Stable Carbonium Ions. LXIII.[1] Diprotonated Aliphatic Alkoxy Alcohols and Their Cleavage in Strong Acid Solution. Stable Secondary Alkoxycarbonium Ions

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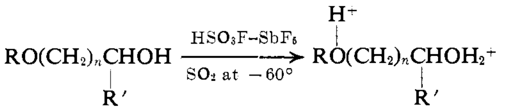
Abstract: Protonation of acyclic alkoxy alcohols has been studied in HSO_3F–SbF_5–SO_2 solution. Diprotonation was observed with negligible exchange rates between −60 and 0°. When the solutions are allowed to warm up, the diprotonated alkoxy alcohols undergo various cleavage reactions depending on the nature of their alkyl groups. The formation of carbonium ions, alkoxycarbonium ions, protonated alcohols, diols, and aldehydes was observed. In order to identify the alkoxycarbonium ions formed they were also generated by ionization of α-chloro ethers in SbF_5–SO_2 solution.

Our recent investigation of protonated dicarboxylic acids and diols,[3,4] leads us now to study the protonation of a series of aliphatic alkoxy alcohols in the strong acid system FSO_3H–SbF_5.

The cleavage of protonated ethers[5] and alcohols[6] yields carbonium ions and protonated alcohols. The cleavage of alkoxy alcohols, however, may also yield diprotonated diols, protonated aldehydes, or alkoxycarbonium ions, depending on which bond is broken. Since the pioneering work of Meerwein, *et al.*,[7] on alkoxycarbonium ions, this field has received considerable interest. Recent papers[8–12] report the observation (nmr) or isolation of a series of stable tertiary alkoxycarbonium ions, dialkoxycarbonium ions, and primary alkoxycarbonium ions formed in the cleavage of diprotonated alkoxy alcohols.

Results and Discussion

I. Protonation of Aliphatic Alkoxy Alcohols. When an alkoxy alcohol is dissolved in FSO_3H–SbF_5–SO_2, a stable and clear solution is obtained. The pmr spectrum at −60° indicates protonation of both the ether and the hydroxyl oxygen atoms. The chemical shifts and coupling constants are summarized in Table I.



$$RO(CH_2)_n\underset{\displaystyle R'}{\underset{|}{C}}HOH \xrightarrow[SO_2\text{ at }-60^\circ]{HSO_3F-SbF_5} R\overset{\displaystyle H^+}{\overset{|}{O}}(CH_2)_n\underset{\displaystyle R'}{\underset{|}{C}}HOH_2^+$$

The OH_2^+ protons which appear around −9.5 ppm in protonated aliphatic alcohols are submitted to additional deshielding due to the proximity of the charge on the ether oxygen. They appear as far downfield as −11.1 ppm. The OH^+ proton, for the same reasons, is deshielded to about −10.5 ppm from TMS.

The chemical shift of the methylene (methine) protons is inversely proportional to the distance of these protons from the charges. The α protons appear around −5.2 ppm; the β protons at about −2.5 ppm.

2-Methoxyethanol (Figure 1). $CH_3O^+(H)CH_2CH_2OH_2^+$ shows the OH_2^+ protons as a triplet at −10.9 ppm. The shape of this triplet is perturbed by the fact that the α- and β-CH_2 protons have identical chemical shifts. (This makes the OH_2^+ triplet an X_2 part of an $A_2B_2X_2$ system.) This effect, which was previously observed on diprotonated glycols,[13] is now observed on all protonated 2-alkoxyethanols. The OH^+CH_3 proton appears as a complex multiplet at −10.1 ppm. The α- and β-CH_2 protons appear at −5.2 ppm and the CH_3 protons as a doublet (J_{H-H} = 3.0 Hz) at −4.65 ppm.

1-Methoxy-2-propanol (Figure 2). $CH_3O^+(H)CH_2CH(OH_2^+)CH_3$ shows the OH_2^+ protons as a doublet (J_{H-H} = 3.0 Hz) at −10.5 ppm overlapping partially the OH_2^+ quartet centered at −10.4 ppm. The CH proton appears as a complex multiplet at −5.7, the CH_2 protons as a triplet (J_{H-H} = 6.0 Hz) at −5.0, the α-CH_3 proton as a doublet (J_{H-H} = 3.0 Hz) at −4.7, and the β-CH_3 as a doublet (J_{H-H} = 6.5 Hz) at −1.9 ppm.

