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A Mild and Convenient Oxidation Procedure for the Conversion of Organoboranes to the Corresponding Alcohols[1]

George W. Kabalka* and Herbert C. Hedgecock, Jr.

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916

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Organoboranes are oxidized efficiently by trimethylamine *N*-oxide dihydrate. The reagent is exceptionally mild, permitting the oxidation of a wide variety of functionally substituted organoboranes. In every instance the yields of product alcohol are as good as or better than the yields obtained using the standard oxidation procedure.

The oxidation of organoboranes has been utilized extensively as a convenient preparation of alcohols (eq 1).[2] In

$$R_3B \xrightarrow{\text{oxidn}} 3ROH \qquad (1)$$

fact, the hydroboration–oxidation sequence is the most efficient route for the anti-Markovnikov hydration of alkenes (eq 2).

$$RCH{=}CH_2 \xrightarrow{BH_3} \xrightarrow{\text{oxidn}} RCH_2CH_2OH \qquad (2)$$

The oxidation of organoboranes has become an increasingly important reaction as the role of organoboranes in organic synthesis has expanded.[3] One of the key features of the organoboranes is that they can be prepared containing a wide variety of functional substituents. These substituents are sometimes sensitive to the oxidation reagents, hydrogen peroxide and sodium hydroxide.[4] The presence of the strong base and oxidant can lead to undesirable side reactions.

In an attempt to minimize side reactions of functionally substituted organoboranes, researchers have resorted to modifying the standard oxidation procedure. Two modifications have been successful: the simultaneous addition of the base and peroxide[5] and the use of milder bases.[6,7] In addition alternate oxidation procedures have been explored. The alternate procedures generally utilize reagents which are inconvenient to handle, difficult to obtain, or are themselves reactive toward certain functional substituents.[8-10]

One reagent has been studied that appeared to offer promise as a mild oxidizing agent, trimethylamine *N*-oxide[11,12] (eq 3). However, anhydrous amine oxides are inconvenient to prepare and the reported procedure utilizes hydrocarbon solvents, whereas most organoboranes are formed in ethereal solvents.

$$R_3B + \bar{O}\text{–}\overset{+}{N}R_3 \longrightarrow R_2B\text{–}OR + :NR_3 \qquad (3)$$

We now wish to report that the commercially available, easily handled, trimethylamine *N*-oxide dihydrate is an efficient reagent for organoborane oxidations. In addition the reagent will tolerate a wide variety of functional substituents and the reactions may be performed in any of the common organic solvents.

Results and Discussion

Temperature and Solvent Effects. Oxidations of organoboranes with trimethylamine *N*-oxide dihydrate (TAO) can be carried out in either hydrocarbon or ethereal solvents. The rate of the oxidations appears to be insensitive to the solvent utilized. This is presumably a consequence of the low solubility of TAO in all of the solvents used in the study.

Table I
Comparison of the Efficiencies of the Trimethylamine *N*-Oxide Dihydrate and Hydrogen Peroxide Oxidation Procedures[a,b]

Organoborane[c]	Registry no.	Product	Registry no.	Yield, %[d] Amine oxide	Yield, %[d] Hydrogen peroxide
Tri-*n*-hexylborane	1188-92-7	1-Hexanol[e]	111-27-3	95	95
Tri-*n*-octylborane	3248-78-0	1-Octanol[e]	111-87-5	95	95
Tri-*sec*-butylborane	1113-78-6	2-Butanol	78-92-2	94	94
Tricyclohexylborane	1088-01-3	Cyclohexanol	108-93-0	94	92
Trinorbornylborane	14289-75-9	*exo*-Norborneol	497-37-0	100	100

[a] The amine oxide procedure was carried out by refluxing 3 equiv of trimethylamine *N*-oxide with the organoborane (1 *M* in diglyme) for 2 hr. [b] The peroxide oxidations were carried out by adding 3 equiv of hydrogen peroxide (30% aqueous solution) and 1 equiv of sodium hydroxide (3 *N*) to the organoborane (1 *M* in tetrahydrofuran) and heating to 60° for 1 hr.[4] [c] The organoborane was prepared via the hydroboration of the corresponding alkene using the standard procedures outlined in ref 4. [d] Yields determined via GLC analysis. [e] Conversion based only on tri-*n*-hexylborane and tri-*n*-octylborane.

