Acknowledgment. The authors are extremely grateful to the Goodyear Tire and Rubber Co. for the use of their high-resolution mass spectrometer and their GC/MS equipment, to Professor N. C. Deno for several helpful suggestions, and to Professor S. D. Darling for running some of the low-resolution mass spectra.

Registry No.—*dl*-1, 3333-27-5; *meso*-1, 3443-36-5; **5**, 141-46-8; **6**, 3041-16-5; **7**, 22347-47-3; **8**, 29908-11-0; **9**, 62005-92-9; **10**, 62005-93-0; **15**, 62005-94-1; **16**, 62005-95-2; dioxane, 123-91-1; ethylene glycol, 107-21-1.

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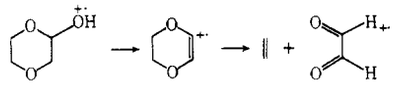
(16) A referee has suggested the following scheme for the production of an ion with *m/e* 58.



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Stereoselectivity in Synthesis and Nucleophilic Displacement Reactions of *cis*- and *trans*-2,3-Dichlorotetrahydropyrans

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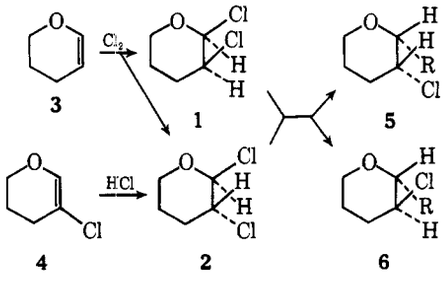
The stereochemistry of addition of chlorine to 3,4-dihydro-2*H*-pyran was reinvestigated and found to depend importantly on solvent polarity. In nonpolar solvents (e.g., pentane) stereoselective syn addition occurred yielding a mixture of *cis*- and *trans*-2,3-dichlorotetrahydropyrans in a ratio of 4:1. In polar solvents (e.g., dichloromethane) the cis:trans product ratio obtained was 1:2. Synthesis of *trans* 2,3-dichlorotetrahydropyran was accomplished by stereospecific syn addition of hydrogen chloride to 5-chloro-3,4-dihydro-2*H*-pyran. A general mechanism for the addition of chlorine to enol ethers which is consistent with the observed solvent dependence is discussed. The stereochemistry of nucleophilic displacement reactions at C-2 of *cis*- and *trans*-2,3-dichlorotetrahydropyrans and *trans*-2,3-dichlorotetrahydrofuran was studied using a variety of nucleophiles including NaSPh, NaOMe, NaN_3, and KOAc in dimethylformamide solution. *cis*-2,3-Dichlorotetrahydropyran yielded exclusively trans products with inversion at C-2. *trans*-2,3-Dichlorotetrahydropyran and -tetrahydrofuran yielded only cis products with C-2 inversion in reactions with NaSPh; with less effective nucleophiles mixtures of cis and trans products were obtained.

In connection with a synthetic program, we required *cis*- and *trans*-2,3-dichlorotetrahydropyran, **1** and **2**, respectively. It was thought by early workers[1] (owing to assumptions about the reaction mechanism) that addition of chlorine to 3,4-dihydro-2*H*-pyran (**3**) yielded only *trans*-2,3-dichlorotetrahydropyran (**2**). In 1965 Lemieux and Fraser-Reid[2] showed the product of this addition in carbon tetrachloride solution to be a 1:1 mixture of cis and trans dichloro compounds **1** and **2**. We have reinvestigated the addition reaction of chlorine to 3,4-dihydro-2*H*-pyran (**3**) and have found reaction conditions whereby the addition occurs with high (4:1) stereoselectivity, yielding largely *cis*-2,3-dichlorotetrahydropyran (**1**). The trans isomer[3] (**2**) was obtained by stereospecific syn addition of hydrogen chloride to 5-chloro-3,4-dihydro-2*H*-pyran (**4**). Using 2,3-dichlorotetrahydropyran and similar 2,3-dichlorotetrahydrofuran preparations of known stereochemical compositions, we have studied the stereochemical consequences of reactions of **1** and **2**, and those of *trans*-2,3-dichlorotetrahydrofuran (**7**), with selected nucleophiles.