3-Ethoxy-1-propanol (Figure 3). $CH_3CH_2O^+(H)CH_2CH_2CH_2OH_2^+$ shows the OH_2^+ triplet (J_{H-H} = 3.0 Hz) at −10.10, the OH^+ quintuplet (J_{H-H} = 3.2 Hz) at −9.30 ppm. All protons α to oxygen appear as a complex multiplet at −5.10, the β-methylene group as a quintuplet (J_{H-H} = 6.0 Hz) at −2.85 ppm, and the methyl triplet (J_{H-H} = 7.0 Hz) at −1.85 ppm.

The following other alcohols were studied: 3-methoxypropanol, 2-methoxybutanol, 2-propoxyethanol, 2-isopropoxyethanol, and 2-butoxyethanol. The nmr spectra indicate that all these species are diprotonated in FSO_3H–SbF_5–SO_2 solution at −60°. The chemical shifts and coupling constants are summarized in Table I.

II. Alkoxycarbonium Ions. In order to identify by an independent route the alkoxycarbonium ions formed in the cleavage of diprotonated alkoxy alcohols, the secondary methoxyethyl-, methoxypropyl-, ethoxy-

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[1] Part LXII: G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, **90**, 2587 (1968).

[2] NATO Postdoctoral Fellow, 1966–1967.

[3] G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **89**, 4752 (1967).

[4] G. A. Olah and J. Sommer, *ibid.*, **89**, 927 (1967).

[5] G. A. Olah and D. H. O'Brien, *ibid.*, **89**, 1725 (1967).

[6] G. A. Olah, J. Sommer, and E. Namanworth, *ibid.*, **89**, 3576 (1967).

[7] H. Meerwein, K. Bodenbenner, P. Borner, F. Kunert, and K. Wunderlich, *Ann.*, 632, 38 (1960); H. Meerwein, V. Hederich, H. Morschel, and K. Wunderlich, *ibid.*, 635, 1 (1960).

[8] B. G. Ramsay and R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **88**, 3058 (1966).

[9] H. Hart and D. Tomalia, *Tetrahedron Lett.*, 3383 (1966).

[10] K. Dimroth and P. Heinrich, *Angew. Chem.*, 78, 714 (1966).

[11] S. Kabuss, *ibid.*, 78, 714 (1966).

[12] G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 2993 (1967).

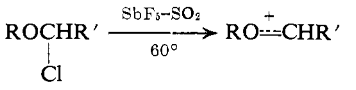
[13] G. A. Olah and J. Sommer, *ibid.*, **89**, 927 (1967).

Table I. Nmr Chemical Shifts of Diprotonated Alkoxy Alcohols in $FSO_3H-SbF_5-SO_2$ Solution at −60° [a]

Alkoxy alcohols	OH_2^+	OH^+	H_1	H_2	H_3	H_4	H_5	H_6
1 + 2 3 + $CH_3OCH_2CH_2OH_2$ H	−10.90 (m)	−10.50 (m)	−4.65	−5.2				
1 + 2 3 + 4 $CH_3OCH_2CH(OH_2)CH_3$ H	−10.50 (d, 3.0)	−10.40 (m)	−4.7 (d, 3.0)	−5.0 (t, 6.0)	−5.7	−1.9 (d, 6.5)		
1 + 2 4 3 + $CH_3OCH(CH_3)CH_2OH_2$ H	−10.90 (m)	−10.10 (m)	−4.65 (d, 3.0)	−5.40 (m)	−5.15	−2.0 (d, 6.0)		
1 + 2 5 4 3 + $CH_3OCH(CH_3)CH_2CH_2OH_2$ H	−10.10 (m, 3.0)	−9.30 (m)	−4.60 (d, 3.1)	−5.20 (m)		−2.90 (q, 7.0)	−2.0 (d, 7.0)	
4 1 + 2 3 + $CH_3CH_2OCH_2CH_2OH_2$ H	−11.10	−10.30	−5.30 (m)			−1.90 (t, 7.0)		
5 1 + 2 4 3 + $CH_3CH_2OCH_2CH_2CH_2OH_2$ H	−10.10	−9.30	−5.10 (m)			−2.85 (qi, 6.0)	−1.85 (t, 7.0)	
5 4 1 + 2 3 + $CH_3CH_2CH_2OCH_2CH_2OH_2$ H	−10.90	−10.1	−5.70			−2.30 (m)	−1.30 (t, 7.0)	
4 1 + 2 3 + $(CH_3)_2CHOCH_2CH_2OH_2$ H	−10.75 (m)	−10.75 (m)	−5.10 (m)			−1.9 (d, 6.5)		
$CH_3CH_2CH_2CH_2\overset{+}{O}CH_2CH_2\overset{+}{O}H_2$ H	−10.85 (m)	−10.05 (m)	−5.20 (m)			−2.30 (m)	−1.70 (m)	−1.20 (t, 7.0)

