involved in cuprate coupling reactions. The values are highly sensitive to solvent polarity; waves that are considerably more negative are observed in nonpolar media. A true indication of the reducing power of organocuprates, routinely employed in ethereal solvents, has been determined. In THF, secondary iodides give two distinct values, whereas the corresponding bromides afford only a single wave at far more negative potentials. This finding is in line with the anticipated propensity of an iodide to undergo a one-electron reduction to afford an intermediate (free) radical that can racemize at carbon. The results also indicate that with tosylates *in THF* the electron sink is at sulfur. As it is the S–O bond that ultimately is broken electrochemically, this suggests that, in their substitution reactions, these substrates participate in a direct two-electron (oxidative addition) process with organocopper(I) reagents.

Experimental Section

Procedures. Tetramethylammonium tetrafluoroborate (TMAF, electrometric grade, Southwest Analytical Co.) was used without further purification. Tetra-*n*-butylammonium tetrafluoroborate (TBAFB, electrometric grade, Southwest Analytical Co.) was recrystallized (200 mmol) once from 180 mL of ethyl acetate and 100 mL of pentane; the resulting white crystals were dried in a vacuum oven (8 torr, room temperature) for 48 h: mp 162–162.5 °C (lit.[22] mp 162.5 °C). Both salts were stored in a desiccator over Drierite (50:50 mixture of indicating and nonindicating, W.A. Hammond Drierite Co., 8 mesh). *N,N*-Dimethylformamide (DMF, Mallinckrodt) was first magnetically stirred over calcium hydride (Alfa) under a nitrogen atmosphere for at least 36 h. Stirring was discontinued and the calcium hydride allowed to settle (ca. 24 h) under a nitrogen atmosphere. The supernatant liquid was decanted and then distilled at reduced pressure (55 °C, 19 torr) from anhydrous copper sulfate (Aldrich, used as received and stored in a vacuum desiccator) onto activated 3A molecular sieves. This distillate was then passed through a column of activated alumina and stored over 3A molecular sieves and activated alumina under an argon atmosphere in the dark.

Dioxane (Aldrich), 1,2-dimethoxyethane (DME, Aldrich), and spectral-grade acetonitrile (CH_3CN, Mallinckrodt) were distilled from calcium hydride at atmospheric pressure and then passed through a column of activated alumina under an argon atmosphere in the dark. Tetrahydrofuran (THF, Mallinckrodt) was distilled from a calcium hydride prestill and finally from sodium benzophenone ketyl.

Cyclohexyl iodide, 1-iodoheptane, *tert*-butyl iodide, cyclohexyl bromide, 1-bromoheptane, and *tert*-butyl bromide were all commercially available. 2-Iodo- and 2-bromooctane were both prepared according to the method of Coulson et al. from 2-octanol.[23] All iodides were distilled from neutral alumina at reduced pressure prior to use and protected from light; the bromides were distilled at atmospheric pressure. Methyl crotonate and cyclohexenone were commercially available and were used without further purification.

Mesylates were prepared according to the method of Crossland et al.[24] using the appropriate alcohol, triethylamine, and methanesulfonyl chloride; tosylates were formed from the corresponding alcohols in pyridine containing *p*-toluenesulfonyl chloride.[25]

Apparatus. A three-compartment cell was used for cyclic voltammetry (CV) studies. The reference and auxiliary electrode compartments were separated from the working electrode compartment by fine-porosity sintered-glass frits. The working electrode was a mercury drop suspended on a mercury-plated platinum wire. The reference electrode was a saturated calomel electrode (SCE). The auxiliary electrode was a platinum wire. The solutions analyzed were $1–16 \times 10^{-3}$ M in substrate with 0.1 M TBAFB in either DMF, CH_3CN, or THF as the solvent. Cyclic voltammograms were obtained with a Bioanalytical Systems Inc. CV-II wave generator and a Houston 200 X-Y recorder. Typical scans were run at 100 mV/s.

Acknowledgment. Financial support supplied by the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the American Cancer Society (JFRA No. 37 to B.H.L.) is gratefully acknowledged.

Registry No. Cyclohex-2-en-1-one, 930-68-7; methyl crotonate, 623-43-8; 1-bromoheptane, 629-04-9; 1-iodoheptane, 4282-40-0; 2-bromooctane, 557-35-7; 2-iodooctane, 557-36-8; cyclohexyl bromide, 108-85-0; cyclohexyl iodide, 626-62-0; *tert*-butyl bromide, 507-19-7; *tert*-butyl iodide, 558-17-8; 2-pentanol tosylate, 3813-69-2; 3-ethenyl-1-butanol tosylate, 25163-50-2; 5-norbornene-2-methanol mesylate, 86646-41-5; tetra-*n*-butylammonium tetrafluoroborate, 429-42-5.

(22) House, H. O.; Feng, E.; Peet, N. P. *J. Org. Chem.* **1971**, *36*, 2371.

(23) Coulson, E. J.; Gerrard, W.; Hudson, H. R. *J. Chem. Soc.* **1965**, 2364.

(24) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.

(25) Fieser, L.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 1180.

Electrophilic Addition of *p*-Nitrobenzenesulfonyl Peroxide to 3,4-Dihydro-2*H*-pyran

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The addition of *p*-nitrobenzenesulfonyl peroxide to 3,4-dihydro-2*H*-pyran (DHP) in alcohols gives high yields of 3-[[(*p*-nitrophenyl)sulfonyl]oxy]-2-alkoxytetrahydropyrans. The stereochemistry of the addition process is dependent on the steric bulk of the attacking alcohol. For small alcohols, trans addition predominates, while bulky alcohols give mostly cis product. The results are compared with analogous haloalkoxylations of DHP.

Our interest in electrophilic additions of sulfonyl peroxides to olefins[1] prompted us to examine their reactions with 3,4-dihydro-2*H*-pyran (DHP). Besides serving as a model for sulfonyl peroxide addition to electron-rich olefins, this system could be used prototypically to develop a method for preparing α-substituted acetals and ketals of current interest from vinyl ethers[2] (eq 1). Furthermore, we hoped to exploit the good leaving properties of the

(1) Hoffman, R. V.; Bishop, R. D. *Tetrahedron Lett.* **1976**, 33.

(2) Creary, X.; Rollin, A. J. *J. Org. Chem.* **1977**, *42*, 4231.

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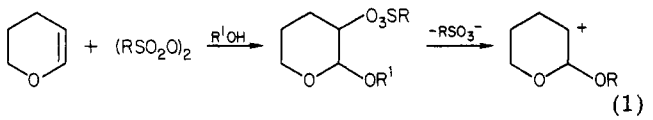
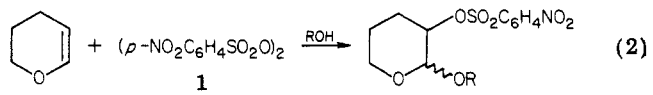


(1)

sulfonyloxy group in subsequent cationic transformations of the pyran system[3] (eq 1). We report here that, indeed, *p*-nitrobenzenesulfonyl peroxide undergoes efficient addition to DHP in the presence of alcohols or other nucleophilic solvents to yield α-sulfonyloxy acetals.

