

Stable Carbonium Ions. LXIII.¹ Diprotonated Aliphatic Alkoxy Alcohols and Their Cleavage in Strong Acid Solution. Stable Secondary Alkoxy-carbonium Ions

George A. Olah and Jean Sommer²

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received October 30, 1967

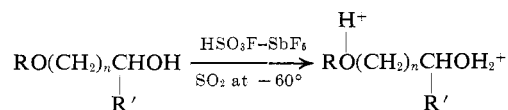
Abstract: Protonation of acyclic alkoxy alcohols has been studied in $\text{HSO}_3\text{F}-\text{SbF}_5-\text{SO}_2$ solution. Diprotonation was observed with negligible exchange rates between -60 and 0° . When the solutions are allowed to warm up, the diprotonated alkoxy alcohols undergo various cleavage reactions depending on the nature of their alkyl groups. The formation of carbonium ions, alkoxy-carbonium ions, protonated alcohols, diols, and aldehydes was observed. In order to identify the alkoxy-carbonium 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 $\text{FSO}_3\text{H}-\text{SbF}_5$.

The cleavage of protonated ethers⁵ and alcohols⁶ yields carbonium ions and protonated alcohols. The cleavage of alkoxy alcohols, however, may also yield diprotonated diols, protonated aldehydes, or alkoxy-carbonium ions, depending on which bond is broken. Since the pioneering work of Meerwein, *et al.*,⁷ on alkoxy-carbonium ions, this field has received considerable interest. Recent papers⁸⁻¹² report the observation (nmr) or isolation of a series of stable tertiary alkoxy-carbonium ions, dialkoxy-carbonium ions, and primary alkoxy-carbonium 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 $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$, 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.

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

- (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).

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). $\text{CH}_3\text{O}^+(\text{H})\text{CH}_2\text{-CH}_2\text{OH}_2^+$ 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 ($J_{\text{H-H}} = 3.0$ Hz) at -4.65 ppm.

1-Methoxy-2-propanol (Figure 2). $\text{CH}_3\text{O}^+(\text{H})\text{CH}_2\text{-CH}(\text{OH}_2^+)\text{CH}_3$ shows the OH_2^+ protons as a doublet ($J_{\text{H-H}} = 3.0$ 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 ($J_{\text{H-H}} = 6.0$ Hz) at -5.0 , the α - CH_3 proton as a doublet ($J_{\text{H-H}} = 3.0$ Hz) at -4.7 , and the β - CH_3 as a doublet ($J_{\text{H-H}} = 6.5$ Hz) at -1.9 ppm.

3-Ethoxy-1-propanol (Figure 3). $\text{CH}_3\text{CH}_2\text{O}^+(\text{H})\text{-CH}_2\text{CH}_2\text{CH}_2\text{OH}_2^+$ shows the OH_2^+ triplet ($J_{\text{H-H}} = 3.0$ Hz) at -10.10 , the OH^+ quintuplet ($J_{\text{H-H}} = 3.2$ 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 ($J_{\text{H-H}} = 6.0$ Hz) at -2.85 ppm, and the methyl triplet ($J_{\text{H-H}} = 7.0$ 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 $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$ solution at -60° . The chemical shifts and coupling constants are summarized in Table I.

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

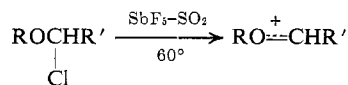
- (13) G. A. Olah and J. Sommer, *ibid.*, **89**, 927 (1967).

