Hz, 1 H), 5.33 (q, $J$ = 2 Hz, 1 H), 5.40 (d, $J$ = 4 Hz, 1 H), 5.44 (m, 1 H), 5.59 (dd, $J$ = 3, 10 Hz, 1 H), 5.79 (dd, $J$ = 2, 10 Hz, 1 H); exact mass calcd for $C_{41}H_{60}O_{11}$ (M - oleandrose - $H_2O$) 728.4136, found 728.4138.

**5-*O*-(*tert*-Butyldimethylsilyl)-10,11-dihydro-10-hydroxyavermectin B1 (9a) and 4″-*O*-(Trimethylsilyl)-5-*O*-(*tert*-butyldimethylsilyl)-10,11-dihydro-10-hydroxyavermectin B1 (9b).** To a solution of 2 g of dry **8** in 20 mL of dichloromethane were added 1 mL of distilled triethylamine, 1 g of *tert*-butyldimethylsilyl chloride, and 100 mg of 4-(*N*,*N*-dimethylamino)-pyridine. The mixture was stirred at 25 °C for 18 h. The product was isolated by flash column chromatography on silica gel with 1:1 ethyl acetate/hexane to yield 1 g of the 5-O-silylated product **9a** as a glassy solid: $^1$H NMR 0.15 (s, 6 H), 0.90 (m, 16 H), 1.10 (d, $J$ = 7 Hz, 3 H), 1.15 (d, $J$ = 7 Hz, 1 H), 1.26 (t, $J$ = 6 Hz, 9 H), 1.53 (s, 3 H), 1.55 (m, 7 H), 1.66 (s, 1 H), 1.78 (s, 3 H), 1.98 (m, 3 H), 2.15–2.40 (m, 6 H), 2.55 (sh d, $J$ = 1 Hz, 1 H), 3.14 (t, $J$ = 9 Hz, 1 H), 3.21 (t, $J$ = 9 Hz, 1 H), 3.31 (d, $J$ = 3 Hz, 1 H), 3.40 (s, 3 H), 3.42 (m, 3 H), 3.43 (s, 3 H), 3.58 (m, 1 H), 3.71 (d, $J$ = 6 Hz, 1 H), 3.77 (m, 2 H), 3.94 (m, 1 H), 3.98 (br s, 1 H), 4.16 (br s, 1 H), 4.44 (br s, 1 H), 4.65 (d, $J$ = 15 Hz, 1 H), 4.71 (d, $J$ = 3 Hz, 1 H), 4.84 (d, $J$ = 15 Hz, 1 H), 4.95 (d, $J$ = 7 Hz, 1 H), 5.23 (s, 1 H), 5.26 (s, 1 H), 5.36 (s, 1 H), 5.37 (d, $J$ = 3 Hz, 1 H), 5.40 (m, 1 H), 5.55 (dd, $J$ = 3, 10 Hz, 1 H), 5.76 (d, $J$ = 10 Hz, 1 H). To a solution of 1 g (1.0 mmol) of **9a** in 10 mL of dry dichloromethane were added 2 mL of molecular sieve dried *N*,*N*-dimethylformamide (DMF), 0.5 mL of distilled triethylamine, and 0.125 mL (1.0 mmol) of chlorotrimethylsilane. After 1 h at 25 °C, another 0.065 mL (0.5 mmol) of chlorotrimethylsilane was added. The reaction was analyzed after another 30 min by TLC (silica gel, 2:1 hexane/ethyl acetate, $R_f$(**9b**) = 0.6, $R_f$(**9a**) = 0.13), which indicated completion. The mixture was quenched with a saturated sodium bicarbonate solution and extracted with dichloromethane. The product was purified by flash column chromatography on silica gel (2:1 hexane/ethyl acetate) to afford 0.65 g of **9b** as a glassy solid: $^1$H NMR 0.12 (s, 15 H), 0.80–1.00 (m, 19 H), 1.05 (d, $J$ = 7 Hz, 3 H), 1.17 (d, $J$ = 6 Hz, 3 H), 1.23 (d, $J$ = 6 Hz, 3 H), 1.28 (m, 1 H), 1.30–1.70 (m, 4 H), 1.51 (s, 3 H), 1.78 (s, 3 H), 1.95 (m, 3 H), 2.12–2.40 (m, 5 H), 3.12 (t, $J$ = 9 Hz, 1 H), 3.20 (t, $J$ = 9 Hz, 1 H), 3.30–3.50 (m, 3 H), 3.38 (s, 3 H), 3.45 (s, 3 H), 3.56 (m, 1 H), 3.60–3.82 (m, 2 H), 3.72 (d, $J$ = 4 Hz, 1 H), 3.96 (m, 1 H), 3.98 (br s, 1 H), 4.65 (dt, $J$ = 2, 15 Hz, 1 H), 4.71 (d, $J$ = 3 Hz, 1 H), 4.86 (dt, $J$ = 2, 15 Hz, 1 H), 4.96 (d, $J$ = 9 Hz, 1 H), 5.25 (d, $J$ = 2 Hz, 1 H), 5.28 (d, $J$ = 2 Hz, 1 H), 5.30 (d, $J$ = 3 Hz, 1 H), 5.35 (s, 1 H), 5.40 (m, 1 H), 5.57 (dd, $J$ = 3, 10 Hz, 1 H), 5.78 (dd, $J$ = 2, 10 Hz, 1 H).

