Organic and Biological Chemistry

Stable Carbonium Ions. LIII.[1a] Diprotonated Aliphatic Glycols and Their Rearrangement in Fluorosulfonic Acid–Antimony Pentafluoride Solution

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Abstract: A series of aliphatic diols have been studied in HSO_3F–SbF_5–SO_2 solution. O-protonation of the diprimary, disecondary, and primary–secondary diols was observed by nmr spectroscopy with negligible exchange rates at −60°. When the solutions are allowed to warm up, different rearrangement reactions occur, depending on the diol studied.

In continuation of our previous work on protonated alcohols and their cleavage to carbonium ions[2] we now report the observation of diprotonated aliphatic diols and their rearrangement in SbF_5–HSO_3F–SO_2 solution.

The behavior of α-glycols under acidic conditions (pinacolic rearrangement) has been investigated extensively and many reviews are available.[3-6] β-Glycols have also been shown to yield aldehydes and ketones under strongly acidic conditions at higher temperature and under pressure[7,8] whereas γ-glycols yield tetrahydrofuran derivatives with subsequent dehydration to 1,4-dienes,[9-11]

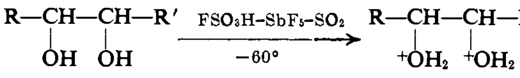
Results and Discussion

In the strong acid system FSO_3H–SbF_5–SO_2, all diprimary, disecondary, and primary–secondary aliphatic diols studied were completely diprotonated and we could observe the well-resolved nmr spectra with negligible exchange rates at −60°.

The following diprotonated glycols were observed: (α-glycols) ethylene glycol, 1,2-propanediol, 2,3-butanediol, 2,2,5,5-tetramethyl-3,4-hexanediol; (β-glycols) 1,3-propanediol, 1,3-butanediol, 3-methyl-2,4-pentanediol, 2,4-pentanediol; (γ-glycols) 1,4-butanediol, 2,5-hexanediol; (δ-glycol) 1,6-hexanediol.

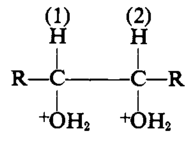
Figures 1–6 are representative of the nmr spectra at −60°. Chemical shifts and coupling constants are summarized in Table I. All spectra show approximately three groups of lines. The protons on oxygen are shifted downfield to −10.5 ± 1 ppm, more shielded in the α-glycols where the two positive charges are closest. The protons bound to the carbon next to the oxygen appear around −5.0 ppm and the protons more remote appear between −2.5 and −1.0 ppm depending on their distance from the positively charged oxygen.

Diprotonated α-Glycols. It was of interest whether two hydroxyl groups on adjacent carbon atoms could be both protonated in our strong acid solution. Diprotonated α-diketones could not be observed and the spectra of diprotonated oxalic acid was not well resolved at −90°.[12] α-Glycols in FSO_3H–SbF_5–SO_2 solution at −60° give well-resolved spectra indicating complete diprotonation.



$$\mathrm{R}-\underset{\mathrm{OH}}{\mathrm{CH}}-\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{R'} \xrightarrow[-60^\circ]{\mathrm{FSO_3H\text{-}SbF_5\text{-}SO_2}} \mathrm{R}-\underset{^+\mathrm{OH_2}}{\mathrm{CH}}-\underset{^+\mathrm{OH_2}}{\mathrm{CH}}-\mathrm{R'}$$

The integration of the spectra of the protonated glycols shows two protons on oxygen in all the cases studied.



$$\mathrm{R}-\overset{\overset{(1)}{\mathrm{H}}}{\underset{^+\mathrm{OH_2}}{\mathrm{C}}}-\overset{\overset{(2)}{\mathrm{H}}}{\underset{^+\mathrm{OH_2}}{\mathrm{C}}}-\mathrm{R}$$

In the symmetric α-glycols studied, we do not observe the resonance absorption lines expected by a first-order treatment. The lines are perturbed by a virtual coupling effect due to the identical chemical shift of the H(1) and H(2) proton. Analogous cases have been observed and discussed earlier.[13]

Ethylene glycol, $^+H_2OCH_2CH_2OH_2{}^+$ (Figure 1), shows two resonance lines of similar shape and equal intensity. The proton on oxygen appears at −11.2 ppm and the line at −5.4 ppm is assigned to the methylene protons.

1,2-Propanediol. The protons on oxygen give the expected triplet ($^{a}J_{\mathrm{H-H}} = 3.5$ Hz) at −11.0 ppm and doublet ($^{b}J_{\mathrm{H-H}} = 3.0$ Hz) at −10.7. The methylene protons appear at −4.6 ppm, the methine protons at

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[1] (a) Part LII: G. A. Olah, D. H. O'Brien, and A. M. White, *J. Amer. Chem. Soc.*, **89**, 5694 (1967); (b) NATO Postdoctoral Research Investigator, 1966–1967.

[2] G. A. Olah, J. Sommer, and E. Namanworth, *J. Amer. Chem. Soc.*, **89**, 3576 (1967).