Table I. Nmr Chemical Shifts of Diprotonated Alkoxy Alcohols in $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$ Solution at -60°

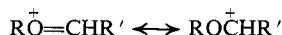
Alkoxy alcohols	OH_2^+	OH^+	H_1	H_2	H_3	H_4	H_5	H_6
$\begin{array}{c} 1 + 2 \quad 3 + \\ \text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}_2 \\ \\ \text{H} \end{array}$	-10.90 (m)	-10.50 (m)	-4.65	—5.2—				
$\begin{array}{c} 1 + 2 \quad 3 + \quad 4 \\ \text{CH}_3\text{OCH}_2\text{CH}(\text{OH}_2)\text{CH}_3 \\ \\ \text{H} \end{array}$	-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)		
$\begin{array}{c} 1 + 2 \quad 4 \quad 3 + \\ \text{CH}_3\text{OCH}(\text{CH}_3)\text{CH}_2\text{OH}_2 \\ \\ \text{H} \end{array}$	-10.90 (m)	-10.10 (m)	-4.65 (d, 3.0)	-5.40 (m)	-5.15	-2.0 (d, 6.0)		
$\begin{array}{c} 1 + 2 \quad 5 \quad 4 \quad 3 + \\ \text{CH}_3\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}_2 \\ \\ \text{H} \end{array}$	-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)	
$\begin{array}{c} 4 \quad 1 + 2 \quad 3 + \\ \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}_2 \\ \\ \text{H} \end{array}$	-11.10	-10.30		—5.30— (m)		-1.90 (t, 7.0)		
$\begin{array}{c} 5 \quad 1 + 2 \quad 4 \quad 3 + \\ \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}_2 \\ \\ \text{H} \end{array}$	-10.10	-9.30		—5.10— (m)		-2.85 (qi, 6.0)	-1.85 (t, 7.0)	
$\begin{array}{c} 5 \quad 4 \quad 1 + 2 \quad 3 + \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}_2 \\ \\ \text{H} \end{array}$	-10.90	-10.1		—5.70—		-2.30 (m)	-1.30 (t, 7.0)	
$\begin{array}{c} 4 \quad 1 + 2 \quad 3 + \\ (\text{CH}_3)_2\text{CHOCH}_2\text{CH}_2\text{OH}_2 \\ \\ \text{H} \end{array}$	-10.75 (m)	-10.75 (m)		—5.10— (m)		-1.9 (d, 6.5)		
$\begin{array}{c} + \quad + \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}_2 \\ \\ \text{H} \end{array}$	-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 $\text{SbF}_5\text{-SO}_2$ solution at -60° .



The secondary alkoxy-carbonium ions may be written as the two resonance forms



The nmr spectra show a substantial deshielding (9.9 ppm) for the methine proton (-5.9 ppm in the

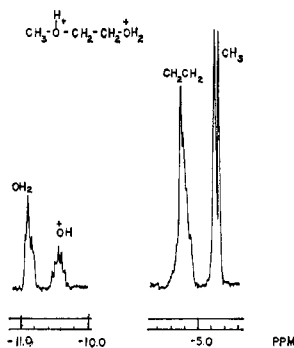


Figure 1.

un-ionized halo ether), and for the other protons a deshielding which decreases as the distance to the $\text{C}^+=\text{O}$ bond increases.

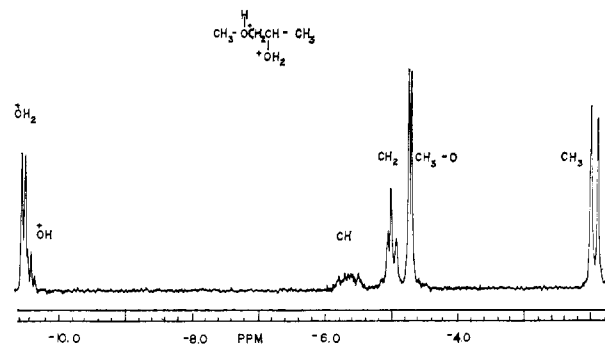


Figure 2.