**10-Fluoro-10,11-dihydroavermectin B1 (10b).** To a solution of 840 mg (0.78 mmol) of **9b** in 10 mL of dichloromethane cooled to −78 °C was added 0.120 mL (0.91 mmol) of (*N*,*N*-diethylamino)sulfur trifluoride. The mixture was stirred at −78 °C for 2 h and TLC analysis showed no more progress in the conversion of starting material to product. The reaction was stopped by the addition of 2 mL of a 7% aqueous sodium carbonate solution, warming the mixture to room temperature, and extracting the product with dichloromethane. The product was isolated by flash column chromatography on silica gel (1:4 ethyl acetate/hexane) and further purified by reverse phase HPLC on the M20 column (91:9 methanol/water) to afford 314 mg of 4″-*O*-(trimethylsilyl)-5-*O*-(*tert*-butyldimethylsilyl)-10,11-dihydro-10-fluoroavermectin B1 (**10a**). Product **10a** was then dissolved in 5 mL of dry THF in a polypropylene flask and 15 mL of a solution of HF–pyridine (prepared by diluting 10 mL of commercially available pyridine–hydrogen fluoride complex in 60 mL of dry THF and 30 mL of distilled pyridine) was then added. After 20 h at room temperature, the reaction mixture was poured into a separatory funnel containing 200 mL of ice–water, carefully neutralized with sodium bicarbonate, and extracted with ether. The ethereal extracts were combined and dried over magnesium sulfate, filtered, and evaporated in vacuo to afford a solid, which was purified by preparative TLC (three 1-mm thick plates eluted in 1:3 hexane/ethyl acetate) to yield 200 mg of **10b** as a glassy solid: $^1$H NMR 0.90 (m, 10 H), 1.20 (m, 10 H), 1.37–2.10 (m), 1.51 (s, 3 H), 1.81 (s, 3 H), 2.10–2.48 (m, 6 H), 2.50 (d, $J$ = 2 Hz, 1 H), 3.17 (t, $J$ = 9 Hz, 1 H), 3.21 (t, $J$ = 9 Hz, 1 H), 3.21 (s, 1 H), 3.45 (s, 6 H), 3.30–3.70 (m, 3 H), 3.80 (m, 2 H), 3.90 (s, 1 H), 3.95 (m, 1 H), 3.98 (d, $J$ = 6 Hz, 1 H), 4.30 (t, $J$ = 6 Hz, 1 H), 4.60–4.90 (m, 4 H), 4.92 (s, 1 H), 5.03 (d, $J$ = 12 Hz, 1 H), 5.34 (s, 1 H), 5.40 (d, $J$ = 4 Hz, 1 H), 5.47 (m, 2 H), 5.58 (dd, $J$ = 3, 10 Hz, 1 H), 5.79 (dd, $J$ = 2, 10 Hz, 1 H); FAB MS 915 (M + Na); exact mass calcd for $C_{41}H_{59}O_{10}F$ (M - oleandrose - water) 730.4092, found 730.4090.