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

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Table I. Nmr Chemical Shifts[a] and Coupling Constants[b] of Diprotonated Aliphatic Diols[c]

	$^+OH_2$	H_1	H_2	H_3	H_4
		Diprimary glycols			
1 1 $^+H_2OCH_2CH_2OH_2^+$	−11.2 (m)	−5.4 (m)			
1 2 1 $^+H_2OCH_2CH_2CH_2OH_2^+$	−9.8 (t) 3.5	−5.0 (m)	−2.6 (qi) 6.5		
1 2 2 1 $^+H_2OCH_2CH_2CH_2CH_2OH_2^+$	−9.6 (t) 3.5	−4.9 (m)	−2.4 (m)		
1 2 3 2 1 $^+H_2OCH_2CH_2CH_2CH_2CH_2OH_2^+$	−9.4	−4.85	−2.4	to −1.4 (cm)	
1 2 3 3 2 1 $^+H_2OCH_2CH_2CH_2CH_2CH_2CH_2OH_2^+$	−9.2	−4.8	−2.8	to −1.8 (cm)	
1 3 1 $^+H_2OCH_2C(CH_3)_2CH_2OH_2^+$	−10.2 (t) 3.5	−4.7 (t)		−1.2 (s)	
a 1a 2a 3 2b 1b b $^+H_2OCH_2CH(CH_3)CH_2CH_2OH_2^+$	a −9.95 b −9.85 (t) 3.5	a −5.1 b	−2.4 (m)	−1.35 (d) 6.5	
		Disecondary Glycols			
2 1 + 1 + 2 $CH_3CH(OH_2)CH(OH_2)CH_3$	−11.05	−5.4 (m)	−1.9 (d) 7.0		
3 1 + 1 + 3 $(CH_3)_3CCH(OH_2)CH(OH_2)C(CH_3)_3$	−11.0 (m)	−5.2 (m)	−1.9 (s)		
3 1 + 2 1 + 3 $CH_3CH(OH_2)CH_2CH(OH_2)CH_3$	−10.5 (d) 4.0	−5.5 (m)	−2.7 (m)	−2.0 (d) 7.0	
3 1 + 2 4 1 + 3 $CH_3CH(OH_2)CH(CH_3)CH(OH_2)CH_3$	−10.05 (d) 4.0	−5.4 (m)	−2.6 (m)	−1.85 (d) 7.0	−1.25 (d) 7.0
3 1 + 2 2 1 + 3 $CH_3CH(OH_2)CH_2CH_2CH(OH_2)CH_3$	−9.5 (d) 3.5	−5.5 (m)	−2.3 (m)	-1.8 (d) 6.0	
		Primary–Secondary Glycols			
a 1a 1b b+ 2 $^+H_2OCH_2CH(OH_2)CH_3$	a −11.0 (t) 3.5 b −10.7 (d) 3.0	a −4.6 (m) b −5.3 (m)	−1.4 (d) 7.0		
a 1a 2 1b b 3 $^+H_2OCH_2CH_2CH(OH_2^+)CH_3$	a −10.25 (t) 3.5 b −10.0 (d) 4.0	a −5.15 (m) b −5.4 (m)	−2.7 (q)	−1.9 (d) 7.0	

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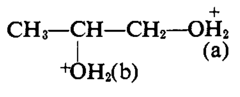
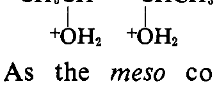
[a] In parts per million referred to external TMS. [b] In hertz as indicated following the multiplicity. [c] The multiplicity of the nmr lines is indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; qi, quintet; m, multiplet; cm, complex.

−5.3 ppm, and the methyl doublet (J_{H-H} = 7.0 Hz) at −1.4 ppm (see Figure 2).



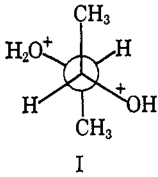
$$CH_3-\underset{^+OH_2(b)}{CH}-CH_2-\overset{+}{O}H_2\ (a)$$

2,3-Butanediol. In the protonated mixture of *meso*- and *dl*-2,3-butanediol the protons on oxygen appear as a triplet at −11.05 ppm. This triplet is due to the superposition of the doublets from the *meso* and

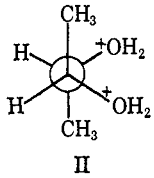


$$CH_3\underset{^+OH_2}{CH}-\underset{^+OH_2}{CH}CH_3$$

dl compounds. As the *meso* compound allows a greater distance between the two positively charged oxygens in its most favorable conformation, I, we may assume that its protons on oxygen are less deshielded (6.3 Hz) than in the *dl* pair II.



