public of Algeria, which has provided support for B.M. at Oregon State University.

Registry No. 1-Methylnaphthalene, 90-12-0; 2-methylnaphthalene, 91-57-6; 5-methylquinoline, 7661-55-4; 8-methylquinoline, 611-32-5; 7-methylquinoline, 612-60-2; 3-methylquinoline, 612-58-8; 3-methylpyridine, 108-99-6; 6-methylquinoline, 91-62-3; 2-methylpyridine, 109-06-8; 2-methylquinoline, 91-63-4; 4-methylquinoline, 491-35-0; 4-methylpyridine, 108-89-4; *tert*-butoxy radical, 3141-58-0; toluene, 108-88-3; H_2, 1333-74-0.

Supplementary Material Available: Tables of computed energy terms from HMO and SCF–PPP calculations (4 pages). Ordering information is given on any current masthead page.

Conformational Change Occasioned by Complexation: "Contra-Anomeric-Effect" Epimerization of 2-Methoxy-1,3-dioxanes in the Presence of Magnesium Bromide[1†]

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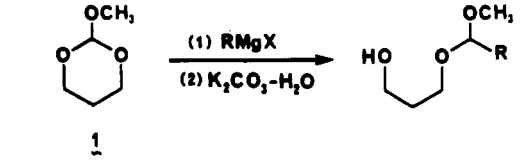
Received December 9, 1986

The complexation of 2-methoxy-1,3-dioxanes with $MgBr_2$ has been investigated in an effort to assess the conformational consequences of binding acidic reagents to small, basic molecules with well-defined conformational minima. Anhydrous $MgBr_2$ has been found to catalyze the epimerization of anancomeric 2-methoxy-1,3-dioxanes and form a 1:1 complex with the ortho esters containing a preponderance (>91%) of the thermodynamically less stable, equatorially substituted 2-methoxy-1,3-dioxane. Preferential coordination of $MgBr_2$ with the "contra-anomeric-effect" epimer having an equatorial 2-OCH_3 provides at least 1.7 kcal/mol of driving force for conformational change. These observations suggest that reagent–substrate complexation can affect the outcome of reactions subject to stereoelectronic control.

Several years ago we reported[2] that the reaction of 2-methoxy-1,3-dioxane (1) with Grignard reagents does not follow the course suggested by the reactions of anancomeric models for the conformational isomers of 1.[3] The failure



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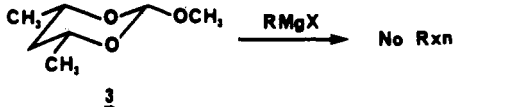

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of the biased models 2 and 3 to reflect the behavior of the conformationally mobile substrate in this prototypical example of a stereoelectronically controlled reaction[4] was attributed to complexation between 1 and the Grignard reagent to give a species having the 2-OCH_3 group effectively "locked" in an equatorial orientation.[2,5]

The results of these studies suggested that dramatic conformational change occasioned by reagent–substrate complexation may have a profound effect on the outcome of reactions subject to stereoelectronic control. In an effort to assess the conformational consequences of binding acidic reagents to small, basic substrates with well-defined conformations, we have explored the behavior of cyclic ortho esters in the presence of Mg^{2+} species.

The ability of ethers to solvate Mg^{2+} ions has been known for more than 80 years.[6] Much of the pioneering work on complex formation between alkaline earth cations and Lewis-type bases was reported by Menschutkin in a remarkable series of papers published at the beginning of this century.[7] Due to the reactivity of RMgX with ortho esters, we have employed $MgBr_2$ in our model studies and have, perforce, repeated much of this early work on "etherates" (a term coined by Menschutkin to describe solvates that involve ether-like oxygen atoms)[7-10] of Mg^{2+}

† Dedicated to Professor Ernest L. Eliel on the occasion of his 65th birthday.