Results

The addition of *p*-nitrobenzenesulfonyl peroxide (**1**, pNBSP) to solutions of dihydropyran in hydroxylic solvents at 0 °C led to a rapid loss of active oxygen (<10 min). Upon workup, high yields (65–90%) of the 1,2-addition products were obtained (eq 2). Products were isolated as mixtures of the cis and trans isomers.



(2)

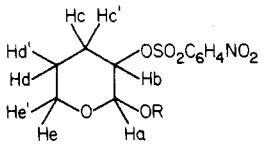
1

2a, R = H
b, R = CH_3
c, R = CH_2CH_3
d, R = $CH(CH_3)_2$
e, R = $C(CH_3)_3$
f, R = $COCH_3$
g, R = CH_2CF_3

The assigned structures of the adducts were consistent with their spectra. All of these cis–trans mixtures had similar IR spectra with bands indicating aliphatic and aromatic C–H's (2960 and 3120 cm^{-1}), the nitro group (1540 cm^{-1}), the sulfonyloxy group (1365 and 1190 cm^{-1}), and the acetal group (~970 cm^{-1} variable). Furthermore, lactol **2a** had a broad O–H band at 3300 cm^{-1} while acetate **2f** showed a strong carbonyl absorption at 1765 cm^{-1}.

The mass spectra of these adducts **2** had several common features that were indicative not only of the structural components but also of a consistent fragmentation pattern throughout the series. While none gave parent ions, all gave ions at *m/e* 286 and 186 for the loss of the alkoxy group from the parent ion and the *p*-nitrobenzenesulfonyl cation,[4] respectively. The majority of the adducts **2** had a base peak at *m/e* 71.[5] The major fragmentation pathways resulting in these ions are shown in Scheme I.

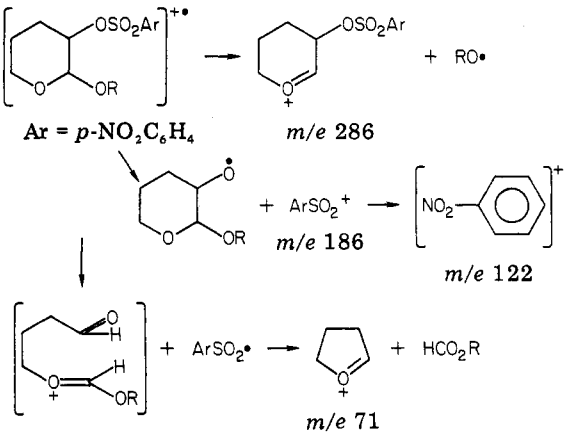
Most helpful were the ^{1}H-NMR spectra of products, which not only indicated their gross structure but yielded the cis:trans ratio by integration. All products **2** had a



2

four-proton aromatic quartet centered at δ 8.3 and a broad four-proton multiplet at δ ~1.8 with a shoulder at 2.1 that

Scheme I. Fragmentation in 3-[[(*p*-Nitrophenyl)-sulfonyl]oxy]-2-alkoxytetrahydropyrans (**2**)

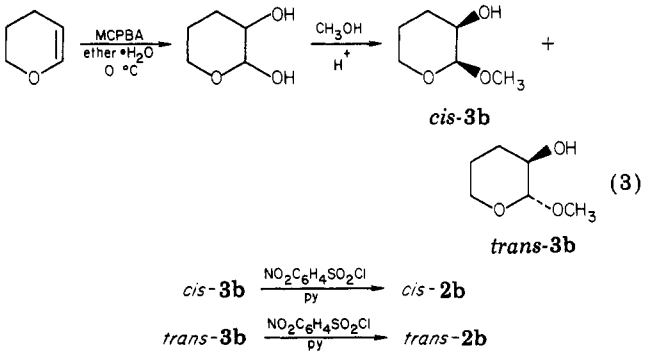


is assigned to the ring protons Hc,c′,d,d′. The ether protons He, He′, and Hb gave complex multiplets between δ 3–4. The anomeric proton Ha gave two doublets, one each for the cis and trans isomers, whose areas totalled one proton. Furthermore, the alkoxy group (OR) resonances were found at characteristic positions but also gave two different absorptions for the cis and trans isomers. Thus the structures of **2** are fully consistent with all the spectral data.

The cis–trans composition of the isomeric mixtures were also determined from their NMR spectra. Anomeric protons in cis 2,3-disubstituted tetrahydropyrans are generally found downfield from those in trans isomers and have smaller coupling constants.[6] In the present case, the anomeric protons in **2** were downfield from the other ring protons (except **2b,c**), the cis peak was at lower field than the trans peak and J_{cis} = 3–4 Hz was smaller than J_{trans} = 5–6 Hz.

Since in some cases the anomeric protons were insufficient for determining the cis:trans ratio, and since the methyl groups of the various alkoxy groups in **2** (-OCH_3, -OCH_2CH_3, -$OCH(CH_3)_2$, -$OC(CH_3)_3$, -$OCOCH_3$) gave individual signals for the cis and trans isomers, it was necessary to correctly assign the relative shift positions of the alkoxy methyl protons in the cis and trans isomers. The alkoxy methyl group was always found at lower field in the cis isomer spectrum than in the trans isomer spectrum. This assignment was made by the following correlations.

Tetrahydropyran-2,3-diol[6c] was treated with acidic methanol. Exchange of the anomeric hydroxyl group gave a mixture of *cis*- and *trans*-**3b** (eq 3), which was separated



(3)

by gas chromatography. Conversion of each isomer to the *p*-nitrobenzenesulfonate revealed that *cis*-**3b** gave *cis*-**2b**

(3) McKillop, A.; Hunt, J. D.; Kienzle, F.; Bigham, E.; Taylor, E. C. *J. Am. Chem. Soc.* **1973**, *95*, 3635.

(4) A common fragment of arylsulfonate esters $ROSO_2Ar$ is the arylsulfonyl cation, $ArSO_2^+$. See, for example: Dannley, R. L.; Hoffman, R. V.; Tornstrom, P. K.; Waller, R. L.; Strivastava, R. B. *J. Org. Chem.* **1974**, *39*, 2543.

(5) Products **2e** and **2f** had *m/e* 71 as the second most abundant ion. The base peaks were *m/e* 57 for **2e** and *m/e* 43 for **2f**, which correspond to the loss of the very stable *t*-Bu cation and the acetyl cation, respectively.

(6) (a) Hall, L. D.; Manville, J. F. *Can. J. Chem.* **1969**, *47*, 361. (b) Sweet, F.; Brown, R. K. *Ibid.* **1968**, *46*, 2283; (c) **1964**, *45*, 1007; (d) **1966**, *44*, 1571. (e) Lemieux, R. V.f Fraser-Reid, B. *Ibid.* **1965**, *43*, 1460.