[a] In parts per million from external TMS. The coupling constants are indicated in hertz next to the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; qi, quintuplet.

ethyl-, and ethoxypropylcarbonium ions have been generated by ionization of the corresponding α-chloro ethers in SbF_5-SO_2 solution at −60°.



$$RO\underset{Cl}{\underset{|}{C}}HR' \xrightarrow[60°]{SbF_5-SO_2} R\overset{+}{O}{=}CHR'$$

The secondary alkoxycarbonium ions may be written as the two resonance forms

$$R\overset{+}{O}{=}CHR' \longleftrightarrow RO\overset{+}{C}HR'$$

The nmr spectra show a substantial deshielding (9.9 ppm) for the methine proton (−5.9 ppm in the un-ionized halo ether), and for the other protons a deshielding which decreases as the distance to the $C^+{=}O$ bond increases.

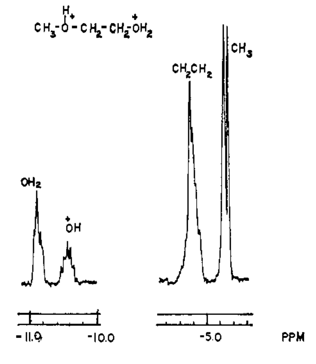


Figure 1.

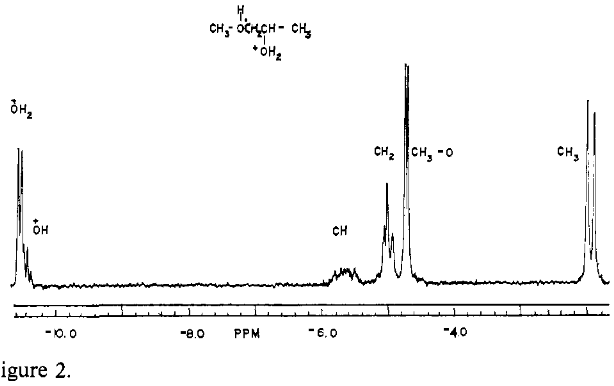


Figure 2.

The chemical shifts and the coupling constants of both the starting halo ethers and the alkoxycarbonium ions are given in Table II.

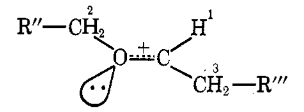
By calculating the activation energy of rotation around the $C^+{=}O$ bond, Ramsey and Taft[8] estimated the π-bond order to be about 0.2 to 0.3 in dimethoxymethylcarbonium ion. Long-range coupling between protons 1 and 2 has been observed in primary alkoxycarbonium ions.[12] We wish now to report some examples of long-range coupling between the protons

Table II. Nmr Chemical Shifts of α-Chloro Ethers (Neat) at −20° and of Their Alkoxycarbonium Ions in SbF_5–SO_2 Solution at −60° [a]