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(5) The fact that model compound 3 is inert to RMgX under conditions leading to endocyclic cleavage of the C(2)–O bond in 1 led to the suggestion[2] that equatorial methyl substituents at C(4) and C(6) in 3 shield the ring oxygens from the approach of the Grignard reagent. This scenario finds support in the observation that *cis*-2-methoxy-4-methyl-1,3-dioxane undergoes cleavage of the endocyclic C(6)–O bond when treated with RMgX: Bailey, W. F.; Croteau, A. A., manuscript in preparation. For a related example, indicating the importance of steric interactions in determining the course of endocyclic C–O bond cleavage in similar systems, see: Bailey, W. F.; Rivera, A. D. *J. Org. Chem.* **1984**, *49*, 4958.
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Table I. Isomerization of 2-Methoxy-1,3-dioxanes

entry	ortho ester[a]	mol equiv $MgBr_2 \cdot OEt_2$	Et_2O, mL	reactn time, h	rec ortho ester,[b] %	cis epimer,[c] %
1	4 + 5	0.70	5	16	65	74
2		0.70	0	16	55	71
3		0.85	5	4	73	82
4		1.00	5	4	74	87
5		1.20	5	0.5	82	85
6		1.20	5	1.5	73	90
7	*d*	1.20	5	3	65	91
8		1.20	5	16	59	87
9	*e*	1.20	0	16	55	91
10		1.20	5	27	50	92
11		1.20	34	3	79	80
12		1.50	5	5	59	91
13		2.00	5	4	50	91
14		3.00	5	4	28	93
15		3.70	20	3	76	89
16	2 + 3	1.20	5	0.5	80	88
17		1.40	5	27	30	96
18	6 + 7	1.00	20	3	70	78
19		1.30	5	3	65	93

[a] Typically, 17–20 mmol of an equilibrium mixture of 2-methoxy-1,3-dioxanes (ca. 65% trans and 35% cis isomer)[11] unless otherwise indicated. [b] Isolated yield of distilled material. [c] Proportion of cis isomer (**3**, **5**, **7**) in recovered material. [d] Contained 97% **4** + 3% **5**. [e] Contained 90% **4** + 10% **5**.

salts and ortho esters. Herein we report rather dramatic evidence for the ability of $MgBr_2$ to alter the preferred conformation of an ortho ester. As detailed below, coordination of $MgBr_2$ with a 2-methoxy-1,3-dioxane provides at least 1.7 kcal/mol of driving force for conformational change and results in formation of a complex with the "contra-anomeric-effect" epimer.

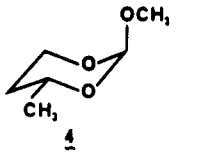
Results and Discussion

Addition of 2-methoxy-1,3-dioxane (**1**) to a solution of $MgBr_2$ in diethyl ether results in the formation of a viscous, immiscible layer. While it would seem a simple matter to isolate, purify, and characterize this etherate, all such attempts proved fruitless.[1] The material is virtually intractable: it could not be induced to crystallize, and any solvent in which it is soluble leads, as expected,[7,8] to destruction of the complex by displacement of the ortho ester by the more basic solvent molecules. Thus, solvents such as CH_3CN displace the ortho ester from $MgBr_2$, while less basic liquids such as ethers do not dissolve the complex. Direct analysis of the magnesium and ortho ester content of the complex using a variety of methods[1] gave irreproducible results due to the rather rapid reaction of ortho ester with $MgBr_2$ to give bromine-containing products.[1] For these reasons, indirect methods were employed to characterize the solvates formed upon addition of anancomeric 2-methoxy-1,3-dioxanes to ethereal solutions of $MgBr_2$.

Preliminary investigation of the complex formed upon addition of an anancomeric 2-methoxy-1,3-dioxane to an ethereal solution of $MgBr_2$ led to the serendipitous discovery that the viscous complex invariably contained a preponderance of the less stable epimer. Regardless of the isomeric composition of the 2-methoxy-1,3-dioxane employed in an experiment, the resulting complex was found to contain much more of the less stable, equatorial 2-methoxy isomer than was initially present. This observation suggests a $MgBr_2$-catalyzed epimerization of the ortho ester and preferential formation of a complex containing the equatorially substituted 2-methoxy-1,3-dioxane.