Table I. Addition of *p*-Nitrobenzenesulfonyl Peroxide to DHP in Hydroxylic Solvents

product	R	yield,[a] %	isomer	anomeric H, δ [e]	alkoxy methyl H's, δ [e]	cis:trans [b]
2a	H	85	cis	4.96 (*J* = 3.0)		32:68
			trans	4.74 (*J* = 4.5)		
2b	CH_3	85	cis	4.58 (m)[c]	3.30 (s)	35:65
			trans	4.37 (m)[c]	3.27 (s)	
2c	CH_2CH_3	77	cis	4.66 (m)[c]	1.11 (t, *J* = 7)	41:59
			trans	4.44 (m)[c]	1.05 (t, *J* = 7)	
2g	CH_2CF_3	15[d]	cis	4.82 (*J* = 3.75)		39:61
			trans	4.60 (*J* = 4.0)		
2d	$CH(CH_3)_2$	80	cis	4.78 (*J* = 3.0)	1.16, 1.07 (d, *J* = 6.5)	48:52
			trans	4.53 (*J* = 4.5)	1.07, 0.96 (d, *J* = 6.5)	
2f	$COCH_3$	91	cis	5.92 (*J* = 3.75)	2.06 (s)	53:47
			trans	5.68 (*J* = 5.5)	2.00 (s)	
2e	$C(CH_3)_3$	91	cis	4.97 (*J* = 3.0)	1.20 (s)	62:38
			trans	4.65 (*J* = 4.5)	1.09 (s)	

[a] Averaged isolated yield of the cis-trans mixture. [b] Cis:trans ratio ± 3% of the uncrystallized mixture. [c] The anomeric protons were an unresolved multiplet instead of the usual doublet. [d] The cis-trans mixture was separated from other components by column chromatography (silica gel, chloroform-hexane). [e] *J* values are in hertz.

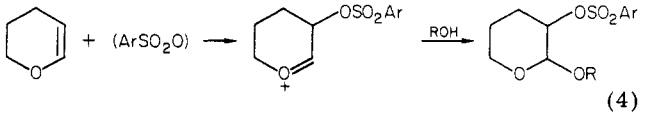
whose methoxy methyl proton absorbed at lower field (δ 3.30) than that for *trans*-**2b** (3.27). By an analogous sequence, isopropyl derivative **3d** was prepared, separated isomerically, and converted to the *p*-nitrobenzenesulfonate derivatives. *cis*-**2d** gave a pair of doublets for the diastereotopic methyl groups of the isopropyl group (δ 1.16 and 1.07, *J* = 6.5 Hz), which were at lower field than the same pair of doublets in *trans*-**2d** (δ 1.07 and 0.96, *J* = 6.5 Hz). This same relationship of alkoxy methyl group protons, cis at lower field and trans at higher field, was found for the other products **2** where both the anomeric proton and the alkoxy methyl group protons could be compared by ratio.

This relationship was further confirmed by repeated crystallization of crude **2b** from methanol–water. The solid obtained after four recrystallizations was enriched (90:10) in *cis*-**2b**, while the mother liquor was enriched in the trans isomer as assigned by ^1H NMR. Sodium naphthalene cleavage[7] of these fractions yielded predominately *cis*-**3b** and *trans*-**3b**, respectively.

With these assignments in hand, the stereochemistry of the addition could be quantitated by ^1H NMR. The results are presented in Table I along with the shift positions of the relevant protons. The data is given for the crude products since recrystallization leads to some fractionation.

Discussion

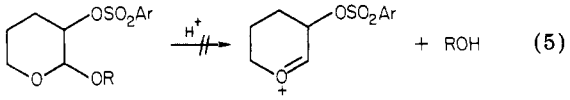
Several general features are apparent in the reaction of pNBSP with DHP. First, addition to the vinyl ether is much more rapid (<10 min) than for a comparable nonactivated olefin like cyclohexene (>3 h).[8] Second, the addition is regiospecific, giving only the Markovnikov product. Third, a wide variety of solvent nucleophiles can be incorporated in the products. These features are only consistent with an electrophilic addition to the olefin (eq 4); free-radical addition is not operative.[9] Thus, the



(4)

general electrophilic properties of sulfonyl peroxides toward electron donors[10] can be extended to include very electron-rich olefins.

The α-sulfonyloxy acetal products obtained are quite stable and do not exhibit normal reactivity of either the acetal function or the *p*-nitrobenzenesulfonate ester. For instance, when trans methoxy product **2b** was treated with acidic methanol for 3 days at 0 °C, no conversion to the cis isomer was observed. Nor was the methoxy group exchangeable with other alcohols or water under acid-catalyzed conditions. The electron-withdrawing nature of the adjacent arenesulfonate group[11] prohibits the normally facile ionization to an oxonium ion (eq 5).



(5)

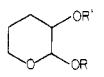
Likewise, ionization of the *p*-nitrobenzenesulfonate group was not facile, since **2b** could be recovered unchanged after refluxing for 1 h in methanol. The inductive effect of the acetal function is sufficient to prevent formation of an adjacent cation under these conditions. In contrast, 2-methoxycyclohexyl *p*-nitrobenzenesulfonate is readily solvolyzed in refluxing methanol.[8]

The data in Table I indicate that product stereochemistry is influenced mainly by the size of the solvent nucleophile. For small R groups of ROH (water, methanol), trans addition is favored. As the size of R becomes larger, more cis product is produced until, for *tert*-butyl alcohol, cis addition is the major path. While the absolute differences along the series are only moderate, the trend in the data is distinct and quite reproducible.

The data for capture by trifluoroethanol are the same as for those ethanol itself, as would be expected if steric factors are the controlling influence on product stereochemistry. (The anomalously low yield of **2g** is accompanied by the production of several other components in the reaction mixture that were not investigated further.