Results

Chlorine Addition to 3,4-Dihydro-2*H*-pyran (3). Effects of variation of solvent and other reaction conditions on the stereoselectivity of addition of chlorine to 3,4-dihydro-2*H*-pyran (**3**) are recorded in Table I. When the addition reaction is carried out in polar solvents (e.g., dichloromethane or tetrahydrofuran) the product mixtures obtained exhibit a cis:trans isomer ratio little different from that observed at thermodynamic equilibrium,[2] i.e., 35% cis (**1**). As the reaction solvent polarity decreases the cis isomer (**1**) content of the product mixture increases to a maximum of about 80% when the addition reaction is carried out in pentane. Variation of reaction temperature from −78 to 25 °C has little effect; at higher temperatures equilibration of **1** and **2** occurs.[2] The concentration of 3,4-dihydro-2*H*-pyran (**3**) is important when nonpolar solvents are used; concentrations of **3** greater than

Table I. Stereoselectivity of Addition of Chlorine to 3,4-Dihydropyran (3)

Solvent	ϵ[a]	Temp, °C	% *cis*-2,3-dichloro-tetrahydropyran (1)[b]
Pentane	1.8 (20 °C)	0	82
		−78	81
		0	73
		−78	75
Carbon tetrachloride	2.2 (20 °C)	0	65
Benzene	2.3	25	65
Diethyl ether	4.7	0	66
Chloroform	5.0	25	50
Ethyl acetate	6.4	0	44
Dichloromethane	9.1	25	38
Tetrahydrofuran		25	36
Nitromethane	45	0	44
Equilibration[c]		25	35

[a] Dielectric constant (at temperature of chlorination unless otherwise indicated) from "International Critical Tables", Vol. 6, E. W. Washburn, Ed., p 83. [b] See Experimental Section for methodology; reproducibility was <±3%. [c] By treatment with titanium tetrachloride in benzene or tetraethylammonium chloride in acetonitrile.

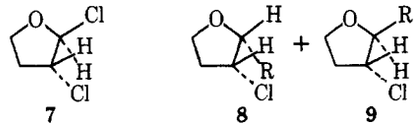
0.1 M increase the trans isomer (2) content of the 2.3-dichloro product. However, further dilution beyond 0.1 M 3 in pentane yields no measurable increase in formation of cis isomer 1.

Hydrogen chloride addition to 5-chloro-3,4-dihydro-2*H*-pyran (4). Synthesis of *trans*-2,3-dichlorotetrahydropyran[3] (2) was accomplished by stereospecific syn addition of hydrogen chloride to 5-chloro-3,4-dihydro-2*H*-pyran (4) in anhydrous benzene. We were unable to detect the presence of any cis isomer (1) in this preparation using ^{1}H NMR spectrometry.

^{1}H NMR Analyses and Molecular Conformation. Important to the present investigation was the direct determination of isomer content of mixtures of 1 and 2 from ^{1}H NMR spectra of benzene solutions. Previously, Lemieux and Fraser-Reid[2] used an indirect method of analysis.

Owing to the strong anomeric effect[4] operative in α-halo tetrahydropyrans[5] both *cis*- and *trans*-2,3-dichlorotetrahydropyrans (1 and 2) exist in conformations in which the C-2 chloro substituent is axial.[2] In trans 2,3-disubstituted tetrahydropyrans, when the atom bonded to C-2 is less electronegative than halogen, the anomeric effect is not totally dominating and other, presumably steric, effects are important in determining conformation. Steric effects are not as important in the analogous cis isomers and, for these compounds, even a relatively weak anomeric effect determines conformation. Assignments of the C-2 H resonances for the cis and trans 2,3-disubstituted tetrahydropyrans included in Table II were made using these considerations and the knowledge that in tetrahydropyrans the resonance for a C-2 equatorial hydrogen appears downfield of the corresponding axial hydrogen resonance.[6] Using these generalizations, stereochemical assignments for the various tetrahydropyrans (1, 2, 5, and 6) were straightforward and fully in accord with expectations based on their method of preparation (see Table III and following discussion), and previous literature assignments.[2,6,7]