The ability of $MgBr_2$ to cause isomerization of acid-labile 2-methoxy-1,3-dioxanes is not without precedent. More strongly acidic reagents such as BF_3 and Amberlyst-15 have been used by Eliel and co-workers to equilibrate anancomeric 2-methoxy-1,3-dioxanes,[11] and an entirely analogous mechanism is undoubtedly responsible for epimerization in the presence of $MgBr_2$. The formation of a complex containing a predominance of the 2-methoxy-1,3-dioxane having an equatorially situated 2-OCH_3 is, however, somewhat surprising, since the axial 2-OCH_3 isomer is the more stable[11] due to the anomeric effect.[12] In this sense, treatment of 2-methoxy-1,3-dioxanes with $MgBr_2$ results in a contra-anomeric-effect isomerization.

The composition of the complex formed from various combinations of $MgBr_2$ and three pairs of anancomeric 2-methoxy-1,3-dioxanes (**2**–**7**) was assessed indirectly by hydrolysis of the solvate (10% aqueous NaOH) and analysis of the recovered ortho ester. The results of these studies are summarized in Table I.



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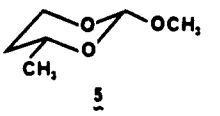

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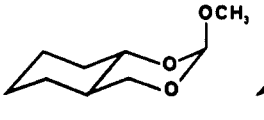

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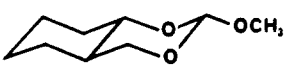

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The data in Table I demonstrate that the ratio of $MgBr_2$ to 2-methoxy-1,3-dioxane has an effect on the proportion of *cis*-2-methoxy isomer recovered from the complex. A plot of the percentage of cis isomer **5** in recovered 2-methoxy-4-methyl-1,3-dioxanes as a function of the quantity of $MgBr_2$ added is shown in Figure 1. Clearly, 1 equiv of $MgBr_2$ is needed to convert the 2-methoxy-4-

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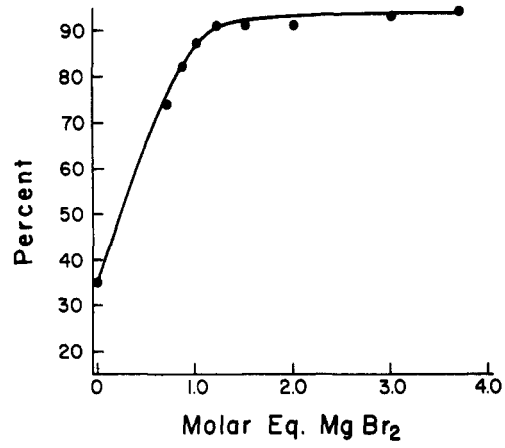
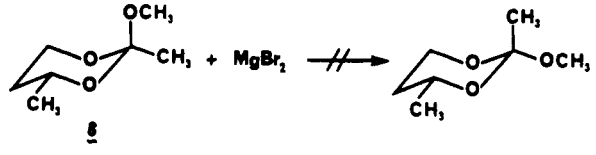


Figure 1. Percent of cis isomer **5** present in the 2-methoxy-4-methyl-1,3-dioxanes recovered from treatment with magnesium bromide as a function of the quantity of magnesium bromide added.

methyl-1,3-dioxanes into a complex containing a high proportion (91 ± 4%) of the cis isomer **5**. This result strongly implies a 1:1 stoichiometry for the complex between $MgBr_2$ and **5**. Entirely analogous results were obtained when other 2-methoxy-1,3-dioxanes were treated with $MgBr_2$ (Table I, entries 16–19).

It should be noted that the proportion of cis isomer in the ortho ester recovered from the complex is a *minimum value*, since epimerization to the thermodynamically more stable trans isomer will occur in the presence of even the weakest acids.[3,11] We have measured the acid-catalyzed equilibrium of **4** ⇌ **5** in diethyl ether solvent at 25 °C using Amberlyst-15 as the catalyst and find, as reported by Eliel and co-workers,[11] that the axially substituted ortho ester is the more stable by $\Delta G^\circ = 0.36 \pm 0.02$ kcal/mol. A measure of the energy change provided by complexation with $MgBr_2$ can be approximated by comparison of the partitioning constant for precipitation of complexed **5** from a solution of essentially pure **4** ($K > 91/9 = 10.1$; Table I, entry 7) with the equilibrium constant for **4** ⇌ **5** in solution ($K = 0.55$). Thus, complexation of the ortho ester provides *at least* 1.7 kcal/mol of driving force for conformational change.