Table II
Oxidation of Tricyclohexylborane in the Presence of Added Reagents[a]

Reagent	Yield, %[b] cyclohexanol	Recovered, %[b] reagent
Benzaldehyde	94	100
Butyrophenone	94	100
Ethyl valerate	94	100
Ethyl cinnamate	94	100
Phenylethylene oxide	94	100
Benzonitrile	94	100
Thiophene	94	100
Bromohexane	94	100
3-Penten-2-one	94	95

[a] The oxidations were carried out by adding 3 equiv of trimethylamine *N*-oxide dihydrate to 10 mmol of tricyclohexylborane in diglyme (1 *M*) and heating the reaction to reflux for 2 hr.[16] [b] Determined by GLC analysis.

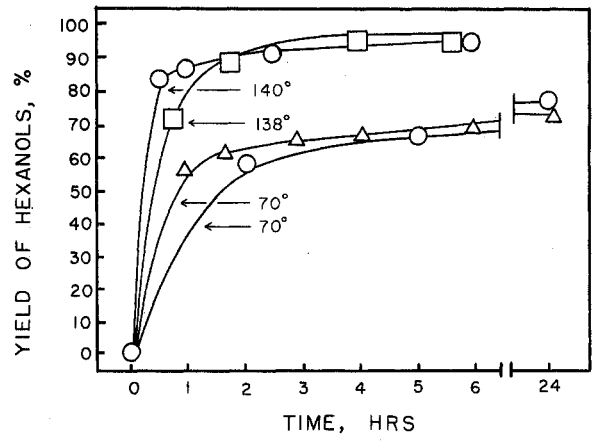


Figure 1. A comparison of the rates of oxidation of tri-*n*-hexylborane with trimethylamine *N*-oxide dihydrate at various temperatures. The reactions were carried out in a variety of solvents: O, diglyme; □, xylene; △, THF.

The rate of the oxidation reaction is temperature dependent. The data indicate that the second and third alkyl groups are removed more slowly than the first, requiring either higher temperatures or longer reaction times.[13] The experimental results are summarized in Figure 1.

TAO permits an essentially quantitative conversion of an organoborane to corresponding alcohol. In all cases the yields of alcohols were as good as or better than the results in which the standard oxidation procedure was employed.[4] The results of a comparative study are summarized in Table I. Diglyme was employed as a solvent in the oxidations, since it is a common hydroboration solvent and permits a convenient oxidation rate.

Specificity. Trimethylamine *N*-oxide dihydrate is a remarkably mild oxidizing agent. A variety of functionality is unaffected by it under the reaction conditions employed. To demonstrate this aspect of the oxidation procedure, tricyclohexylborane was oxidized in the presence of added reagents. In nearly every case the added reagents were found to be unchanged at the end of the oxidation. The results are summarized in Table II.

TAO thus appears to be a milder oxidant than hydrogen peroxide. A series of functionally substituted alkenes was then hydroborated and oxidized using both the TAO procedure and the standard procedure.[4] In a number of these cases isomeric products are possible owing to the effect of the functional group on the direction of the hydroboration reaction.[14] Furthermore, certain of the intermediate organoboranes are prone to reactions such as cyclization.[15] The results are presented in Table III, in which only the major product is considered.

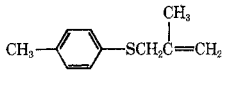
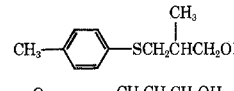
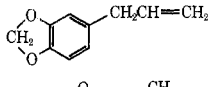
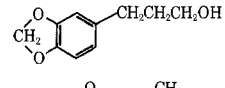
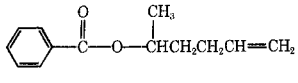
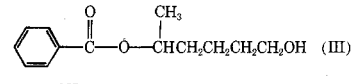
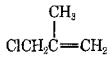
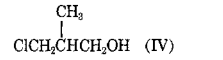
Conclusions

The use of trimethylamine *N*-oxide dihydrate as an oxidizing agent for organoboranes should be considered as a viable alternative to the standard oxidation procedure. The reagent is more convenient and far safer to handle than hydrogen peroxide. Furthermore, the yields of alcohols are at least as good as, and in some cases better than, those obtained in the peroxide procedure.