In 2,3-disubstituted tetrahydrofurans 8 and 9 (R ≠ Ph)



7 8 9

Table II. Proton Magnetic Resonance Chemical Shifts (δ) and Coupling Constants (J) for C-2 H (Anomeric) Hydrogens of Cis and Trans 2,3-Disubstituted Tetrahydropyrans and -furans

	Cis		Trans	
Compd	δ (ppm)	$J_{C\text{-}2H,C\text{-}3H}$, Hz	δ (ppm)	$J_{C\text{-}2H,C\text{-}3H}$, Hz[b]
1, 2	5.86[a]	3	5.93	<1
7			6.16	s
5,6 R = SPh	5.33	3	5.21	4
8, 9[c] R = SPh	5.42	4	5.47	1
5, 6 R = OMe	4.49	3	4.35	4
8, 9 R = OMe	4.69	4	4.84	s
5, 6 R = N_3	5.12	3	4.82	6
8, 9 R = N_3	5.14	4	5.39	s
5, 6 R = OAc	6.02	3	5.66	5
8, 9 R = OAc	6.18	4	6.10	s
6 R = Ph			4.00	10
8 R = Ph	4.90	4		

[a] Spectra were obtained in carbon tetrachloride except for 1 and 2 for which benzene was used and 5, 6, R = SPh, for which dimethyl sulfoxide-d_6 was used. [b] s = singlet. [c] 9, R = SPh, was prepared by reaction of 3-chloro-4,5-dihydrofuran and thiophenol in liquid sulfur dioxide (see Experimental Section).

Table III. Stereochemistry of Products Formed by Reaction of *cis*- and *trans*-2,3-Dichlorotetrahydropyran (1 and 2) and *trans*-2,3-Dichlorotetrahydrofuran (7) with Selected Nucleophiles in Dimethylformamide at 25 °C

		Products		
Nucleophile (M^+Y^-)	α-Halo ether	% cis (5 or 8, R = Y)	% trans (6 or 9, R = Y)	% elimination (4)
NaSPh	1[a]	17	63	20
	2	100		
	7	100		
NaOMe	1[a]	16	62	22
	2	80	20	
	7	89	11	
NaN_3	1[a]	18	84	
	2	91	9	
	7	90	10	
KOAc	1[a]	12	88	
	2	69	31	
	7	61	39	
PhMgBr	1[a]		100	
	2		100	
	7	100		

[a] As prepared by addition of chlorine to 3 (0.1 M) in pentane at 0 °C (see Table I, Experimental Section), containing ~20% of 2.

assignments of stereochemistry are based on the magnitude of $J_{2,3}$. Trans compounds exhibit $J_{2,3} \leq 1$ Hz (eq,eq) and cis compounds exhibit $J_{2,3} \simeq 4$ Hz (eq,ax).[8,9]

3-Chloro-2-phenyltetrahydropyran[10] (6, R = Ph) exhibits $J_{2,3} = 10$ Hz, which is indicative of trans diaxial hydrogens. 3-Chloro-2-phenyltetrahydrofuran (8, R = Ph) was assigned cis stereochemistry by comparison with assignments of *cis*- and *trans*-3-methyl-2-phenyltetrahydrofuran.[11]

Nucleophilic Displacement Reactions. For a study of the stereoselectivity achievable in nucleophilic displacement reactions of *cis*- and *trans*-2,3-dichlorotetrahydropyrans (1 and 2), dimethylformamide (DMF) was selected as reaction solvent because of its utility as an aprotic medium for S_N2 reactions.[12] Results of reactions of 1, 2, and 7 with selected nucleophiles in DMF are recorded in Table III. Evaluation of

results of reactions of *cis*-2,3-dichlorotetrahydropyran (1) required correction to remove the contribution of the trans isomer (2) present to the extent of 20% (Table I). Owing to the trans diaxial relationship of the C-3 hydrogen and the C-2 chloro substituent in the cis isomer (1) some elimination occurs with the more basic nucleophiles.