An upper limit on the energy change associated with complexation is provided by the observation that orthoacetate **8** is not epimerized by $MgBr_2$. Treatment of **8** with 1.2 equiv of $MgBr_2$ for 0.5 h results in no detectable isomerization: 72% of **8** was recovered unchanged, and bromine-containing decomposition products accounted for the remaining material. Since **8** is more stable than its epimer by at least 4 kcal/mol,[13] this result suggests that the energetic preference for complex formation with a 2-methoxy-1,3-dioxane having an equatorial 2-OCH_3 is certainly less than this value.



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(13) The energy difference between **8** and its epimer can be approximated as 4.34 kcal/mol by assuming additivity of conformational free energies: the ΔG° values (axial → equatorial) for a 2-CH_3 and 2-OCH_3 group are −3.98[11] and +0.36 kcal/mol. The actual energy difference between **8** and its epimer is unknown, but the true value may well be larger than that calculated due to additional gauche interactions present in the *gem*-disubstituted compounds. For a discussion of the assumptions inherent in calculations based on additivity of conformational free energies, see: Eliel, E. L.; Enanoza, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8072.

The experiments outlined in Table I also indicate that long reaction times (Table I, entries 8–10, 17) or high molar ratios of $MgBr_2$ to ortho ester (Table I, entries 13, 14) result in a low recovery of ortho ester due to $MgBr_2$-induced decomposition. Not surprisingly, diethyl ether competes with 2-methoxy-1,3-dioxanes for coordination with $MgBr_2$.[7,8] Use of large volumes of ether leads to higher total recoveries of ortho ester but decreases in the cis isomer content (Table I; compare entries 7 and 11, 14 and 15). Significantly, the proportion of cis isomer in the recovered 2-methoxy-1,3-dioxane remains essentially invariant at ca. 90%, provided that at least 1 equiv of $MgBr_2$ is in contact with the ortho ester for 1.5 h or more.

The possibility that the high proportion of equatorial 2-OCH_3 isomer in the complex was due to preferential destruction of the trans isomer by reaction with $MgBr_2$ was considered but excluded on the basis of the fact that the total recovery of cis isomer often greatly exceeds the amount initially present (Table I). Indeed, the epimerization was successfully conducted on a preparative (i.e., 16-g) scale, resulting in conversion of an equilibrium mixture of the isomeric bicyclic ortho esters **6** and **7** into 88% isomerically pure **7** in 81% isolated yield.

The fact that the magnesium bromide complexes of anancomeric 2-methoxy-1,3-dioxanes contain the less stable ortho ester having an equatorial 2-methoxy group is strong evidence that the exocyclic (methoxy) oxygen is involved in coordination with magnesium in these complexes. Were this not the case, it would be difficult to account for the driving force leading to virtually complete isomerization of the axially substituted ortho esters **2**, **4**, and **6** to their equatorially substituted epimers **3**, **5**, and **7** upon treatment with $MgBr_2$. In view of the data presented in Figure 1 establishing a 1:1 stoichiometry for complexation of $MgBr_2$ with **5**, it is tempting to propose a structure for the complex that involves a tetracoordinate magnesium with the ortho ester acting as a bidentate ligand. This proposal is at best tentative, since although tetracoordination is common for Mg^{2+}, solvates are known with both higher and lower coordination numbers.[9] Alternatively, the stoichiometry may reflect the average composition of a solvate in which the ortho ester acts as a bridging ligand between $MgBr_2$ units.