Experimental Section

Proton NMR spectra were recorded on a Varian Associates A-60 spectrometer. All chemical shifts are reported in parts per million downfield from tetramethylsilane.

Table III
Comparison of the Trimethylamine *N*-Oxide and the Hydrogen Peroxide Oxidation Procedures for a Series of Functionally Substituted Organoboranes[a]

Alkene	Registry no.	Product[b]	Yield, %[c] $(CH_3)_3\overset{+}{N}-\overset{-}{O}\cdot 2H_2O$[d]	Yield, %[c] H_2O_2–OH^-[e]
	54844-24-5	 (I)	92	83
	94-59-7	 (II)	75	75
	54844-25-6	 (III)	94	91
	563-47-3	 (IV)	67	60
$ClCH_2CH_2CH_2CH{=}CH_2$	928-50-7	$ClCH_2CH_2CH_2CH_2CH_2OH$ (V)	95	89

[a] The organoboranes were formed via the hydroboration of the alkenes listed in the table. [b] Only the major product is indicated. [c] By GLC analysis. [d] Oxidations were carried out by adding 3 equiv of trimethylamine *N*-oxide dihydrate to 10 mmol of the organoborane in diglyme (1 *M*) and heating for 2 hr.[16] [e] Oxidations were carried out by adding 3 equiv of H_2O_2 (30%, aqueous) and 1 equiv of NaOH (3 *N*) to 10 mmol of organoborane (1 *M*) in diglyme. The reaction mixture was then heated to 60° for 1 hr.

Table IV
Hydroboration–Oxidation of Representative Alkenes. Experimental Details

Alkene	Registry no.	Quantity, g	Oxidn reflux time, hr	Product	Yield, %	Bp, °C
1-Hexene	592-41-6	2.53	3	1-Hexanol[a]	95	156
1-Octene	111-66-0	3.36	2	1-Octanol[a]	95	196
(*E*)-2-Butene	624-64-6	1.69	1	2-Butanol[b]	94	101
Cyclohexene	110-83-8	2.48	1	Cyclohexanol	94	160
Norbornene		2.72	1	*exo*-Norborneol	100	176

[a] Product contains 6% of the secondary isomer. [b] Product contains no 1-butanol.

All melting points and boiling points are uncorrected. The gas chromatography work was performed on a Varian Aerograph 90-P. The following columns were used: 5% SE-30 on Chromosorb W, 10 ft × 0.25 in.; 9% Carbowax 20M on Chromosorb W, 10 ft × 0.25 in. Commercially available samples of (*E*)-2-butene, 1-hexene, 1-octene, cyclohexene, norbornene, safrole, 3-chloro-2-methylpropene, 5-chloro-1-pentene, and trimethylamine *N*-oxide dihydrate were used without further purification (Aldrich).

Products were isolated by distillation at reduced pressures. The samples were characterized and the data compared to known values.

Oxidations. General Procedures. A. Trimethylamine *N*-Oxide Dihydrate. The organoborane (10 mmol) dissolved in 20 ml of diglyme was contained in a 50-ml, N_2-flushed flask fitted with a reflux condenser and mercury bubbler, vented to a hood. TAO (30 mmol, 3.33 g) was added all at once to this solution and the reaction mixture was gently refluxed with efficient stirring for 2 hr.[17] The reaction product was isolated by extraction. The contents of the reaction flask were transferred to a separatory funnel. The flask was rinsed with 50 ml of ether and the ether solution was added to the separatory funnel. The mixture was extracted three times with 25 ml of saturated aqueous NaCl. The ether layer was separated and dried over anhydrous magnesium sulfate, and the product was distilled.

B. Hydrogen Peroxide. The organoborane (10 mmol) dissolved in 20 ml of tetrahydrofuran was contained in a 50-ml, N_2-flushed flask fitted with a septum inlet and a reflux condenser.[18] Aqueous sodium hydroxide (10 mmol, 3.33 ml of 3 *N* solutions) was added followed by the slow addition, via syringe, of hydrogen peroxide (30 mmol, approximately 3.3 ml of a 30% aqueous solution). The reaction mixture was heated to 60° for 1 hr to ensure completion of the oxidation. The alcoholic products were isolated by saturating the mixture with sodium chloride and separating the THF layer, which was back extracted with saturated sodium chloride solution. The THF layer was dried ($MgSO_4$) and the product isolated by distillation.