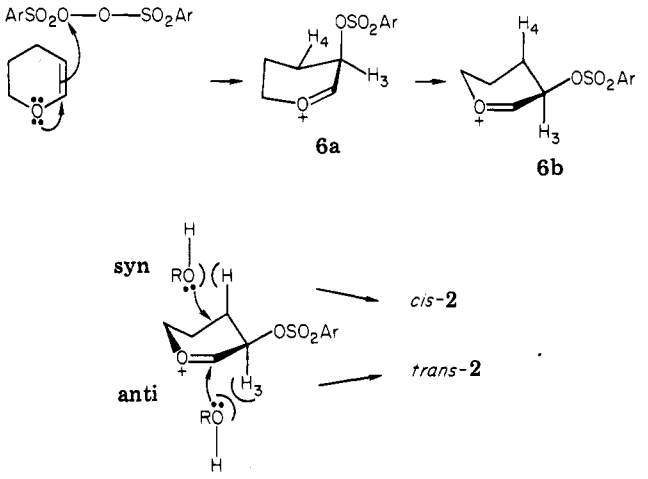
(7) Clossen, W. D.; Wriede, P.; Bank, S. *J. Am. Chem. Soc.* **1966**, *88*, 1581.
(8) R. V. Hoffman, Unpublished.
(9) Carey, F. A.; Sundberg, R. J. "Advanced Organic Chemistry, Part B"; Plenum Press: New York, 1977; pp 81–85.
(10) (a) Aromatic π systems, see: Dannley, R. L.; Tornstrom, P. K. *J. Org. Chem.* **1975**, *40*, 2278. Dannley, R. L.; Knipple, W. R. *Ibid.* **1973**, *38*, 6. Dannley, R. L.; Gagen, J. E.; Zak, K. *Ibid.* **1973**, *30*, 1. Levi, E. M., Kovacic, P.; Gormish, J. F. *Ibid.* **1970**, *26*, 4536. (b) Olefin π systems, see: ref 1; Bolte, J.; Kergmard, A.; Vincent, S. *Tetrahedron Lett.* **1965**, 1529. Bolte, J.; Kergmard, A.; Vincent, S. *Bull Soc. Chim. Fr.* **1972**, 301. (c) Amine N donors, see: Hoffman, R. V.; Belfoure, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 2183. Hoffman, R. V.; Belfoure, E. L. *Ibid.* **1979**, *101*, 5687. Hoffman, R. V.; Poelker, D. J. *J. Org. Chem.* **1979**, *44*, 2464. Hoffman, R. V.; Cadena, R. *J. Am. Chem. Soc.* **1977**, *99*, 8226.
(11) Lambert, J. B.; Mark, H. W.; Holcomb, A. G.; Magyar, E. S. *Acc. Chem. Res.* **1979**, *12*, 317.

Table II. Equilibrium Cis:Trans Ratios for 2,3-Disubstituted Tetrahydropyrans

	cis:trans
3b, R′ = H; R = CH_3	35:65[a]
3d, R′ = H; R = *i*-Pr	35:65
3e, R′ = H; R = *t* Bu	41:59
4, R′ = R = CH_3	38:62
5, R′ = H; R = CH_2CH_2Cl	40:60[b]

[a] Literature value 39:61, ref 6d. [b] Reference 6c.

Scheme II

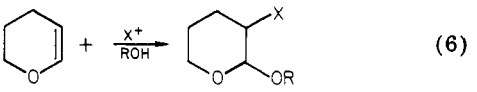


Perhaps the low nucleophilicity of the trifluoroethanol results in a sufficiently low rate of capture that the intermediate oxonium ion decomposes via alternate routes.)

Control experiments show that the cis and trans isomers do not interconvert under the reaction conditions. In order to judge whether these kinetic product ratios parallel a change in product stabilities, we measured the equilibrium cis:trans ratios for **3b,d,e** and 2,3-dimethoxytetrahydropyran (**4**) by acid-catalyzed exchange (Table II). These ratios are the same within experimental error (±3%) and agree excellently with that determined for 2-(2-chloroethyl)-3-hydroxytetrahydropyran(**5**).[6c] Since the size of the alkoxy group at C-2 does not influence the cis:trans ratio in **3**, and since the arylsulfonyloxy group at C-3 has an effective steric bulk comparable to that of either hydroxy or methoxy,[12] it is likely that the equilibrium cis:trans ratio in the products **2** should also be ~40:60. Thus the changing product ratios seen in Table I are due to changing rates of nucleophilic capture of the intermediate cation by solvent from the syn and anti faces with increasing bulk.

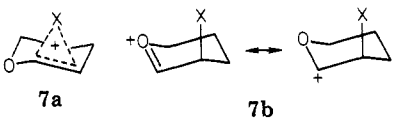
These data are nicely accommodated by considering the cation formed by peroxide addition. Attack on the DHP π-bond yields the axially substituted oxonium ion **6a** (Scheme II). Since there is no electronic interaction between the arylsulfonyloxy group and the adjacent charged center,[1] the more stable equatorial isomer (**6b**) is favored, and capture of this ion by nucleophile gives product. Axial approach of the nucleophile from the syn side of **6b** involves 1,3-diaxial steric interaction with H_4, while axial approach from the anti side involves 1,2-diaxial steric interaction with H_3. It is clear that for additions to sp^2-hybridized cyclohexyl systems (e.g., cyclohexanones), 1,2-diaxial interactions are more severe than 1,3-diaxial interactions.[13] Thus, syn nucleophilic capture of ion **6b** should be kinetically preferred over anti capture by these steric considerations. On the other hand, data in Table II indicate that the trans isomer is thermodynamically favored regardless of the size of the capturing alcohol. The changing product ratios (syn:anti) in Table I therefore reflect kinetic vs. thermodynamic control of the mixture. For small nucleophiles, steric interactions with H_3 *and* H_4 are small; thermodynamic control leads to a product mixture in which the trans isomer predominates to the same extent (~60:40) as found for the thermodynamic ratio (Table II). As the size of the capturing alcohol becomes larger, steric interactions are larger and syn attack, giving *cis*-**2**, is favored kinetically. Increased kinetic control results in more cis isomer for larger nucleophiles.[14]

This study provides an interesting contrast to the observation for other electrophilic additions to the pyran system. The most recent studies are those of Duggan and Hall,[15] which complement other earlier work[6a,e,16] on haloalkoxylations of pyran (eq 6). When the electrophile



(6)

is iodine or bromine, the stereochemistry of addition is nearly exclusively trans. However, when the electrophile is chlorine, then the stereochemistry is mostly trans, with some cis also being observed (Table III). These results have been rationalized in terms of contributions of the cationic intermediates from halogen addition. When the electrophile is bromine or iodine, a bridging interaction as in **7a** is an important mode of carbocation stabilization



7a **7b**

and thus trans addition is the stereochemical result. (Bridged ion **7a**, (X = Br, I) is also obtained by ionization of 1,2-disubstituted tetrahydropyrans and similarly controls the stereochemistry of exchange.[6a,e]) Small amounts of cis product are attributed to a small amount of conversion of **7a** to **7b**, which can afford either the cis or trans product. When the electrophile is chlorine, it has been argued that bridging is unimportant,[12,6e] products are derived principally from **7b**, and, thus, cis products are found in greater proportion.

A comparison of the data in Table III reveals that halogens, even chlorine, exert a markedly different stereochemical control on the addition to DHP relative to pNBSP. While it is well accepted that bromine and iodine are capable of bridging as in **7a**, chlorine is not thought to give bridged ions[6a,e,14,15] in pyrans. In fact, chloroalkoxylation gives mostly trans isomer (85%) regardless of the size of the capturing alcohol (Table III). Although the

(12) Hirsch, J. A. "Topics in Stereochemistry"; Eliel, E. L., Allinger, H. L., Eds.; Interscience: New York, 1967; Vol. I, pp 199–222.