α-Chloro ether	H_1	H_2	H_3	H_4	H_5
2 1 3 $CH_3CH(Cl)OCH_3$	−5.80 (q,5.5)	−3.60 (s)	−1.85 (d,5.5)		
2 1 3 4 $CH_3OCH(Cl)CH_2CH_3$	−5.85 (t,5.5)	−3.80 (s)	−2.20 (m)	−1.25 (t,7.5)	
$CH_3CH_2OCH(Cl)CH_3$	−5.95 (q,5.5)	−3.95 (m)	−1.95 (d,5.5)	−1.45 (t,7.5)	
4 2 1 3 5 $CH_3CH_2OCH(Cl)CH_2CH_3$	−5.90 (t,5.5)	−4.00 (m)	−2.20 (m)	−1.45 (t,7.5)	−1.25 (t,7.0)
Alkoxycarbonium ion					
2 + 1 3 $CH_3\overset{+}{O}{=}CHCH_3$	−9.50 (d,4.0)	−5.30 (s)	3.20 (d,4.0)		
2 + 3 $CH_3\overset{+}{O}{=}C(CH_3)_2$[b]		−5.0 (s)	−3.18 (s)		
3 2 + 1 4 $CH_3CH_2\overset{+}{O}{=}CH_2CH_3$	−9.85 (q,4.0)	−5.55 (q,7.0)	−3.07 (d)	−1.70 (t)	
3 2 + 1 4 $CH_3CH_2\overset{+}{O}{=}CHCH_2CH_3$	−9.95 (m)	−5.51 (q,7.0)	−3.52 (q,6.5)	−1.70 (t,7.0)	−1.10 (t,6.5)
3 + 1 2 4 $CH_3\overset{+}{O}{=}CHCH_2CH_3$	−9.90 (m)	−5.30 (s)	−3.60 (q,9.70)	−1.25 (t,7.0)	

[a] In parts per million from external TMS. Multiplicity: q, quartet; s, singlet; d, doublet; t, triplet; m, multiplet. The coupling constants are given in hertz next to the multiplicity. For simplification, long-range coupling constants observed in the alkoxycarbonium ion do not figure in this table. [b] Prepared by cleavage of $(CH_3O)_2C(CH_3)_2$ in SbF_5–FSO_3H–SO_2 at −60°.

2 and 3 in secondary alkoxycarbonium ions. Coupling



of this type has been explained in terms of hyperconjugation of the π orbitals with the CH(2) and CH(3) σ orbitals in substituted ethylenes by Hoffmann.[14]

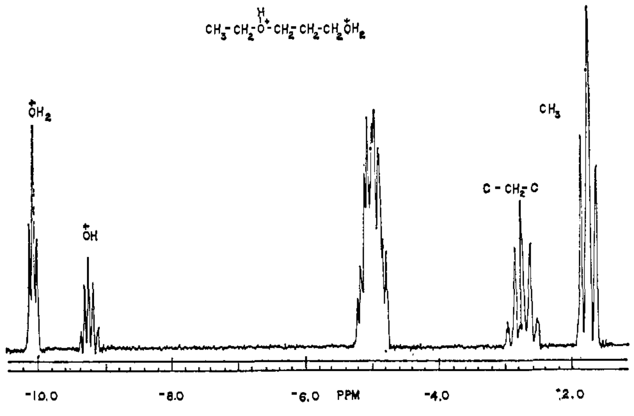
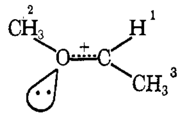


Figure 3.

We did not observe any *cis–trans* isomers in the secondary alkoxycarbonium ions studied. This is obviously due to the high energy difference between the *cis* and *trans* configurations.

Methoxymethylcarbonium Ion (Figure 4). The methine proton appears as a quartet of quartets ($J_{1,3}$ = 4.0, $J_{1,2}$ = 0.8 Hz) at −9.50 ppm. The methoxy protons (2) appear as a five-line multiplet ($J_{2,3}$ = $J_{2,1}$ = 0.8 Hz)



at 5.30 ppm and the CH_3(3) proton appears as a doublet of quartets at −3.20 ppm. The long-range coupling has been confirmed by decoupling experiments. Irradiation of the H(2) multiplet collapses the H(1) and H(3) lines, respectively, to a quartet and a doublet.

