; **36**, 97337-67-2; **37**, 27994-30-5; β-**38**, 97337-68-3; α-**38**, 97337-69-4; **39**, 3590-59-8; **41**, 97337-70-7; **43**, 97337-71-8; $CH_3OSnBu_3$, 1067-52-3; $Pd(PPh_3)_4$, 14221-01-3; $CH_3OH$, 67-56-1; $CH_3ONa$, 124-41-4; $Bu_3SnOPh$, 3587-18-6; 1-phenyl-3-(4-bromophenyl)-3-hydroxy-1-propene, 1669-60-9; 4-methylpentan-2-one, 108-10-1; propanal, 123-38-6; 7-methyloct-3-en-5-one, 17577-93-4; cinnamyl alcohol, 104-54-1; 7-oxabicyclo[3.2.1]oct-2-en-6-one, 4720-83-6.

# Reductive Alkylation of Illinois No. 6 Coal. Chemical and Spectroscopic Evidence Concerning the Principal Oxygen-Containing Groups in the Coal

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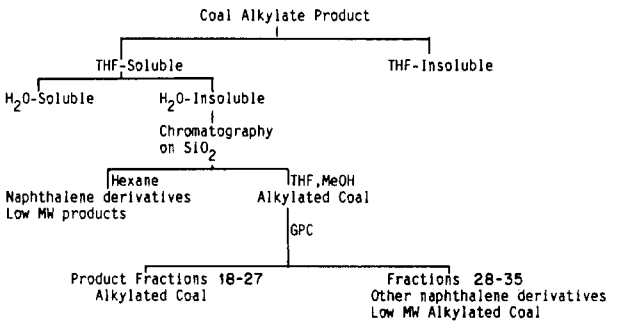
The reductive alkylation of a representative Illinois No. 6 high volatile bituminous coal from the Illinois No. 6 seam has been carried out with potassium naphthalene(-1) as the reducing agent and several primary alkyl iodides as the alkylating agents, and the properties of the soluble products have been investigated. Chemical and spectroscopic studies of the products obtained in reactions with methyl-$d_3$ and methyl-$^{13}C$ iodide indicate that only 2 ether linkages/100 C are cleaved in the reductive alkylation, that there are 5 C-alkylation and 7 O-alkylation reactions/100 C, and that there are 0.1 primary alkyl methyl ethers/100 C, 2.2 hindered aryl methyl ethers/100 C, 3.3 unhindered aryl methyl ethers/100 C, 0.6 unhindered dihydroxyaryl methyl ethers/100 C, and 0.8 methyl carboxylates/100 C. The nature of the oxygen-containing compounds in this coal is discussed.

Although CP MAS NMR spectroscopy, diffuse reflectance FTIR spectroscopy, and related methods for the study of solids provide important information about the structural elements of coal, it is clear that even more information could be obtained if the coal could be studied in homogeneous solution. Consequently, procedures for the conversion of the intractable solid into soluble products without significant degradation of the structure have long been sought. In some instances, this objective can be realized by reduction or by alkylation. For example, the reduction of a low volatile, bituminous coal from the Lower Kittaning Seam with 88% carbon(daf) with potassium in ammonia yields a product that is 90% soluble in pyridine.[1] Regrettably, the lower rank bituminous coals cannot be successfully solubilized with these procedures.[2] The most suitable method for these coals was discovered by Sternberg and his associates.[3,4] They found that many coals reacted with potassium naphthalene(-1) to form polyanions that could be alkylated. The reaction products are often quite soluble in common organic solvents such as tetrahydrofuran or pyridine and, as a consequence, can be investigated in homogeneous solution.[5]

A systematic study of a low rank bituminous coal from the Illinois No. 6 seam revealed that reductive alkylation with potassium naphthalene(-1) as the reducing agent provided a higher yield of soluble products than reductive alkylation with potassium in liquid ammonia or potassium–sodium alloy in glyme solvents.[2] A study of the reaction variables indicated that the reduction step was most effectively accomplished with potassium rather than lithium or sodium and with biphenyl or naphthalene rather than anthracene or other polycyclic aromatic hydrocarbons.[6] The reactivity patterns observed in the alkylation reactions, methyl iodide > butyl iodide and butyl iodide > butyl bromide > butyl chloride, established that the alkylation reaction was well characterized as an $S_N2$ process.[6] Although the structure of the alkylating agent often influences the solubility of the product, the methylation, butylation, and octylation of Illinois No. 6 coal yielded only modestly different amounts of soluble products.

**Scheme I**




The proton and carbon NMR spectra of the reductive methylation and butylation products of this Illinois coal have been reported.[6,7] However, the NMR data did not permit an unequivocal assignment of the interesting oxygen-containing structural elements even when the reactions were carried out with highly enriched reagents such as methyl-$^{13}C$ and butyl-1-$^{13}C$ iodide. Accordingly, we have extended our study by the investigation of the alkylated coals prepared with methyl-$d_3$ and methyl-$^{13}C$ iodide by using both chemical and spectroscopic methods to define the nature and quantity of the O-alkylated products.

## Results

The empirical formula of the representative Illinois No. 6 coal used in this study was $C_{100}H_{87.0}O_{13.1}S_{1.9}N_{0.75}$; it contained 8.2% ash. The reductive alkylation reaction was carried out as shown in eq 1 and 2.

$$\text{coal} \xrightarrow[5\text{ days, }25\text{ °C}]{\text{K, } C_{10}H_8\text{, THF}} \text{coal polyanion} \quad (1)$$

$$\text{coal polyanion} \xrightarrow[2\text{ days, }25\text{ °C}]{\text{RI, THF}} \text{coal alkylate product} \quad (2)$$

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(2) Stock, L. M. *Coal Sci.* **1982**, *1*, 210.
(3) Sternberg, H. W.; Delle Donne, C. L.; Pantages, P.; Moroni, E. C.; Markby, R. E. *Fuel* **1971**, *50*, 432.
(4) Sternberg, H. W.; Delle Donne, C. L. *Fuel* **1974**, *53*, 172.
(5) The results obtained from several laboratories have been reviewed in ref 2.
(6) Alemany, L. B.; Stock, L. M. *Fuel* **1982**, *61*, 250.
(7) Alemany, L. B.; Stock, L. M. *Fuel* **1982**, *61*, 1088.

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