The fact that $MgBr_2$ complexes preferentially with the less stable, contra-anomeric-effect epimer of a 2-methoxy-1,3-dioxane lends credence to the suggestion that the behavior of 2-methoxy-1,3-dioxane (**1**) when treated with a Grignard reagent[2] (vide supra) is the result of a two-step process: complexation of **1** with a Mg^{2+} species ($RMgX$, MgX_2, R_2Mg), followed by stereoelectronically favorable[4] cleavage of the endocyclic C(2)–O bond of the equatorial conformer of **1**. More generally, the results presented above indicate that reagent–substrate complexation can affect the outcome of reactions subject to stereoelectronic control.[4] Indeed, it is precisely such reactions, involving basic substrates and acidic reagents, that are most likely to involve formation of a reagent–substrate complex. Consequently, the assumption, implicit in many studies of reactions subject to stereoelectronic control,[4] that conformationally mobile substrates will follow the course suggested by the behavior of conformationally biased models should be made with caution where conformational change may be occasioned by complexation of reagent with substrate prior to reaction.

Experimental Section

Melting points and boiling points are uncorrected. Boiling points reported for bulb-to-bulb distillations (Kugelrohr) refer to bath temperatures. Proton magnetic resonance spectra were

recorded in $CDCl_3$ solution on Varian EM-360 or Bruker WH-90 instruments, and shifts are referenced with respect to internal Me_4Si. Carbon-13 magnetic resonance spectra were obtained in $CDCl_3$ solution with a Bruker WH-90 spectrometer; shifts are referenced with respect to internal Me_4Si, and peak multiplicities are reported for off-resonance, proton-decoupled spectra. Analytical gas–liquid chromatography (GLC) was accomplished on a Perkin-Elmer Model 3920B instrument fitted with flame-ionization detectors and 10-ft, 10% FFAP on Chromosorb W NAW (60/80-mesh) columns. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

All operations involving magnesium bromide were conducted in an atmosphere of dry argon inside a glovebag using glassware that had been dried at 140 °C for at least 3 h and allowed to cool in an atmosphere of dry argon. Diethyl ether (Mallinckrodt, anhydrous) was freshly distilled under argon from dark purple solutions of sodium/benzophenone. Magnesium bromide monoetherate was either prepared by the method of Ashby and Arnott[14] or obtained commercially (Aldrich), and the $MgBr_2$ to ether ratio of samples was determined by EDTA titration of magnesium using Eriochrome T as indicator.

Quantities of *meso*-2,4-pentanediol were prepared as previously described,[12] and *trans*-2-(hydroxymethyl)cyclohexanol [bp 101–105 °C (1.5 mm) [lit.[15] bp 104–105 °C (0.7 mm)]] was obtained by methanolysis of *trans*-2-(acetoxymethyl)-1-(acetoxymethoxy)-cyclohexane.[16] The 2-methoxy-1,3-dioxanes (**2–5, 8**) were prepared following the method of Eliel and Nader.[3]

***t*-2-Methoxy- and *c*-2-Methoxy(*r*-4a,*t*-8a)-1,3-dioxadecahydronaphthalene (6 and 7, Respectively).** A solution of 29.1 g (223 mmol) of *trans*-2-(hydroxymethyl)cyclohexanol and 29.4 g (280 mmol) of trimethyl orthoformate in 40 mL of cyclohexane containing a catalytic quantity of *p*-toluenesulfonic acid was heated with stirring, and the azeotrope of cyclohexane/methanol was removed through a short Vigreux column until the still head temperature reached 80 °C. At this point heating was stopped, the mixture was cooled to room temperature and stirred with 1.5 g of anhydrous K_2CO_3 to neutralize the acid catalyst. The suspension was filtered, the solid was washed well with ether, and the solvents were removed at reduced pressure (ca. 20 mm). The residue was distilled through a short Vigreux column to give 31.6 g (84%) of product as a mixture of isomers, bp 118–126 °C (20 mm). Separation of the epimeric ortho esters was accomplished by fractional distillation of the mixture through a 40 × 1.5 cm vacuum-jacketed spinning-band column fitted with a Teflon band and operating at a reflux ratio of 20:1. Distillates were collected and stored over small quantities of anhydrous K_2CO_3. The lower boiling (axial 2-OCH_3) *t*-2 isomer (**6**) was collected [bp 91–93.5 °C (10 mm)] and the pot residue was distilled with a Kugelrohr apparatus to give the higher boiling (equatorial 2-OCH_3) *c*-2 epimer (**7**) [bath temperature 115–130 °C (20 mm)]. Analytical samples of **6** and **7** were obtained by preparative GLC on a 10-ft, 15% FFAP on Chromosorb W NAW (60/80-mesh) column at 180 °C, and their structures were established on the basis of the following data.