Hydroboration. The hydroborations were carried out using standard procedures.[19] The procedure using BH_3–THF was as follows. The alkene (30 mmol) was dissolved in 20 ml of diglyme in a 50-ml, N_2-flushed, round-bottomed flask equipped with a septum inlet and a reflux condenser. The solution was cooled to 0° by means of an ice–water bath and the BH_3–THF (10 mmol, 5 ml of a 2 *M* solution) was added via a syringe. The hydroboration was permitted to proceed for 0.5 hr at 0° and then the mixture was allowed to warm to room temperature. The THF could be removed by distillation prior to the oxidation or during the oxidation.

Oxidations with Added Reagents. These oxidations were carried out as described above except that 10 mmol of the extra reagent was added to the reaction mixture. The percentage of added reagent (and alcohol product) was determined via gas chromatographic analyses utilizing an internal standard.

Aliphatic Alcohols. In each case 30 mmol of the alkene in 20 ml of diglyme was hydroborated with 10 mmol (5 ml of 2 *M* solution) of BH_3·THF. The resultant organoborane was oxidized with trimethylamine *N*-oxide dihydrate (30 mmol, 3.33 g) by refluxing for the indicated time. The products were analyzed by GLC and isolated by distillation.

The experimental details are summarized in Table IV.

3-*p*-Tolylthio-2-methylpropene. *p*-Tolylthiol (0.3 mmol, 24.2 g) was treated with 1 equiv of aqueous sodium hydroxide (50 ml, 6 *N*). The mixture was stirred at room temperature for 4 hr. The water was removed at room temperature under reduced pressure. The residual salt was mixed with 50 ml of methanol. 3-Chloro-2-methylpropene (0.3 mmol, 27.5 g) was added to the mixture and stirred overnight. The mixture was added to 100 ml of H_2O and the product was extracted with 3 × 50 ml of ether. The ether layer was dried over anhydrous $MgSO_4$ and the product was distilled: bp 67° (0.3 mmHg); yield 43 g, (80%); NMR (neat) δ 1.8 (s, 3, CH_3C=), 2.2 (s, 3, CH_3Ar), 3.4 (s, 2, $-CH_2S$), 4.8 (broad s, 2, H_2C=C), 7.2 ($A_2'X_2'$, 4, ArH).

Anal. Calcd for $C_{11}H_{14}S$: C, 74.09; H, 7.92; S, 17.99. Found: C, 74.20; H, 8.06; S, 18.40.

5-Benzoxy-1-hexene. 5-Hexen-2-one (0.30 mol, 30 g) was slowly added to aqueous $NaBH_4$ (0.1 mol, 1 *M*). The mixture was stirred for 1.5 hr and the product, 1-hexen-5-ol, was isolated by extraction into ether and then distilled: bp 135° (740 mmHg) [lit. bp 138–139° (752 mmHg)];[20] yield of alcohol 90% (27 g); NMR ($CDCl_3$) δ 1.2 (d, 3, $-CH_3$, J = 6 Hz), 1.5 (m, 2, $-CH_2C$=C), 2.1 (m, 2, $-CH_2-$), 3.0 (s, 1, –OH), 3.8 (sextet, 1, methine), 5.1 (m, 2, H_2C=C), 5.8 (m, complex, 1 H). The benzoate ester was prepared by adding benzoyl chloride (0.3 mol, 42 g) to 1-hexen-5-ol (0.27 mol, 27 g) dissolved in 50 ml of pyridine. The product was isolated by pouring the reaction mixture into 100 g of ice–water. The 5-benzoxy-1-hexene was extracted with 3 × 50 ml of ether. The ether layer was dried over anhydrous $MgSO_4$ and the product was distilled: bp 95° (0.5 mmHg); NMR ($CDCl_3$) δ 1.4 (d, 3, $-CH_3$, J = 6 Hz), 2.0 (m, broad, 4, $-CH_2CH_2-$), 5.2 (sextet, 1, methine), 5.1 (m, 2, H_2C=C–), δ 5.9 (m, 1, –C=CH–), 7.6 (m, 3, ArH), 8.3 (m, 2, ArH).