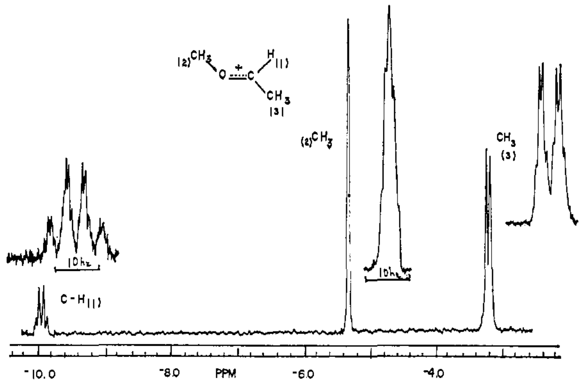
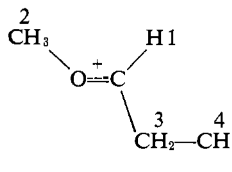


Figure 4.

Methoxyethylcarbonium Ion (Figure 5). The methine



proton is deshielded to −9.90 ppm as a multiplet, but the coupling, $J_{1,3}$, with the methylene protons is sur-

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(14) L. Hoffmann, *Mol. Phys.*, **1**, 326, (1958).

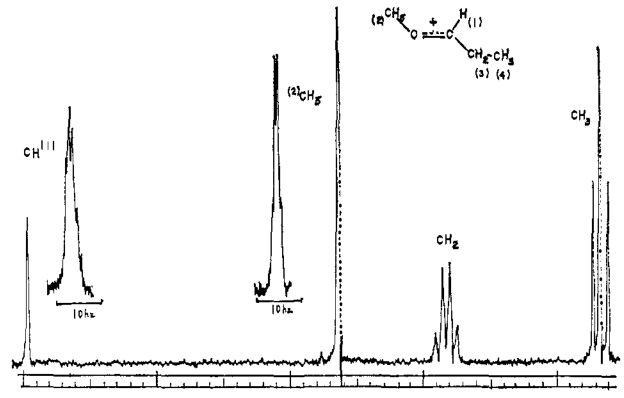


Figure 5.

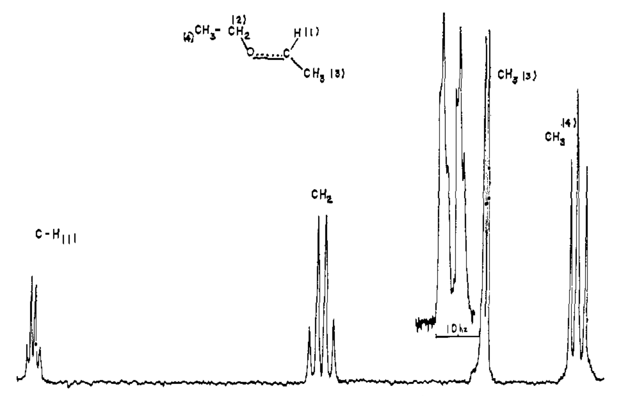


Figure 6.

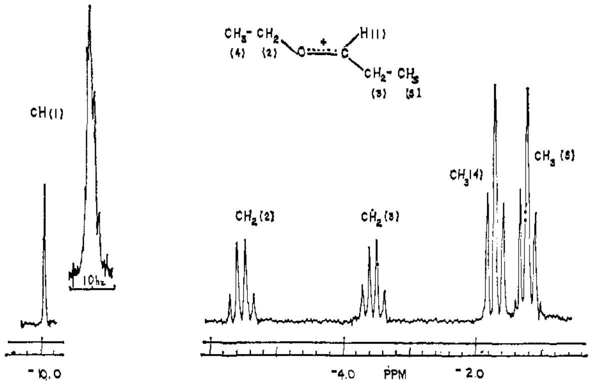
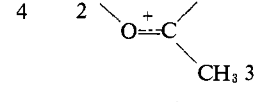


Figure 7

prisingly small ($J_{1,3} \simeq 0.7$ Hz) compared to the preceding example and the same effect is observed in the other alkoxyethylcarbonium ions. This effect due to unequal rotamer distribution around the $^{+}CH-CH_2$ bond has been reported in various systems by Karabatsos and coworkers.[15-17] It is interesting to note that in this case where the π-bond order is inferior to 1, the effect is very important.

The methylene protons appear as a quartet ($J_{3,4}$ = 7.0 Hz) at −3.60 ppm and the methoxy protons as a multiplet at −5.30 ppm. These protons are coupled to both 1 and 3 protons but the resolution was insufficient to measure accurately $J_{1,2}$ and $J_{1,3}$ in this case. The methylene triplet appears at −1.25 ppm ($J_{3,4}$ = 7.0 Hz).