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

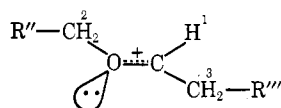
By calculating the activation energy of rotation around the $\text{C}^+=\text{O}$ bond, Ramsey and Taft⁸ estimated the π -bond order to be about 0.2 to 0.3 in dimethoxy-methylcarbonium ion. Long-range coupling between protons 1 and 2 has been observed in primary alkoxy-carbonium ions.¹² We wish now to 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 Alkoxy-carbonium Ions in $\text{SbF}_5\text{-SO}_2$ Solution at -60° ^a

α -Chloro ether	H ₁	H ₂	H ₃	H ₄	H ₅
$\begin{array}{c} 2 \quad 1 \quad 3 \\ \text{CH}_3\text{CH}(\text{Cl})\text{OCH}_3 \end{array}$	-5.80	-3.60	-1.85		
$\begin{array}{c} 2 \quad 1 \quad 3 \quad 4 \\ \text{CH}_3\text{OCH}(\text{Cl})\text{CH}_2\text{CH}_3 \end{array}$	-5.85	-3.80	-2.20	-1.25	
$\begin{array}{c} 4 \quad 2 \quad 1 \quad 3 \quad 5 \\ \text{CH}_3\text{CH}_2\text{OCH}(\text{Cl})\text{CH}_2\text{CH}_3 \end{array}$	-5.95	-3.95	-1.95	-1.45	
$\begin{array}{c} 4 \quad 2 \quad 1 \quad 3 \quad 5 \\ \text{CH}_3\text{CH}_2\text{OCH}(\text{Cl})\text{CH}_2\text{CH}_3 \end{array}$	-5.90	-4.00	-2.20	-1.45	-1.25
Alkoxy-carbonium ion					
$\begin{array}{c} 2 \quad + \quad 1 \quad 3 \\ \text{CH}_3\text{O}=\text{CHCH}_3 \end{array}$	-9.50	-5.30	3.20		
$\begin{array}{c} 2 \quad + \quad 3 \\ \text{CH}_3\text{O}=\text{C}(\text{CH}_3)_2^b \end{array}$		-5.0	-3.18		
$\begin{array}{c} 3 \quad 2 \quad + \quad 1 \quad 4 \\ \text{CH}_3\text{CH}_2\text{O}=\text{CHCH}_2\text{CH}_3 \end{array}$	-9.85	-5.55	-3.07	-1.70	
$\begin{array}{c} 3 \quad 2 \quad + \quad 1 \quad 4 \\ \text{CH}_3\text{CH}_2\text{O}=\text{CHCH}_2\text{CH}_3 \end{array}$	-9.95	-5.51	-3.52	-1.70	-1.10
$\begin{array}{c} 3 \quad + \quad 1 \quad 2 \quad 4 \\ \text{CH}_3\text{O}=\text{CHCH}_2\text{CH}_3 \end{array}$	-9.90	-5.30	-3.60	-1.25	

^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 alkoxy-carbonium ion do not figure in this table. ^b Prepared by cleavage of $(\text{CH}_3\text{O})_2\text{C}(\text{CH}_3)_2$ in $\text{SbF}_5\text{-FSO}_3\text{H-SO}_2$ at -60° .

2 and 3 in secondary alkoxy-carbonium ions. Coupling



of this type has been explained in terms of hyperconjugation of the π orbitals with the $\text{CH}(2)$ and $\text{CH}(3)$ σ orbitals in substituted ethylenes by Hoffmann.¹⁴

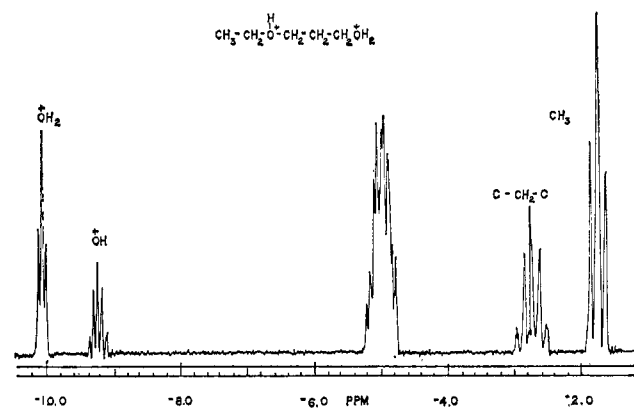
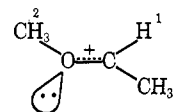


Figure 3.