3-*p*-Tolythio-2-methyl-1-propanol (I). 3-*p*-Tolythio-2-methylpropene (30 mmol, 5.34 g) was hydroborated with 10 mmol of BH_3·THF at 0° for 1 hr. Oxidation was performed by refluxing the resultant organoborane with 30 mmol of TAO in diglyme for 30 min. GLC analysis (SE-30) indicated a 92% yield of I. The product was isolated by distillation: bp 112–113° (0.15 mmHg); NMR ($CDCl_3$) δ 1.0 (d, 3, $-CH_3$, J = 7 Hz), 1.9 (broad m, 1, CH), 2.3 (s, 3, $ArCH_3$), 2.9 [m (AB), 2, SCH_2], 3.0 (s, 1, –OH), 3.6 (d, 2, $-CH_2O$, J = 6 Hz), 7.3 ($A_2'X_2'$, 4, ArH).

Anal. Calcd for $C_{11}H_{16}OS$: C, 67.28; H, 8.22; S, 16.34. Found: C, 67.20; H, 8.16; S, 16.53.

3-(3,4-Methylenedioxyphenyl)-1-propanol (II). Safrole (30 mmol, 4.86 g) was hydroborated with 10 mmol of BH_3·THF at 0° for 1 hr. The resultant organoborane was oxidized by refluxing with 30 mmol of TAO in diglyme for 1 hr. GLC analysis (Carbowax) indicated a 75% yield of product II; 12% of the secondary isomer was also present. The product was isolated by distillation: bp 124–128° (2 mmHg) [lit. bp 170–172° (8 mmHg)];[21] NMR ($CDCl_3$) δ 1.8 (m, 2, $-CH_2-$), 2.7 (t, 2, $ArCH_2-$, J = 7 Hz), 3.7 (t, 2, $-CH_2O$, J = 6.5 Hz), 3.0 (s, 1, –OH), 6.0 (s, 2, OCH_2O), 6.8 (s, 3, ArH).

5-Benzoxy-1-hexanol (III). 5-Benzoxy-1-hexene (30 mmol, 6.12 g) was hydroborated with BH_3·THF at 0° for 1 hr. The resultant organoborane was oxidized by refluxing with 30 mmol of TAO in diglyme for 30 min. GLC analysis (SE-30) indicated a 95% yield of III. The product was isolated by distillation: bp 121–125° (0.05 mmHg); NMR ($CDCl_3$) δ 1.5 (broad envelope, 9, alkyl), 3.3 (s, 1, OH), 3.7 (t, 2, $-CH_2O$, $J \cong$ 6.5 Hz), 5.2 (m, 1, OCH–), 7.6 (m, 3, ArH), 8.2 (m, 2, ArH).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.05; H, 8.06.

3-Chloro-2-methyl-1-propanol (IV). 3-chloro-2-methylpropene (30 mmol, 2.72 g) was hydroborated with 10 mmol of BH_3·THF for 1 hr at 0°. The resultant organoborane was oxidized with TAO by refluxing in diglyme for 1 hr. GLC analysis (Carbowax) indicated a 67% yield of product. The product was isolated by distillation: bp 65–66° (9–10 mmHg) [lit. bp 76° (21 mmHg)];[22] NMR (neat) δ 0.9 (d, 3, $-CH_3$, J = 7 Hz), 1.9 (m, 1, –CH–), 3.5 (d, 2, $-CH_2Cl$, J = 6 Hz), 3.6 (d, 2, $-CH_2O$, J = 5.5 Hz), 4.6 (s, 1, –OH).

5-Chloro-1-pentanol (V). 5-Chloro-1-pentene (30 mmol, 3.14 g) was hydroborated with BH_3·THF at 0° for 1 hr. The resultant organoborane was oxidized by refluxing with 30 mmol of TAO in

diglyme for 1 hr. GLC analysis (SE-30) indicated a 95% yield of V. The product was isolated by distillation: bp 74° (5 mmHg) [lit. bp 121° (30 mmHg)];[23] NMR ($CDCl_3$) δ 1.6 (m, broad, 6, aliphatic), 3.6 (m, broad, 4, $-CH_2O$ and CH_2Cl), 3.9 (s, 1, OH).

Acknowledgment. We wish to thank the Research Corporation for support of this study.