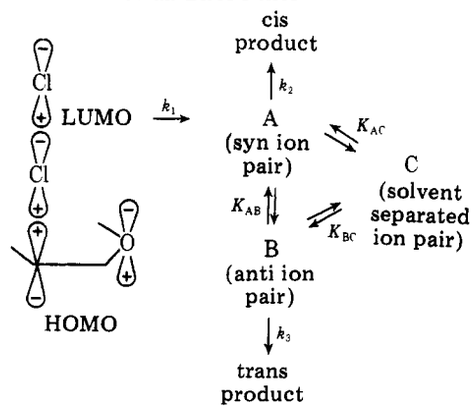
Reaction of phenylmagnesium bromide with either *cis*- or *trans*-2,3-dichlorotetrahydropyran (1 or 2) yields *trans*-2-phenyl-3-chlorotetrahydropyran (6, R = Ph).[10] In contrast, similar reaction of *trans*-2,3-dichlorotetrahydrofuran (7) with phenylmagnesium bromide yielded *cis*-2-phenyl-3-chlorotetrahydrofuran (8, R = Ph) analogous to the result obtained by reaction of phenylmagnesium bromide with *trans*-2,3-dichloro-3-methyltetrahydropyran.[8]

Discussion

Addition of Chlorine to Enol Ethers. Lemieux and Fraser-Reid[2] investigated the addition of halogens to several cyclic enol ethers in carbon tetrachloride solution and proposed as a general mechanism polar attack of halogen on the olefinic bond with formation of a carbonium ion (or ions) which, upon attack of halide ion, leads predominantly to thermodynamic products. Igarashi et al.[14] have extended this work by study of the addition of chlorine to tri-*O*-acetyl-D-glucal in a variety of solvents. They established that (a) product formation is under kinetic, not thermodynamic, control and (b) the stereoselectivity of addition is sensitive to solvent polarity.

Igarashi et al.[14] and later workers[15,16] have proposed modification to the mechanism of Lemieux and Fraser-Reid.[2] The results (Table I) of the present study are fully consistent with earlier findings.[14-16] However, we draw somewhat different conclusions concerning the implications of these data for those mechanistic parameters which determine the stereoselectivity of addition. Chlorine addition occurs in a bimolecular process (Ad_E2) in which the carbon–chlorine bonds are formed in separate steps.[17] Consideration of the initial step—formation of a carbonium ion intermediate—in frontier orbital terms[18] indicates a preferred reaction geometry in which the chlorine molecule is oriented perpendicular to the π system of the enol ether and leads to a "syn" ion pair in which the chloride ion is on the same face of the carbonium (oxonium) ion molecular backbone as the bonded chloro substituent. The net stereoselectivity of the chlorine addition reaction depends on the fate of this initially formed "syn" intimate ion pair (A, Scheme I). Direct collapse of A is the principal reaction pathway for

Scheme I. Addition of an Electrophile (e.g., Cl_2) to an Enol Ether



cyclic enol ethers in solvents with weak ion-solvating ability (Table I) and leads to a cis 2,3-dichloro ether product.[19]

As the ion-stabilizing ability of the reaction solvent increases other fates for ion pair A become increasingly probable. Separation of ion pair A results in solvated ions (C) which may recombine forming either "syn" intimate ion pair A or "anti" intimate ion pair B leading, upon collapse, to the observed (Table I) mixtures of cis and trans 2,3-dichloro ethers. In solvents of intermediate polarity (e.g. chloroform, ethyl acetate) the fate of A depends largely on the relative rates of ion collapse (k_2) and solvation (k_{AC}).

Interconversion of the syn and anti intimate alkoxycarbonium ion pairs A and B requires, in effect, migration of a chloride ion from one face of the cyclic alkoxycarbonium ion to the other. In contract, in acyclic analogues[20] interconversion between syn and anti isomers can occur by rotation of the carbonium ion center about the C–C bond (K_{AB}). Note that rotation of the C-3 carbon about this bond has no direct effect upon the stereochemistry of the product formed by intimate ion pair collapse although such rotation may be important in relieving steric or electronic strains.[21]

While any discussion of structural and conformational features of alkoxycarbonium ions (e.g., A, B, and C, Scheme I) is speculative,[2,14,15] results from both experimental[22] and theoretical[23] studies make clear that the dominant factor providing stabilization is π electron donation by oxygen. As a consequence, the C_2–O bond possesses substantial double bond character and bridged chloronium species are unimportant in alkoxycarbonium ion stabilization.