**10,11-Dihydroavermectin B1 (2) and 8,11-Dihydro-$\Delta^9$-avermectin B1 (12).** To a solution of 1 g (1.0 mmol) of dry **9a** in 10 mL of distilled dichloromethane was added 1 mL of distilled triethylamine, followed by 1.0 g (3 mmol) of dichlorotriphenylphosphorane in one portion. The mixture was stirred at 20 °C for 3 h before TLC analysis (1:1 ethyl acetate/hexane, $R_f$ (sm) = 0.5, $R_f$(product) = 0.6) indicated completion of reaction. The reaction mixture was flash filtered through a short column of silica gel with 1:1 ethyl acetate/hexane to remove the phosphine oxide and ammonium salt. The filtrate was evaporated in vacuo to afford 950 mg of a yellow glassy solid (identified by NMR as a mixture of allylic chlorides **11a** and **11b**), which was dissolved in 2 mL of toluene and 2 mL of tri-*n*-butyltin hydride. This mixture was then heated in a 100 °C oil bath for 18 h. The cooled mixture was then flash chromatographed on silica gel (3:1 hexane/ethyl acetate) to remove the tin compounds. The isolated product mixture (ca. 2:1 **12a**:**12b** isomer ratio by NMR, a single spot by TLC on silica gel) was further separated by reverse phase HPLC (M20 column, 90:10 methanol/water) to afford 450 mg of 5-*O*-(*tert*-butyldimethylsilyl)-10,11-dihydroavermectin B1 (12a) (eluting first) and 280 mg of 5-*O*-(*tert*-butyldimethylsilyl)-8,11-dihydro-$\Delta^9$-avermectin B1 (**12b**) (next major peak). The former product **12a** was desilylated with HF–pyridine (as described for 10-fluoro-10,11-dihydroavermectin B1, **10b**) to provide **2**, which was indistinguishable from that obtained by hydrogenation of **1**. The latter compound **12b** (280 mg) was desilylated with HF–pyridine to yield 180 mg of **12** as a glassy solid: $^1$H NMR 0.88 (d, $J$ = 7 Hz, 3 H), 0.93 (d, $J$ = 7 Hz, 3 H), 0.93 (t, $J$ = 9 Hz, 3 H), 1.01 (d, $J$ = 12 Hz, 1 H), 1.05 (d, $J$ = 6 Hz, 3 H), 1.25 (d, $J$ = 6 Hz, 3 H), 1.27 (d, $J$ = 7 Hz, 3 H), 1.40–1.80 (m), 1.58 (s, 3 H), 1.82 (s, 3 H), 2.01 (dd, $J$ = 6, 12 Hz, 1 H), 2.04 (d, $J$ = 10 Hz, 1 H), 2.10–2.44 (m, 6 H), 2.47 (d, $J$ = 2 Hz, 1 H), 3.04 (q, $J$ = 10 Hz, 1 H), 3.16 (dt, $J$ = 2, 9 Hz, 1 H), 3.18 (s, 1 H), 3.22 (t, $J$ = 9 Hz, 1 H), 3.38 (s, 3 H), 3.42 (s, 3 H), 3.43–3.62 (m, 3 H), 3.67 (t, $J$ = 10 Hz, 1 H), 3.75 (m, 2 H), 3.92 (s, 1 H), 3.98 (m, 1 H), 4.02 (d, $J$ = 6 Hz, 1 H), 4.14 (t, $J$ = 9 Hz, 1 H), 4.24 (m, 1 H), 4.73 (d, $J$ = 4 Hz, 1 H), 4.97 (dd, $J$ = 10, 15 Hz, 1 H), 5.11 (dd, $J$ = 3, 10 Hz, 1 H), 5.25 (d, $J$ = 2 Hz, 1 H), 5.32 (m, $J$ = 6 Hz, 1 H), 5.37 (d, $J$ = 4 Hz, 1 H), 5.51 (s, 1 H), 5.60 (dd, $J$ = 3, 10 Hz, 1 H), 5.79 (dd, $J$ = 2, 10 Hz, 1 H), 5.80 (m, 1 H); exact mass calcd for $C_{48}H_{74}O_{14}$ 874.5079, found 874.5091.