Registry No.—I, 54844-22-3; II, 7031-03-0; III, 54844-23-4; IV, 10317-10-9; V, 5259-98-3; *p*-tolylthiol, 106-45-6; 5-hexen-2-one, 109-49-9; 1-hexen-5-ol, 626-94-8.

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(17) If 20% excess of the amine *N*-oxide dihydrate is used the reaction needs to be refluxed for only 30 min. Excess amine *N*-oxide also increases the rate of reactions run at 70°.
(18) Oxidations were carried out in diglyme as well as THF. The results were identical.
(19) The hydroborations may also be carried out using the commercially available borane dimethyl sulfide complex (Aldrich).
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Mechanisms and Stereochemistry of Displacement of Methoxide Ion by Hydroxide Ion from Phosphorus in Phospholanium and Phosphorinanium Salts

Kenneth L. Marsi

Department of Chemistry, California State University, Long Beach, Long Beach, California 90840

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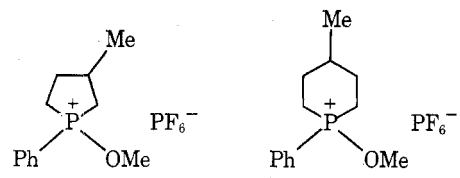
The synthesis of the cis and trans isomers of 1-methoxy-3-methyl-1-phenylphospholanium hexafluorophosphate is reported. Hydroxide displacement of methoxide from the trans isomer leads to 3-methyl-1-phenylphospholane 1-oxide with 51% retention and 49% inversion of configuration at phosphorus, while cleavage of the cis isomer gives the same product with 42% retention and 58% inversion. The cis and trans isomers of 4-methyl-1-phenylphosphorinane 1-oxide were also prepared and methylated with retention to yield the corresponding *cis*- and *trans*-1-methoxy-4-methyl-1-phenylphosphorinanium hexafluorophosphates. Alkaline cleavage of the cis and trans phosphorinanium salts leads to complete inversion of configuration as a result of nucleophilic attack at phosphorus. ^{18}O-Labeling experiments reveal that, under reaction conditions employed, nucleophilic attack at methoxy carbon occurs to the extent of 11% in the phospholanium salts and 9% in the phosphorinanium salts. The stereochemistry of nucleophilic displacement at phosphorus in both systems can be rationalized in terms of stereoelectronic vs. ring strain effects in phosphorane intermediates.

As part of a continuing study of the effect of ring size on the mechanism and stereochemistry of displacement of leaving groups from phosphorus in heterocyclic phosphonium salts,[1] we wish to report results of hydroxide ion displacement of methoxide ion from *cis*- and *trans*-1-methoxy-3-methyl-1-phenylphospholanium (**1**) and *cis*- and *trans*-1-methoxy-4-methyl-1-phenylphosphorinanium (**2**) hexafluorophosphates.



1 2

Synthesis of and Assignment of Stereochemistry to Alkoxyphosphonium Salts. These compounds were prepared by alkylation of the stereoisomerically pure phosphine oxides[1d,f] with trimethyloxonium hexafluorophosphate (eq 1). As expected, alkylation occurred with retention of configuration at phosphorus as shown previously for the phosphetane oxide system.[2] It was also possible to alkylate the oxides by use of methyl fluorosulfonate ("Magic Methyl"). ^1H NMR analysis of methoxyphosphonium fluorosulfonates formed also indicated stereospecific alkylation. However, because the fluorosulfonate salts were difficult to obtain in a pure crystalline form for the purpose of elemental analysis, trimethyloxonium hexafluorophosphate was used and found to be superior in this respect. Characteristics of these compounds are listed in Table I.

$$R_3P{=}O + (CH_3)_3O^+\ PF_6^- \longrightarrow R_3P^+OCH_3\ PF_6^- + (CH_3)_2O \quad (1)$$

The cis and trans stereochemistry for isomers of **1** was established indirectly by an X-ray crystal structure determination.[3] The stereostructure of the isomers of **2** was assigned by ^1H NMR analysis of the oxides (**3**) from which they were derived, together with corroborating physical properties of the oxides. With respect to cyclohexane, the conformational preferences for methyl and phenyl[4] are such that for the 1,4-trans arrangement of these two groups