(13) Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions"; American Chemical Society: Washington, DC, 1976; pp 121–127.

(14) A referee has suggested an alternate explanation for the changing product ratios. In solvents of varying polarity and/or nucleophilicity, the rate of capture may be sufficiently different as to dictate whether **6a** has a long enough lifetime to isomerize to **6b**. This possibility can be discounted by considering the product ratios in trifluoroethanol and ethanol. The former is a much poorer nucleophile than the latter so the lifetime of **6a** should be quite different in TFE than in ethanol. The fact that both give the same cis:trans ratio implies that **6a** has a sufficient lifetime in *both* solvents to convert to **6b** and that steric effects in the capturing alcohol are most important.

(15) Duggan, A. J.; Hall, S. S. *J. Org. Chem.* **1977**, *42*, 1057.

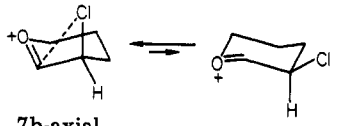
(16) Gaydou, E. M. *Tetrahedron Lett.* **1972**, 4055.

Table III. Product Stereochemistry of Electrophilic Additions to DHP

ROH, R =	cis:trans OCl[a]	OBr[a]	NBS[b]	Br_2[b]	I_2[c]	pNBSP[d]
H						32:68
CH_3	15:85		0:100	13:87	0:100	35:65
CH_2CH_3	15:85		0:100			41:59
$CH_2CH_2CH_3$	15:85	10:90	0:100			
sec-C_4H_9	20:80					
$CH(CH_3)_2$	15:85		0:100			48:52
$C(CH_3)_3$	15:85					62:38
$COCH_3$	32:68		0:100			53:47
$CH_2C_6H_5$	33:67					
CH_2CF_3						39:61

[a] Reference 15. [b] Reference 16. [c] Reference 6e. [d] This work.

effective steric bulk of chlorine and an arenesulfonyloxy group is the same,[12] the chlorine in ion **7b** prefers an axial

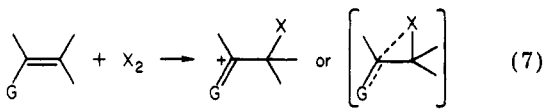


7b-axial 7b-equatorial

rather than equatorial conformation, thus giving mainly trans addition. The most likely source of this conformational bias is electronic interaction of chlorine with the neighboring cation. (This is equivalent to bridging.) The strength of this interaction dictates the position of equilibrium and hence the increased amount of trans isomer.

Chlorination, therefore, like bromination, does give bridging interaction in vinyl ether additions. This interaction is, however, weaker and thus does not override other structural effects. As Hall points out,[14] chloroacetoxylation in acetic acid gives less trans isomer. The greater ionizing power of acetic acid stabilizes ion **7** and renders **7a** less important. Thus the equilibrium is shifted slightly to **7b**, and a greater proportion of cis isomer is possible.

There is a lively discussion in the current literature concerning the halogenation of activated olefins such as vinyl ethers, styrenes, and others. At issue is the importance of halogen bridging when the carbocation is otherwise stabilized by resonance interactions (eq 7).[17] While



(7)

8a 8b

it appears that an open cation **8a** is an acceptable description of the intermediate, product studies also indicate that there is hindered rotation about the C_α–C_β bond for both bromination *and* chlorination. One way to reconcile these observations is to note that while halogen bridging may be largely overshadowed kinetically by resonance stabilization in the formation of the intermediate, it is sufficiently strong enough to influence the conformation of the intermediate ion from which the products are derived. Such is not the case for better bridging atoms such as sulfur where bridging is detected kinetically in the formation of the intermediate and by complete trans stereospecificity in the products for the same activated olefin systems.[17e,18]

The dihydropyran system supports this model well. Halogen bridging to the resonance-stabilized carbocation influences the axial–equatorial equilibrium of the halogen addend but is too weak to control it. It is noteworthy that pNBSP provides a limiting model for olefin addition in that an electrophile of moderate size is added that does not give any neighboring-group stabilization.

Experimental Section

pNBSP was prepared according to Dannley.[19] DHP was distilled before use (bp_{665} 80–81 °C). Alcohols and solvents were reagent grade and used as received except for trifluoroethanol. Melting points and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 231 spectrometer, ^1H NMR spectra were taken on a Jeol-PS-100 instrument, and mass spectra were obtained on a Hewlett-Packard 5995 GC/MS using the direct inlet. Elemental analyses were performed by Micanal Laboratories, Tucson, AZ.

3-[[(*p*-Nitrophenyl)sulfonyl]oxy]-2-hydroxytetrahydropyran (2a). Caution: The reaction between pNBSP and DHP is very vigorous in the absence of solvent. To a cooled (0 °C) solution of DHP (375 mg, 4.46 mmol) and water (2.5 mL) in acetone (50 mL) was added pNBSP (1.5 g, 3.7 mmol). After stirring at 0 °C for 20 min, a potassium iodide test indicated complete consumption of the peroxide. The acetone was removed in vacuo, and the residue was dissolved in methylene chloride and washed with saturated sodium chloride until the washings were neutral. The organic phase was dried ($MgSO_4$) and evaporated to yield **2a** (965 mg, 88%) as a white solid, which was essentially pure by ^1H NMR examination. Recrystallization from ethyl acetate–hexane gave pure **2a** as a mixture of cis and trans isomers: mp 94–95 °C, IR (KBr) 3300 (br), 3110, 2960, 1610, 1535, 1365, 1200, 930, 820, 745, 613 cm^{-1}; mass spectrum, *m/e* (relative intensity) 39 (11.5), 41 (31.4), 43 (55), 46 (11.8), 50 (14.2), 71 (100), 76 (19.5), 75 (12), 122 (14.3), 186 (10.9); ^1H NMR (acetone-d_6) δ 8.45, 8.22 (4 H, aromatic quartet, J = 8 Hz), 4.96 (d, J = 3 Hz) and 4.74 (d, J = 4.5 Hz) [1 H total, cis and trans anomeric H], 4.39 (m, 1 H), 3.88 (m, 1 H), 3.42 (m, 1 H), 2.2–1.2 (m, 4 H). The OH proton is variable. Anal. Calcd for $C_{11}H_{13}NO_7S$: C, 43.56; H, 4.29; N, 4.62. found: C, 43.50; H, 4.33; N, 4.52.