The more effective syn addition of hydrogen chloride to 4 (as compared with addition of chlorine to 3) is readily accounted for by comparing the intermediate intimate ion pairs initially formed in the respective reactions. The total internuclear distance in the transition state for hydrogen chloride addition (Cl- - -H- - -C) is shorter than that for addition of chlorine (Cl- - -Cl- - -C). This and the lack of electronic repulsion between the chloro substituent in ion pair A and the chloride ion formed by hydrogen chloride addition to 4 (which in this case possess an anti relationship) predicts a "tighter" ion pair and greater reaction stereoselectivity.

Reactions of 1, 2, and 7 with Nucleophiles. Reaction of *cis*-2,3-dichlorotetrahydropyran (1) with five nucleophiles in dimethylformamide yielded, in each case, only trans (i.e., inverted) products (Table III). The results for reactions of the trans 2,3-dichloro ethers 2 and 7 are more complex. Both 2 and 7 yielded only products of inversion in reactions with sodium thiophenoxide; with weaker nuclephiles varying amounts of retention products were observed. With these trans 2,3-dichloro ethers the relative percentages of inversion products were of the order $PhS^- > N_3^- \simeq MeO^- > AcO^-$. This varies somewhat with a nucleophilicity scale ($PhS^- > AcO^- > N_3^-$) determined by relative rates of reaction with methyl iodide in DMF.[24] Since 1 reacted solely by inversion with all nucleophiles studied and acetate ion, the bulkiest nucleophile, was ineffective in achieving replacement with inversion when allowed to react with trans compounds 2 and 7, it is probable that in these instances unfavorable steric interactions between the axial chloro substituent at C-3 and the incoming nucleophile are important.[27] The results of the present study extend and agree, only in part, with previous studies of displacement reactions of α-halo ethers.[25-30]

Experimental Section

Solvents used were commercial AR grade solvents and were not further purified unless otherwise noted. Mass spectra were obtained on CEC 21-110 and Du Pont 21-491B mass spectrometers. ^1H NMR spectra were obtained with a Varian HA-100 spectrometer. Chemical shifts are recorded in parts per million downfield from internal tetramethylsilane.

Chlorination of 3,4-Dihydro-2*H*-pyran (3). General Procedure. Chlorine was passed slowly through a stirred solution of 0.84 g (10 mmol) of 3,4-dihydro-2*H*-pyran in 100 mL of solvent (see Table I) until a yellow color persisted. The solvent and excess chlorine were then removed by distillation (<40 °C) in vacuo. The resulting residue

was dissolved in benzene and analyzed directly by ^{1}H NMR spectrometry. ^{1}H NMR spectra of all preparations (Table I) revealed the presence of only *cis*- and *trans*-2,3-dichlorotetrahydropyrans (**1** and **2**); in no instance was evidence for starting material or other transformation products observed. The ratios of **1** (cis) to **2** (trans) were determined by excision of the respective C-2 H resonances from photocopies of the strip chart-recorded spectra and comparison of their weights.

***trans*-2,3-Dichlorotetrahydropyran (2).** To 1.2 g (10 mmol) of 5-chloro-3,4-dihydro-2*H*-pyran (**4**)[31] in 160 mL of benzene (distilled from calcium hydride) was added anhydrous hydrogen chloride until the solution appeared saturated (as monitored by wet litmus paper). Gas addition was continued for an additional 10 min; the flask was then stoppered tightly and allowed to stand at room temperature for 2 h. The excess hydrogen chloride was removed by passing nitrogen through the solution and the solvent was removed. The ^{1}H NMR spectrum (benzene) of the residue revealed only one resonance assignable to C-2 H (δ 5.93). This material, essentially pure *trans*-2,3-dichlorotetrahydropyran (**2**), was used directly for nucleophilic displacement reactions.