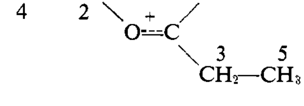
Ethoxymethylcarbonium ion (Figure 6) shows the



$$\overset{4}{CH_3}-\overset{2}{CH_2}-\overset{+}{O}{=}C(\overset{1}{H})-\overset{3}{CH_3}$$

methine proton as a quartet ($J_{1,3}$ = 4.0 Hz). The $CH_3(3)$ appears as a doublet ($J_{3,1}$ = 4.0 Hz) of triplets ($J_{2,3}$ = 0.8 Hz) and the $CH_3(4)$ as a triplet ($J_{2,4}$ = 7.0 Hz) at −1.70 ppm.

Ethoxyethylcarbonium ion (Figure 7) shows the methine proton as a complex multiplet at −9.95 ppm. Here again the coupling with the α-methylene protons is very small ($J_{1,3} \simeq 0.7$ Hz) compared to the same coupling in the alkoxymethylcarbonium ion ($J_{1,3}$ = 4.0 Hz). The α-methylene protons appear as a quartet



$$\overset{4}{CH_3}-\overset{2}{CH_2}-\overset{+}{O}{=}C(\overset{1}{H})-\overset{3}{CH_2}-\overset{5}{CH_3}$$

($J_{2,4}$ = 7.0 Hz) at −5.51 ppm and the β-methylene protons at −3.52 as a quartet ($J_{3,5}$ = 6.5 Hz). The 4 and 5 methyl protons appear respectively at −1.70 and −1.10 ppm.

III. Pathways of Cleavage of Diprotonated Alkoxy Alcohols. When the solutions of diprotonated alkoxy alcohols $RO^{+}H(CH_2)_nCH(OH_2^{+})R$ in SbF_5-FSO_3H solution are allowed to warm, cleavage may occur at three bonds: $R-O^{+}$, $O^{+}-(CH_2)_2$, or $CH-OH_2^{+}$. In the strong acid system, cleavage occurs under nonequilibrium conditions, and the products are rate controlled. For example, when ethanol and propionaldehyde were protonated in the strong acid system used and their solutions mixed and allowed to react for 24 hr, no change or formation of the ethoxyethylcarbonium ion was observed. A quantitative discussion of the cleavage products, however, is not possible because many of the products formed are unstable in the reaction medium at the temperatures where they are formed in the cleavage reactions. Yield estimates of products therefore cannot be given and only a qualitative picture can be derived based on observable products in the strong acid system by the nmr method used. Cleavage of the diprotonated hydroxy ethers can be interpreted in terms of the following three main mechanistic pathways (though others may also be involved). (1) Cleavage of the alkyl group R from the protonated ether alcohols with formation of a carbonium ion and diprotonated diol is favored by a tertiary or secondary alkyl group and does not occur when R is smaller than *n*-propyl. When R is ethyl or methyl, this cleavage would lead to a primary carbonium ion, without the possibility of rearrangement to a secondary carbonium ion by hydride shift.

$$\underset{H}{R\overset{+}{O}}CH_2\underset{^{+}OH_2}{CH}R \longrightarrow R^{+} + H_2\overset{+}{O}CH_2\underset{\overset{+}{O}H_2}{CH}R'$$

(2) Cleavage of the $RO^{+}(H)-CH_2$ bond yields a protonated alcohol and a protonated hydroxycarbonium ion which may rearrange to a stable protonated

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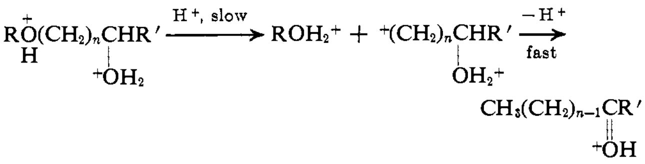
(15) G. J. Karabatsos and H. Nelson, *J. Am. Chem. Soc.*, 87, 2864 (1965).
(16) G. J. Karabatsos and H. Nelson, *Tetrahedron*, 23, 1079 (1967).
(17) G. J. Karabatsos and K. L. Krummel, *ibid.*, 23, 1097 (1967).