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**Registry No.** 1, 65195-55-3; 2, 116522-33-9; 3, 71827-03-7; 4, 116521-80-3; 5, 116555-48-7; 6, 118920-20-0; 7, 116522-61-3; 8, 116555-52-3; 9a, 118893-15-5; 9b, 118920-21-1; 10a, 118920-22-2; 10b, 116522-13-5; 11a, 118920-23-3; 11b, 118920-24-4; 12, 118893-16-6; 12a, 116522-54-4; 12b, 116522-56-6; NBA, 79-15-2.

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## Ionic Chlorination (Bromination) of Alkanes and Cycloalkanes with Methylene Chloride (Bromide)/Antimony Pentafluoride[1]

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### Introduction

Halonium ions[2] of cyclic and acyclic nature are of increasing interest as reactive intermediates and reagents

(1) Synthetic Methods and Reactions. 137. Part 136, see: Olah, G. A.; Wu, A.; Farooq, O. *J. Org. Chem.*, in press.

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**Table I. $SbF_5$-Catalyzed Chlorination and Bromination of Alkanes (Cycloalkanes) with Methylene Chloride and Bromide**

| hydrocarbon | haloalkane (cycloalkane) | % yield Cl | % yield Br |
|---|---|---|---|
| adamantane | 1-haloadamantane | 80 | 74 |
| cyclopentane | cyclopentyl halide | 74 | 70 |
| isobutane | *tert*-butyl halide | 76 | 75 |
| propane | isopropyl halide | 69 | 64 |
| neopentane | *tert*-amyl halide | 88 | 72 |

for organic synthesis. Following the first preparation and characterization of dialkyl halonium ions as stable fluoroantimonates by Olah and December,[2] a large number of symmetrical and unsymmetrical dialkyl halonium ions were prepared,[2,3] and their alkylating ability, as well as intermolecular exchange reactions, were studied.[4,5] Continuing study of halonium ions led to the development of a nonvolatile and safer chloromethylating agent in the form of chloromethyl halonium ion prepared by the reaction of $SbF_5$ with $CH_2Cl_2$.[6] This reagent combination was used to prepare a series of other chloromethyl halonium ions as well as chloromethylmethyl halonium ions.[6] In the preparation of stable carbocations via ionization of the corresponding fluorides (alcohols, etc.) in $SbF_5$–$SO_2$ or $SO_2ClF$ solution, methylene chloride is used on occasion as a cosolvent. In our experience, at low temperatures (–60 to –78 °C) and short times for tertiary ions, this does not lead to chloride-quenched products, but with more reactive secondary systems and particularly when the temperatures are raised and the samples are kept for longer periods of time, such quenching occurs. On the basis of these initial observations, we now want to report that excess methylene chloride (bromide) with $SbF_5$ can be used as an effective halogenating agent for saturated hydrocarbons with longer reaction times and at room temperature.

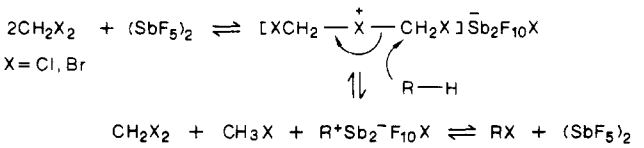
## Results and Discussion

When adamantane was allowed to react in the presence of $SbF_5$ with excess of $CH_2Cl_2$ initially at –78 °C and then at ambient temperature for 24 h, 1-chloroadamantane was obtained as isolated product after workup in 80% yield. Under the same reaction conditions when isobutane was reacted, 2-methyl-2-chloropropane was obtained in 76% yield. Hydrocarbons containing secondary C–H bonds such as cyclopentane gave under identical reaction conditions a 74% yield of the cyclopentyl chloride (Table I). Neopentane, containing only primary C–H bonds, gave isomerized 2-chloro-2-methylbutane as the only isolated product.

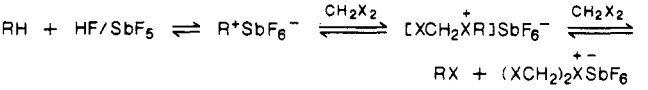
The reaction of related alkanes and cycloalkanes in the presence of $SbF_5$ with excess methylene bromide proceeds similarly, giving comparable yields of the corresponding bromoalkanes (cycloalkanes) (Table I).