Reactions of *cis*- and *trans*-2,3-Dichlorotetrahydropyrans (1 and 2) and *trans*-2,3-Dichlorotetrahydrofuran (7)[32] with Nucleophiles. General Procedure. To a vigorously stirred mixture of 10 mmol of a nucleophile (Table III) in 20 mL of dimethylformamide[33] was added 5 mmol of the appropriate dichloro ether (or dichloro ether mixture) in 10 mL of dimethylformamide.[33] With the exception of reactions involving potassium acetate and sodium azide the nucleophiles were soluble in dimethylformamide; for these nucleophiles suspensions were used. After 30 min (18 h for potassium acetate) the solution (mixture) was poured into 150 mL of water and extracted with benzene (two 75-mL portions). The combined benzene extracts were washed with 100 mL of water and dried with sodium sulfate and the benzene was removed in vacuo (<40 °C). ^{1}H NMR spectra (Table II) of the residues were obtained directly. Mass spectra of all previously unknown compounds (**5, 6, 8, 9,** R $\neq$ OMe or OAc) exhibited parent ions and fragment ions consistent with the assigned structures. Yields in all displacement reactions were high, although no attempt was made to determine them accurately owing to the difficulty in removing the last traces of dimethylformamide. Side products, as based on the appearance of extraneous doublets in the anomeric proton region of the ^{1}H NMR spectra, were visible only for the KOAc and NaOMe reactions of **1** and **2.** In these instances the expected products constituted >95% of the isolated material. The side products were not identified but are thought to be *cis*- and *trans*-2,3-dimethoxy- and 2,3-diacetoxytetrahydropyrans.

Demonstration That the Product-Forming Step in the Reaction of Chlorine with 3,4-Dihydro-2*H*-pyran is Irreversible, i.e., under Kinetic Control. The chlorination of 0.84 g (10 mmol) of 3,4-dihydro-2*H*-pyran (**3**) was carried out in pentane by the general procedure yielding 82:18 *cis*-: *trans*-2,3-dichlorotetrahydropyrans. This mixture, free of solvent, was then added to 100 mL of dichloromethane containing 0.84 g of 3,4-dihydro-2*H*-pyran and the chlorination was repeated. Analysis of the ^{1}H NMR spectrum (benzene) of the resulting product mixture, as described in the general procedure, showed 57.4% cis (**1**) (predicted value 59.5% if under kinetic control, 38% if under thermodynamic equilibrium; see Table I).

***cis*- and *trans*-3-Chloro-2-thiophenyltetrahydrofurans (8, 9).** One gram (10 mmol) of 3-chloro-4,5-dihydrofuran[34] and 2.2 g (20 mmol) of thiophenol were added to 2 mL of liquid sulfur dioxide at −20 °C.[35] After 10 h at −20 °C the sulfur dioxide was allowed to evaporate at room temperature and the excess thiophenol was removed in vacuo. The ^{1}H NMR spectrum of this crude mixture (Table II) revealed that approximately equal amounts of *cis*- and *trans*-3-chloro-4,5-dihydrofurans (**8** and **9,** R = SPh) had been formed.

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Registry No.—**1,** 52809-66-2; **2,** 7429-32-5; **3,** 110-87-2; **4,** 6581-49-3; **5** (R = SPh), 61900-17-2; **5** (R = OMe), 6559-29-1; **5** (R = N_3), 61900-18-3; **5** (R = OAc), 14750-43-7; **6** (R = SPh), 61900-19-4; **6** (R = OMe), 6559-30-4; **6** (R = N_3), 61900-20-7; **6** (R = OAc), 14750-42-6; **6** (R = Ph), 61900-21-8; **7,** 13129-90-3; **8** (R = SPh), 61900-22-9; **8** (R = OMe), 29120-54-5; **8** (R = N_3), 61900-23-0; **8** (R = OAc), 61900-24-1; **8** (R = Ph), 61900-25-2; **9** (R = SPh), 61900-26-3; **9** (R = OMe), 29120-53-4; **9** (R = N_3), 61900-27-4; **9** (R = OAc), 61900-28-5; NaSPh, 930-69-8; NaOMe, 124-41-4; NaN_3, 26628-22-8; KOAc, 127-08-2; PhBr, 108-86-1; 3-chloro-4,5-dihydrofuran, 17557-40-3; thiophenol, 108-98-5.

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