***c*-2-Methoxy(*r*-4a,*t*-8a)-1,3-dioxadecahydronaphthalene (7):** IR (neat) 1450, 1368, 1310, 1210, 1150, 1130, 1075, 1060, 1005, 920, 870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.17 (s, 1 H), 3.94 (dd, J = 4.0, 10.0 Hz, 1 H), 3.60–3.13 [overlapping patterns, i.e., 3.60–3.13 (m, 2 H), 3.43 (s, 3 H)], 2.10–0.70 (br m, 9 H); ^{13}C NMR ($CDCl_3$) δ 112.2 (d, C(2)), 79.4 (d, C(8a)), 70.0 (t, C(4)), 52.6 (q, OCH_3), 40.1 (d, C(4a)), 31.3 (t), 25.6 (t), 25.0 (t), 24.4 (t). Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.81; H, 9.14.

***t*-2-Methoxy(*r*-4a,*t*-8a)-1,3-dioxadecahydronaphthalene (6):** IR (neat) 1450, 1390, 1345, 1208, 1138, 1075, 1032, 990, 958 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.28 (s, 1 H), 3.92–3.29 [overlapping patterns, i.e., 3.92–3.29 (m, 3 H), 3.29 (s, 3 H)], 1.86–0.80 (br m, 3 H); ^{13}C NMR ($CDCl_3$) δ 109.3 (d, C(2)), 72.1 (d, C(8a)), 63.5 (t, C(4)), 52.6 (q, OCH_3), 40.8 (d, C(4a)), 31.4 (t), 26.3 (t), 25.2 (t), 24.7 (t). Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 63.03; H, 9.24.

General Procedure for Epimerization of 2-Methoxy-1,3-dioxanes. A 250-mL Erlenmeyer flask was charged with a weighed amount of magnesium bromide monoetherate and a measured volume of anhydrous ether (Table I). Dissolution of the magnesium bromide was effected by gentle agitation. When small volumes of ether were used, homogeneous dissolution was not achieved; rather, a two-phase mixture with a viscous bottom layer formed.[10] The desired amount of 2-methoxy-1,3-dioxane was weighed into the flask, and the flask was closed with a septum cap. The contents of the flask were mixed by gentle agitation at periodic intervals during the course of the reaction period. The capped argon-filled flask was removed from the glovebag and chilled in an ice bath for 15 min, and the mixture was stirred vigorously with a glass rod as 40 mL of ice-cold 10% aqueous sodium hydroxide was added to hydrolyze the magnesium bromide. The resulting suspension was extracted with two 40-mL portions of ether, and the combined ethereal extracts were dried ($MgSO_4$). The drying agent was removed by filtration into a flask containing a small amount of anhydrous K_2CO_3 to avoid epimerization of the isomeric 2-methoxy-1,3-dioxanes by adventitious acid. The filtrate was concentrated by rotary evaporation, and the residue was distilled with a Kugelrohr apparatus. The distillate was collected over a small quantity of anhydrous K_2CO_3. Quantitiative analyses of the product mixtures were performed by GLC analysis and/or by integration of the ^1H NMR absorptions due to the methoxy or H(2)-methine protons of the isomeric 2-methoxy-1-3-dioxanes. GLC analyses of the product mixtures were conducted with 10-ft, 10% or 15% FFAP on Chromosorb W NAW (60/80-mesh) columns using temperature programming (initial temperature 100 °C for 2 min, heating rate 16 °C/min, final temperature 200 °C for 2 min). The trans isomers (axial 2-methoxy) of the ortho esters employed in the study had the shorter retention times on both columns.

Acknowledgment. This investigation was supported by a grant from the Research Foundation of the University of Connecticut. We thank Allan Croteau for preparing several of the ortho esters used in this study.

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