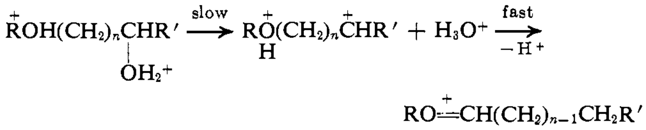
aldehyde or ketone or undergo elimination and polymerization.



$$\underset{H}{R\overset{+}{O}}(CH_2)_n\underset{{}^+OH_2}{CHR'} \xrightarrow{H^+,\text{ slow}} ROH_2^+ + {}^+(CH_2)_n\underset{OH_2^+}{CHR'} \xrightarrow[\text{fast}]{-H^+} CH_3(CH_2)_{n-1}\underset{\overset{\|}{{}^+OH}}{CR'}$$

This bond breakage takes place more easily than that of CH_2–OH_2^+ bond because the latter would yield a primary carbonium ion.

(3) Cleavage of the CH–OH_2^+ bond yields an alkoxycarbonium ion.



$$\overset{+}{R}OH(CH_2)_n\underset{OH_2^+}{CHR'} \xrightarrow{\text{slow}} \underset{H}{R\overset{+}{O}}(CH_2)_n\overset{+}{C}HR' + H_3O^+ \xrightarrow[-H^+]{\text{fast}} RO\overset{+}{=}CH(CH_2)_{n-1}CH_2R'$$

The alkoxycarbonium ion itself may cleave in the acid system with formation of R^+ and a protonated aldehyde.

Diprotonated 2-methoxyethanol, $CH_3O^+(H)CH_2CH_2$-OH_2^+, cleaves at +70° to the methoxymethylcarbonium ion (half-life 30 min). This ion is very stable but cleaves slowly further with formation of protonated acetaldehyde.

Diprotonated 1-methoxy-2-propanol cleaves slowly at −10° to a mixture of protonated acetone, methanol, and methoxyethylcarbonium ion.

Diprotonated 2-methoxy-1-propanol cleaves slowly at the same temperature to give protonated propionaldehyde and protonated methanol.

Diprotonated 2-methoxybutanol cleaves to protonated methanol and butyraldehyde.

Diprotonated 2-ethoxyethanol is very stable and cleaves slowly at room temperature with formation of ethoxymethylcarbonium ion.

Diprotonated 3-ethoxypropanol cleaves slowly at 0° to a mixture of ethoxyethylcarbonium ion, protonated ethanol, and propionaldehyde.

Diprotonated 2-propoxyethanol yields diprotonated glycol at −50° with a half-life of about 30 min.

Diprotonated 2-butoxyethanol cleaves with formation of trimethylcarbonium ion and diprotonated glycol. Half-life of this reaction is about 30 min at −10°.

Experimental Section

Materials. 1-Methoxy-2-propanol was prepared by treating sodium methoxide with propylene oxide in methanol following the procedure of Chitwood and Freure.[18] 2-Methoxy-1-propanol was made by treating propylene oxide with methanol in acidic conditions.[19] 2-Propoxy-1-ethanol, 2-isoproxyethanol, and 2-butoxyethanol were prepared by reaction of ethylene oxide on the corresponding alcohols in the presence of base.[20] α-Chloroethyl methyl ether, α-chloropropyl methyl ether, α-chloroethyl ethyl ether, and α-chloropropyl ethyl ether were prepared following the procedure described in "Organic Syntheses"[21] with the following modifications. The reactions were carried out at −10° for the preparation of the α-chloroethyl ethers and at −35° for the α-chloropropyl ethers. The reaction products were all vacuum distilled or transferred at −30°. Only the main fractions of the distillates were used.

Nmr Spectra. Varian Associates Model A-56/60A or HA-60 nmr spectrometers with variable-temperature probes were used for all spectra. The decoupling experiments were done on a Varian Associates Model HA-100 nmr spectrometer. The protonation of the ether alcohols in FSO_3H-SbF_5-SO_2 solution was carried out at −70° according to the procedure previously described.[4] The ionization of the α-chloro ethers in SbF_5-SO_2 solution was effected at −70° according to a procedure described in earlier work.[12] Cleavage of the protonated alkoxy alcohols was studied directly in the nmr sample tubes. All the peak areas in the spectra were integrated and the integration supported the spectra assignments.

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