Gaseous byproducts formed during the progress of reactions were analyzed in all the reactions and were found to consist of $CH_3F$, $CH_3X$ (X = Cl, Br), and $CH_4$. The overall concentration of the gaseous products in the initial stage of reaction from –78 °C to room temperature was low but became significant during reaction at room temperature. The amount of $CH_3F$ formed was observed to increase during the reaction at the expense of $CH_3Cl$ (as well as $CH_3Br$).

**Scheme I**




**Scheme II**




When bis(halomethyl) halonium ions $[(XCH_2)_2X^+]$ prepared under stable ion conditions from $SbF_5$ and $CH_2X_2$ (X = Cl, Br) according to our previously reported procedure[6] were added to adamantane in an excess of methylene halide at –78 °C and the reaction was continued for the same length of time as the parent reaction at room temperature, 1-haloadamantanes were obtained after appropriate workup in yields similar as described in Table I.

Formation of halogenated alkanes (cycloalkanes) RX along with methyl halides in the reaction of alkanes (cycloalkanes) R–H with $SbF_5$–$CH_2X_2$ can be best explained by Scheme I.

The reaction of $SbF_5$–$CH_2X_2$ (as well as prepared halonium ion) with alkanes takes prolonged reaction times to give satisfactory yields of alkyl halides. This is probably due to the indicated equilibria of alkyl halides with $SbF_5$ to form carbocation equilibria. Since $SbF_5$ (always containing some HF) is also known to react with alkanes and polycyclic hydrocarbons,[7] e.g. adamantane, to form the corresponding cations, formation of alkyl halides can in part also be explained via halomethylalkyl halonium ions shown in Scheme II.

The reaction of alkyl halides with $SbF_5$ to form carbocations[7] and that of methyl halides to form the corresponding polarized complexes (RX → $SbF_5$) and dimethyl halonium ions (RXR),[2,3,8] respectively, is well known.

When a solution of *dimethyl halonium ions* prepared under stable ion conditions from $SbF_5$ and methyl halides in $SO_2ClF$ at –78 °C[2] is added to the alkanes of the present investigation in $CH_2X_2$ at –78 °C and the reaction is allowed to continue as previously, the corresponding alkyl halides are obtained in similar yield, indicating again the equilibria depicted in Scheme III. The haloalkane products formed may, of course, themselves form with $SbF_5$ ionic equilibria as shown in Schemes I and II.

Halogen exchange of methyl halides with $SbF_5$ forms methyl fluoride and mixed antimony halides. Mixed antimony halides as Lewis acids are also known as halogenating agents.[9] The process of halogen exchange continues until all $SbF_5$ is converted to $SbX_5$ with simultaneous formation of $CH_3F$, thus eventually shifting the equilibria to the formation of halogenated products (Scheme IV).

Further investigation for determining the possible path of the ionic halogenation reaction was carried out on the

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(3) Peterson, P. E. *Acc. Chem. Res.* **1971**, *4*, 407 and references therein.
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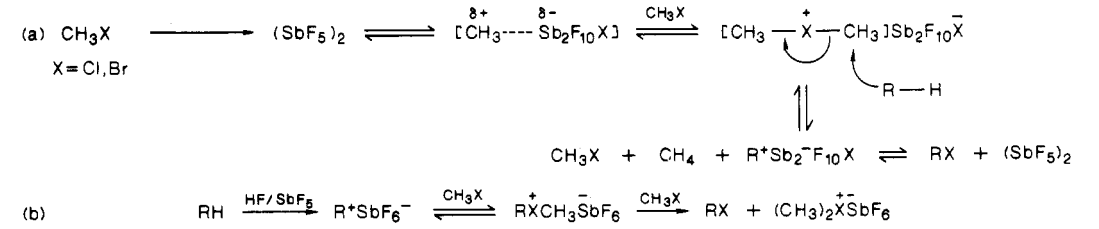
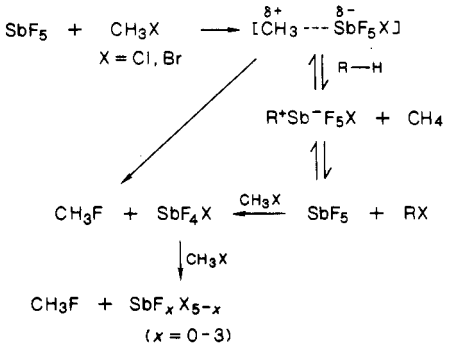
**Scheme III**