3-[[(*p*-Nitrophenyl)sulfonyl]oxy]-2-methoxytetrahydropyran (2b). The same general procedure was followed for all of the 2-alkoxy derivatives **2b–e**. While reactions were normally run on a 1-mmol scale, they could be scaled up significantly (10 g) without decrease in yield. The crude product was normally of high purity, and the cis:trans ratios were determined on the crude product since recrystallization always led to fractionation of the isomers (cis isomer less soluble than trans). The melting

(17) (a) Bromination of styrenes and vinyl ethers: Bienvenue-Goetiz, E.; Dubois, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 5388 and references therein. (b) Bromination of styrenes: Naae, D. G. *J. Org. Chem.* **1980**, *45*, 1394. (c) Bromination of styrene: Ruasse, M. F.; Argile, A.; Dubois, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 7645. (d) Chlorination of styrene: Yates, K.; Leung, H. W. *J. Org. Chem.* **1980**, *45*, 1401 and references therein. (e) Schmid, G. H.; Garratt, D. G. In "The Chemistry of Double Bonded Functional Groups"; Patai, S., Ed.; Wiley: London, 1976; Supplement A, Part 2, Chapter 9.

(18) (a) Toyoshima, K.; Okuyama, T.; Fueno, T. *J. Org. Chem.* 1978, *43*, 2789. (b) Schmid, G. H.; Tidwell, T. T. *Ibid.* **1978**, *43*, 460.

(19) Dannley, R. L.; Gagen, J. E.; Stewart, O. J. *J. Org. Chem.* **1979**, *35*, 3076.

points of the crude and recrystallized cis–trans mixtures tended to have fairly wide ranges (~2–12 °). A typical preparation of 3-[[(*p*-nitrophenyl)sulfonyl]oxy]-2-methoxytetrahydropyran (**2b**) is given here. To a cooled (0 °C) solution of DHP (75 mg, 0.89 mmol) and methanol (30 mL) in methylene chloride (30 mL) was added pNBSP (300 mg, 0.75 mmol). The colorless mixture was stirred 30 min, at which time a potassium iodide test indicated the peroxide was consumed. The solvent was evaporated, the residue was dissolved in methylene chloride, and the solution was extracted with saturated sodium chloride until the washings were neutral (3 × 30 mL). The organic phase was dried ($MgSO_4$) and evaporated to give **2b** as a pale yellow oil (215 mg, 92%). Recrystallization from methanol–water gave pure **2b** as a mixture of cis and trans isomers: mp 59–72 °C; IR (KBr) 3118, 2960, 1610, 1536, 1365, 1190, 740, 618 cm^{-1}; mass spectrum, *m/e* (relative intensity) 41 (16.6), 43 (36.2), 45 (10.2), 61 (15.4), 71 (100), 76 (11.1), 122 (11.9); ^1H NMR ($CDCl_3$) δ 8.29, 8.12 (aromatic quartet, *J* = 8 Hz, 4 H), multiplets at 4.58 and 4.37 (1 H total, cis and trans anomeric H), 3.9–3.2 (m, 3 H), 3.30, 3.27 (s, cis and trans methoxy CH_3, 3 H total) 2.4–1.2 (m, 4 H). Anal. Calcd for $C_{12}H_{15}NO_7S$: C, 45.42; H, 4.73; N, 4.42. Found: C, 45.30; H, 4.88; N, 4.52.

3-[[(*p*-Nitrophenyl)sulfonyl]oxy]-2-ethoxytetrahydropyran (2c). Compound **2c** (pale yellow oil, 79%) was recrystallized from ether–hexane to give a cis–trans mixture: mp 79–88 °C; IR (KBr) 3120, 2960, 1611, 1540, 1365, 1188, 970, 742, 682, 618 cm^{-1}; mass spectrum, *m/e* (relative intensity) 41 (18.0), 43 (27.9), 47 (12.6), 50 (8.8), 71 (100), 76 (14.2), 122 (14.5); ^1H NMR ($CDCl_3$) δ 8.38, 8.12 (aromatic quartet, 4 H), 4.8–4.3 (multiplet with prominent peaks at 4.66 and 4.44, 2 H total, cis and trans anomeric H and NsOCH), 3.9–3.2 (m, 4 H), 2.4–1.4 (m, 4 H), 1.11 and 1.05 (t, *J* = 7 Hz, 3 H total, cis and trans ethoxy–CH_3 triplets).

3-[[(*p*-Nitrophenyl)sulfonyl]oxy]-2-isopropoxytetrahydropyran (2d). Compound **2d** (pale yellow solid, 80%) was recrystallized by dissolving the crude **2d** in a minimum of chloroform, adding two volumes of ether, and taking the solution to turbidity with petroleum ether. Pure **2d** (fine needles) separates as a mixture of the cis and trans isomers: mp 85–87 °C; IR (KBr) 3120, 2960, 1610, 1535, 1365, 1190, 970, 920, 745, 692, 615 cm^{-1}; mass spectrum *m/e* (relative intensity) 41 (16.4), 43 (43), 71 (100), 76 (10), 83 (10.7), 122 (12.1); ^1H NMR ($CDCl_3$) δ 8.28, 8.12 (aromatic quartet, *J* = 8 Hz, 4 H), 4.78 (d, *J* = 3.0 Hz) and 4.53 (d, *J* = 4.5 Hz, anomeric H, 1 H total), 4.7–4.3 (m, 1 H), 3.72 (heptet, *J* = 6.5 Hz, isopropylmethine, 1 H) 4.02–3.3 (m, 2 H), 2.2–1.2 (m, 4 H), 1.16 (d, *J* = 6.5 Hz), 1.07 (d, *J* = 6.5 Hz, diastereotopic isopropyl-CH_3 of *cis* isomer) and 1.07 (d, *J* = 6.5 Hz), 0.96 (d, *J* = 6.5 Hz, diastereotopic isopropyl-CH_3 of trans isomer, 6 H total).

3-[[(*p*-Nitrophenyl)sulfonyl]oxy]-2-*tert*-butoxytetrahydropyran (2e). Compound **2e** (white oily solid, 91%) was recrystallized from chloroform–ether–petroleum ether to give fine white needles of a cis–trans mixture: mp 101–104 °C; IR (KBr) 3120, 2960, 1610, 1535, 1365, 1200, 930, 820, 745, 613 cm^{-1}; mass spectrum, *m/e* (relative intensity) 41 (20.1), 43 (12.4), 57 (100), 71 (25.9), 83 (19), 117 (16.1), 122 (13.5), 286 (10.4); ^1H NMR ($CDCl_3$) δ 8.38 and 8.12 (aromatic quartet, 4 H), 4.97 (d, *J* = 3 Hz) and 4.65 (d, *J* = 4.5 Hz, cis and trans anomeric H, 1 H), 4.8–4.2 (m, 1 H), 4.0–3.3 (m, 2 H), 2.3–1.2 (m, 4 H), 1.2 (s) and 1.09 (s, cis and trans *t*-Bu CH_3, 9 H total). Anal. Calcd for $C_{15}H_{21}NO_7S$: C, 50.13; H, 5.85; N, 3.89. Found: C, 50.19; H, 5.88; N, 3.88.