We did not observe any *cis-trans* isomers in the secondary alkoxy-carbonium 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)

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



at 5.30 ppm and the $\text{CH}_3(3)$ proton appears as a doublet of quartets at -3.20 ppm. The long-range coupling has been confirmed by decoupling experiments. Irradiation of the $\text{H}(2)$ multiplet collapses the $\text{H}(1)$ and $\text{H}(3)$ lines, respectively, to a quartet and a doublet.

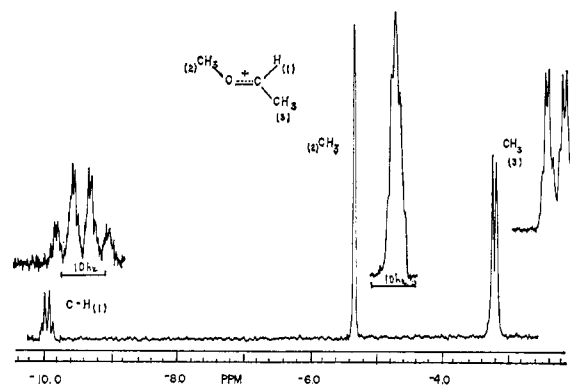
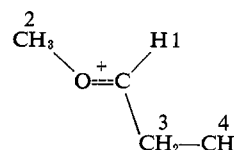


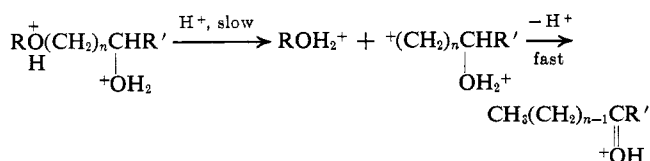
Figure 4.

Methoxyethylcarbonium Ion (Figure 5). The methine



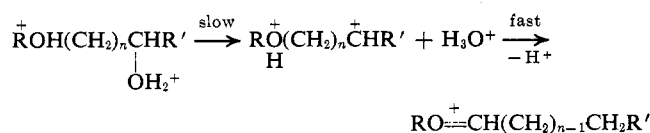
proton is deshielded to -9.90 ppm as a multiplet, but the coupling, $J_{1,3}$, with the methylene protons is sur-

aldehyde or ketone or undergo elimination and polymerization.



This bond breakage takes place more easily than that of $\text{CH}_2\text{-OH}_2^+$ bond because the latter would yield a primary carbonium ion.

(3) Cleavage of the CH-OH_2^+ bond yields an alkoxy-carbonium ion.



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

Diprotonated 2-methoxyethanol, $\text{CH}_3\text{O}^+(\text{H})\text{CH}_2\text{CH}_2\text{-OH}_2^+$, cleaves at $+70^\circ$ 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-isopropoxyethanol, 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 $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$ solution was carried out at -70° according to the procedure previously described.⁴ The ionization of the α -chloro ethers in $\text{SbF}_5\text{-SO}_2$ 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.

Acknowledgment. Support of this work by a grant from the National Institutes of Health is gratefully acknowledged. The award of a postdoctoral fellowship to Dr. Jean Sommer by NATO is also acknowledged.

(18) H. C. Chitwood and B. T. Freure, *J. Amer. Chem. Soc.*, **68**, 680 (1946).

(19) W. Reeve and A. Sadle, *ibid.*, **72**, 1251 (1960).

(20) L. H. Cretcher and W. H. Pittenger, *ibid.*, **46**, 1503 (1924).

(21) H. Gilman, Ed., "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p 369.