**Scheme IV**



preparation of stable alkyl carbocation, e.g. 1-adamantyl carbocation, via 1-fluoroadamantane, $SbF_5$, and $SO_2ClF$ at −78 °C, which was subsequently allowed to react with $CH_2X_2$ (X = Cl, Br) and $CH_3X$ (X = Cl, Br), respectively, under the similar conditions as previous reactions to afford solely 1-adamantanol after aqueous workup. The present evidence might suggest that Schemes I and III(a) are the likely paths for the title reaction.

Reaction of halomethyl halonium carbocations have not so far been investigated in any system except in the preparation of some other onium ions.[6] A halomethyl halonium ion, as shown in Scheme I, can abstract a hydride from an alkane and generate a carbenium ion responsible for the formation of the observed alkyl halide. formation of carbenium ions may equally be attributed to the reactions of the intermediately formed dimethyl halonium ions and $CH_3X$–$SbF_5$ complex with the alkanes via hydride abstractions.

## Experimental Section

Antimony pentafluoride (Aldrich), isobutane and propane (Air Product), cyclopentane and adamantane (Aldrich), and neopentane (Alfa) all were commercially available compounds of high purity. Methylene halides (Aldrich) were dried over $P_2O_5$ under reflux prior to use.

Analysis of liquid products was performed on a Varian Gas Chromatograph (Model 3700) equipped with a quartz silica capillary column coated with DB-1, and that of gaseous products on a Hewlett Packard gas chromatograph (Model 5730A) equipped with a stainless steel column packed with BEEA. GC–MS spectra were recorded on a Finnigan Mat Model 700 GC–MS spectrometer equipped with an ion-trap detector and interfaced with a Varian Associates Model 3500 gas chromatograph. NMR spectra were recorded on a Varian (VXR-200) superconducting NMR spectrometer.

**General Procedure for Halogenation of Alkanes.** To a well-stirred solution of $SbF_5$ (fresh distilled; 15 mmol) in methylene chloride or bromide (30 mL) was added 12 mmol of alkane under dry argon at −78 °C. The reaction mixture was stirred for about 2 h at −78 °C and then slowly warmed up to room temperature at which it was allowed to continue for about 24 h. Working up the reaction mixture in ice–bicarbonate followed by extraction in $CH_2Cl_2$ and removal of the solvent afforded alkyl halides, which were subsequently purified by column chromatography (silica gel, hexane as eluent). The alkyl halides were identified in the GC (by comparing the retention time with authentic compounds), GC–MS, and $^{13}C$ NMR spectra.

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# Hydrolysis of Substituted Crown Ether Acetals

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A number of studies have been made of the hydrolysis of a wide variety of cyclic and acyclic acetals.[1] However, very little is known about the hydrolysis of macrocyclic acetals with the poly(oxyethylene) unit, the so-called crown ether acetals.[2] This is largely attributable to much difficulty in the synthesis of such acetals from carbonyl compounds and oligoethylene glycols by the conventional methods.[3]

Gold et al. prepared a series of 2-methyl-substituted crown ether acetals from acetaldehyde and oligoethylene glycols by using ion-exchange resins[4] and studied the effects of added alkali-metal ions on the acid-catalyzed hydrolysis of these acetals.[2a,b] We recently reported on the effects of ring size on the hydrolysis of 2,2-diphenyl-substituted crown ether acetals,[2c] which were formed by a redoxical acetalization of diphenyldiazomethane with 2,3-dichloro-5,6-dicyanobenzoquinone in the presence of oligoethylene glycols.[5] Successful extension of this redox reaction to other diazoalkanes, providing variously substituted new crown ether acetals,[6] prompted us to investigate the substituent effects in the hydrolysis of these macrocyclic acetals (**1**). Hydrolysis of corresponding dimethyl acetals (**2**) was also made in the same conditions to know the effects of structural change in the alcohol moieties.

## Results and Discussion

The rate constants and the activation parameters were collected for the HCl-catalyzed hydrolysis of variously

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