3-[[(*p*-Nitrophenyl)sulfonyl]oxy]-2-acetoxytetrahydropyran (2f). The same procedure as for **2b** using DHP (250 mg, 3 mmol), glacial acetic acid (15 mL) in methylene chloride (50 mL), and pNBSP (1.0 g, 2.4 mmol) gave **2f** as a dark yellow-brown oil (660 mg, 80%). Recrystallization from ethyl acetate–hexane gave pale tan crystals of **2f** as a mixture of cis and trans isomers: mp 78–82 °C; IR (KBr) 3120, 2960, 1765 (C=O), 1613, 1540, 1365, 1210, 745, 683 cm^{-1}; mass spectrum, *m/e* (relative intensity) 41 (8.4), 43 (100), 50 (7.6), 71 (33.9), 76 (9.3), 122 (9.7); ^1H NMR ($CDCl_3$) δ 8.38 and 8.12 (aromatic quartet, the upfield doublet (8.12) is actually split into two doublets (Δδ = 0.02) presumably for cis–trans isomers, *J* = 8 Hz, 4 H), 5.92 (d, *J* = 3 Hz) and 5.68 (d, *J* = 4 Hz, cis and trans anomeric H, 1 H total), 4.75–4.4 (m, 1 H), 4.0–3.3 (m, 2 H), 2.4–1.3 (m, 4 H), 2.06 (s) and 2.00 (s, superimposed on multiplet, cis and trans acetoxy CH_3, 3 H total).

3-[[(*p*-Nitrophenyl)sulfonyl]oxy]-2-(2,2,2-trifluoroethoxy)tetrahydropyran (2g). To a cold (0 °C) solution of DHP (310 mg, 3.7 mmol) and 2,2,2-trifluoroethanol[20] (9.75 g, 97.5 mmol) in dry dichloromethane (100 mL) was added pNBSP (790 mg, 1.95 mmol). The mixture was stirred at 0 °C for 3.5 h under a nitrogen atmosphere. Completion of the reaction was confirmed by a negative potassium iodide test for active oxygen. The reaction mixture was washed with saturated sodium chloride solution until neutral (3 × 80 mL) and dried ($MgSO_4$). Removal of the solvent gave a yellow oil (910 mg), which contained five components by TLC on silica gel (2:1 chloroform–hexane). Resolution of the mixture by silica gel flash chromatography[21] (5:1 chloroform–hexane) yielded **2f** as a yellow oil (110 mg, 15%) as a mixture of cis and trans isomers: IR (NaCl plates) 3110, 2960, 1611, 1539, 1365, 1190, 975, 830, 618 cm^{-1}; mass spectrum, *m/e* (relative intensity) 41 (19.3), 43 (40.1), 55 (11.2), 71 (100) 76 (14.8), 83 (16.5), 109 (10.1), 122 (17.0), 186 (16.1), 286 (4.1); ^1H NMR ($CDCl_3$) δ 8.37, 8.08 (4 H, aromatic quartet, *J* = 8 Hz), 4.82 (d, *J* = 3.75 Hz) and 4.60 (d, *J* = 4.0 Hz, 1 H total, cis and trans anomeric H), 4.48 (m, 1 H), 4.1–3.4 (m, 4 H), 2.4–1.2 (m, 4 H).

Determination of Cis:Trans Ratio. The integrated ratio of the cis and trans anomeric protons and/or the ratios determined for the alkoxy methyl group resonances for the cis and trans isomers were used. In cases where both were used, the values agreed ±5%. It was found by comparison of cis:trans ratios that recrystallization, regardless of solvent, gave enrichment of the cis isomer in the precipitate. The kinetic product ratios given in Table I were determined on the crude product mixture so as to avoid this fractionation.

Preparation of *cis*- and *trans*-3-Hydroxy-2-methoxytetrahydropyran (3b). Tetrahydropyran-2,3-diol[6c] (1.0 g) in absolute methanol (10 mL) was treated with 3 drops of methanesulfonic acid, refluxed 90 min, and allowed to stand at room temperature overnight. Solid potassium carbonate was added until the solution was basic to moist litmus. The methanol was removed in vacuo and the residue taken up in methylene chloride and filtered. Gas chromatographic analysis (2 m, 20% Carbowax-20M, 155 °C, 60 cc/min He) showed two peaks that were collected separately. The first peak was *cis*-2-methoxy-3-hydroxytetrahydropyran (**3b**) while the second peak was *trans*-**3b** as determined by ^1H NMR.[6d] These isomers could also be prepared conveniently by first preparing *trans*-**3b** from 3,4-dihydropyran, *m*-chloroperbenzoic acid, and methanol and then performing an acid-catalyzed equilibration.[6d]

***cis*-3-[[(*p*-Nitrophenyl)sulfonyl]oxy]-2-methoxytetrahydropyran (2b).** *cis*-**3b** (40 mg, 0.3 mmol) was dissolved in dry pyridine (5 mL), and *p*-nitrobenzenesulfonyl chloride (135 mg, 0.61 mmol) was added in one portion after cooling to 0 °C. A fine white precipitate began to form immediately. After standing 6 h at 0 °C, water was added dropwise (10 drops), and the mixture was diluted with water (40 mL) and extracted with ether. The ether extract was washed with 2.5 M HCl (3 × 15 mL) and water (10 mL), dried ($MgSO_4$), and evaporated to give *cis*-**2b** as a yellow oil (40 mg, 42%) that had the same R_f value on TLC examination (silica gel, chloroform) as **2b** from peroxide addition to DHP. ^1H NMR examination ($CDCl_3$) showed a single isomer: δ 8.39, 3.12 (aromatic quartet, 4 H, *J* = 8 Hz), 4.58 (m, 1 H), 3.9–3.2 (m, 3 H), 3.30 (s, 3 H, methoxy CH_3), 2.4–1.2 (m, 4 H).

***trans*-3-[[(*p*-Nitrophenyl)sulfonyl]oxy]-2-methoxytetrahydropyran (*trans*-2b).** *trans*-**3b** was prepared in the same way as *cis*-**2b**. ^1H NMR examination ($CDCl_3$) showed a single isomer: δ 8.39, 8.12 (aromatic quartet, 4 H, *J* = 8 Hz), 4.37 (m, 1 H), 3.9–3.2 (m, 3 H), 3.27 (s, 3 H, methoxy CH_3), 2.4–1.2 (m, 4 H). Thus it is seen that *trans*-**2b** has *both* the anomeric proton *and* the methoxymethyl absorptions upfield from those in *cis*-**2b**.

Preparation of *cis*- and *trans*-3-Hydroxy-2-isopropoxytetrahydropyran (3d). Tetrahydropyran-2,3-diol[6c] (750 mg) in isopropyl alcohol (10 mL) was treated with 3 drops of methanesulfonic acid and refluxed 3 h. Potassium carbonate was added until the solution was basic to moist litmus, and the solution was filtered. Isopropyl alcohol was removed in vacuo and the residue taken up in ether and filtered. Gas chromatographic analysis as

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(21) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

for **3b** showed two peaks corresponding to the cis and trans isomers. The cis isomer was collected and identified by ^{1}H NMR.[6d] These isomers could also be conveniently prepared by acid-catalyzed isopropyl alcohol exchange of *trans*-**3b**.

***cis*-3-[[(*p*-Nitrophenyl)sulfonyl]oxy]-2-isopropoxytetrahydropyran (*cis*-2).** *cis*-**2d** was prepared from *cis*-**3d** as described for *cis*-**2b**. The mixture stood 3 h at 0 °C and was then poured into ice water (25 mL) and extracted into dichloromethane (3 × 25 mL). The organic layer was washed with 2.5 M HCl (2 × 10 mL) and water and then dried and evaporated to give *cis*-**2d** as a yellow oil, which slowly solidified (15 mg). Examination by ^{1}H NMR ($CDCl_3$) gave the following: δ 8.45, 8.12 (aromatic quartet, 4 H, J = 8 Hz), 4.78 (d, J = 3.0, 1 H, anomeric H), 4.7–4.4 (m, 1 H), 3.76 (heptet, J = 6.5, 1 H), 4.02–3.2 (m, 2 H), 2.2–1.2 (m, 4 H), 1.16 and 1.07 (doublets, J = 6.5 Hz, 6 H total, diastereotopic CH_3 groups of isopropyl group). Thus it is seen that the *cis*-**2d** has both the anomeric proton and the isopropoxy methyl group absorptions at lower field than those of the trans isomer, which was determined from a mixture of *cis*- and *trans*-**2d**.

Conversion of *cis*-2b and *trans*-2b to *cis*-3b and *trans*-3b. It was observed that nosylates **2** upon recrystallization returned solid that was enriched in the cis isomer while the filtrate was enriched in the trans isomer. A mixture of *cis*- and *trans*-**2b** was recrystallized five times from methanol–water. The solid product was >90% *cis*-**2b** as determined by ^{1}H NMR: δ 4.58 (anomeric H) and 3.30 (methoxy CH_3). The filtrate from the last recrystallization was found to be >90% trans by ^{1}H NMR: δ 4.36 (anomeric H) and 3.27 (methoxy CH_3). These individual isomers were cleaved to the corresponding hydroxy compounds **3** by using sodium naphthalene.[7] A solution of sodium naphthalene (0.3 M, 9 mL, 2.7 mmol) in THF under nitrogen was cooled to −78 °C and *cis*-**2b** (200 mg, 0.63 mmol) dissolved in a minimum of dry THF was added by syringe. After 5 min the reaction was removed from the bath, and after an additional 5 min at room temperature, water (1 mL) was added. The mixture was dried ($MgSO_4$) and filtered to give an orange solution, which showed only *cis*-**3b** by GC analysis. This material was collected and identified as *cis*-**3b** by ^{1}H NMR. Identical cleavage of *trans*-**2b** gave a solution which by GC contained only *trans*-**3b**, which was also collected and identified by ^{1}H NMR. This confirms our correlation of chemical shift assignments in *cis*- and *trans*-**2b**. Because only one isomer of **2d** was prepared, we felt it important to confirm the chemical shift correlation between the anomeric protons and the isopropyl methyl groups for *cis*-**2d** and *trans*-**2d**. A cis–trans mixture of **3d** was recrystallized twice from methanol–water and once from chloroform–ether–petroleum ether as described in the preparation of **2d**. The solid obtained from this sequence was shown to be >85% *cis*-**2d** by ^{1}H NMR: δ 7.78 (d, J = 3.0, cis anomeric He, 1.16 and 1.07 (pair of doublets, J = 6.5 Hz, diastereotopic isopropoxy CH_3). The filtrate from the final recrystallization was >80% *trans*-**2d** by ^{1}H NMR: δ 4.53 (d, J = 4.5 Hz, trans anomeric H), 1.07, 0.96 (pair of doublets, J = 6.5 Hz, diastereotopic isopropoxy CH_3). *cis*-**2d** was cleaved with sodium naphthalene exactly as described above. Gas chromatography showed >80% *cis*-**3d** to be present, and this was collected and identified by ^{1}H NMR. Likewise, cleavage of *trans*-**2d** gave 80% *trans*-**3d**. These experiments confirm that *both* the anomeric proton *and* the isopropyl CH_3 groups are downfield from the trans isomer in **2d**. These data and integrated ratios of other compounds in the series **2a–e** served to show the generality of this phenomenum, thus cis:trans ratios in **2** could be determined either from the anomeric proton signals or the alkoxy group signals.

Stability of *trans*-2b. *trans*-**2b** was dissolved in methanol (20 mL), and 3 drops of methanesulfonic acid were added. After standing 3 days at room temperature, the methanol was evaporated and the residue was dissolved, in dichloromethane and washed with saturated sodium chloride until the washings were neutral. The solution was dried ($MgSO_4$) and evaporated. Only *trans*-**2b** was present; thus product equilibration is not occurring under the reaction conditions and the product ratios in Table I are indeed the kinetic ones.

Equilibration of 3b,d,e and 4. *trans*-**3b** (100 mg) was dissolved in the appropriate alcohol with 3 drops of methanesulfonic acid and refluxed 5 h. Addition of potassium carbonate, filtration, and solvent removal gave equilibrium mixtures of **3b,d,e** whose cis:trans ratios are given in Table II. Compound **4** was equilibrated identically in methanol.

Registry No. 1, 6209-72-9; *cis*-**2a**, 86728-55-4; *trans*-**2a**, 86728-56-5; *cis*-**2b**, 86728-57-6; *trans*-**2b**, 86728-58-7; *cis*-**2c**, 86728-59-8; *trans*-**2c**, 86728-60-1; *cis*-**2d**, 86728-61-2; *trans*-**2d**, 86728-62-3; *cis*-**2e**, 86728-63-4; *trans*-**2e**, 86728-64-5; *cis*-**2f**, 86728-65-6; *trans*-**2f**, 86728-66-7; *cis*-**2g**, 86728-67-8; *trans*-**2g**, 86728-68-9; *cis*-**3b**, 6559-11-1; *trans*-**3b**, 6559-02-0; *cis*-**3d**, 86728-69-0; *trans*-**3d**, 6559-06-4; *cis*-**3e**, 86728-70-3; *trans*-**3e**, 6559-08-6; *cis*-**4**, 86728-71-4; *trans*-**4**, 6559-03-1; *cis*-**5**, 86728-72-5; *trans*-**5**, 86728-73-6; DHP, 110-87-2; *p*-$NO_2C_6H_4SO_2Cl$, 98-74-8; H_2O, 7732-18-5; $HOCH_3$, 67-56-1; $HOCH_2CH_3$, 64-17-5; $HOCH(CH_3)_2$, 67-63-0; $HOC(CH_3)_3$, 75-65-0; HO_2CCH_3, 64-19-7; $HOCH_2CF_3$, 75-89-8; tetrahydropyran-2,3-diol, 86728-74-7.