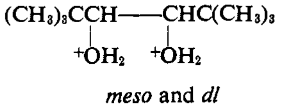
I



II

The methine protons appear as a multiplet at −5.4 ppm. The methyl doublet (J_{H-H} = 7.0 Hz) at −1.9 ppm seems to contain some additional lines. This has been explained earlier.[13]

2,2,5,5-Tetramethyl-3,4-hexanediol. The protons on oxygen appear as a broad line at −11.0 ppm, the



$$(CH_3)_3C\underset{^+OH_2}{CH}-\underset{^+OH_2}{CH}C(CH_3)_3$$

meso and *dl*

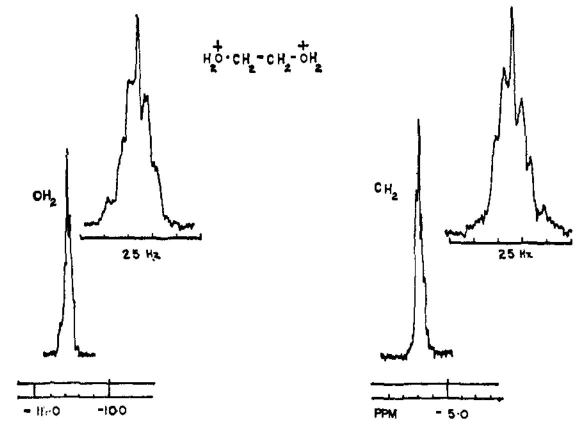


Figure 1.

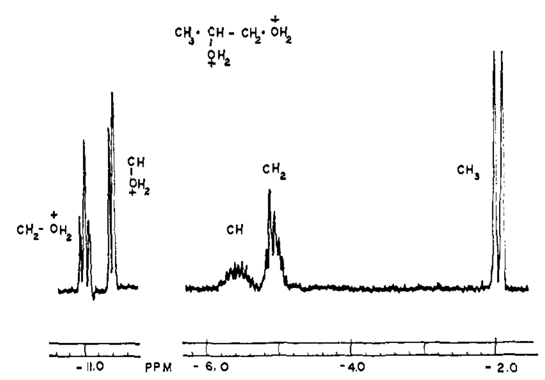
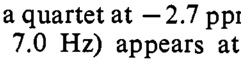


Figure 2.

methine protons as a multiplet at −5.2 ppm, and the methyl protons as a singlet at −1.9 ppm. The integration of the three lines as well as their deshielding are in accord with a fully diprotonated species. It is interesting to note in this case that the strong steric hindrance of the *t*-butyl groups (especially in the *dl* pair) does not hinder diprotonation of this α-glycol.

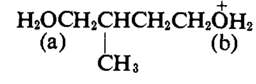
Diprotonated β-, γ-, and δ-Glycols. 1,3-Propanediol (Figure 3), $H_2O^+CH_2CH_2CH_2OH_2^+$, shows a triplet (J_{H-H} = 3.5 Hz) at −9.8 ppm. The α-methylene protons appear as a seven-line multiplet at −4.9 ppm, and the β-methylene appear as a five-line multiplet (J_{H-H} = 6.5 Hz) at −2.4 ppm.

1,3-Butanediol. The protons on oxygen appear as a triplet (J_{H-H} = 3.5 Hz) at −10.26 ppm (H_a) and a doublet (J_{H-H} = 4.0 Hz) at −10.0 ppm (H_b). The α-methylene protons and the methine proton appear as multiplets respectively at −5.15 and −5.6 ppm. The β-methylene gives a quartet at −2.7 ppm and the methyl doublet (J_{H-H} = 7.0 Hz) appears at −1.9 ppm (see Figure 4).


$$CH_3\underset{{}^{+}OH_2\,(b)}{\underset{|}{CH}}CH_2CH_2\overset{(a)}{O}H_2^{+}$$

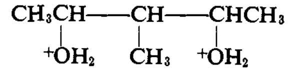
1,4-Butanediol $(CH_2CH_2OH_2^+)_2$ shows the OH_2^+ protons as a triplet (J_{H-H} = 3.5 Hz) at −9.6 ppm, the α-methylene protons as a multiplet at −4.9 ppm, and the β-methylene as a seven-line multiplet at −2.4 ppm.

2-Methyl-1,4-butanediol shows the OH_2^+ protons a and b as two interfering triplets (J_{H-H} = 3.5 cps) at −9.85 and −9.95 ppm. The α-methylene protons and the methine proton appear as multiplets at around −5.1 ppm. The β-methylene and the methyl doublet (J_{H-H} = 6.5 Hz) appear respectively at −2.4 and −1.35 ppm.


$$\underset{(a)}{H_2\overset{+}{O}}CH_2\underset{CH_3}{\underset{|}{CH}}CH_2CH_2\underset{(b)}{\overset{+}{O}H_2}$$

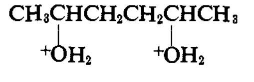
1,5-Pentadiol, $^{+}H_2OCH_2CH_2CH_2CH_2CH_2OH_2^{+}$, shows the OH_2^+ triplet at −9.4 ppm (J_{H-H} = 3.5 Hz) and the α-methylene as a multiplet at −4.8 ppm. The rest of the protons appear as a complex multiplet between −2.4 and −1.4 ppm.

3-Methyl-2,4-pentanediol shows the OH_2^+ protons as a doublet (J_{H-H} = 4.0 Hz) at −10.05 ppm, the α-methine multiplet at −5.4 ppm, the β-methine multiplet at −2.6 ppm, the β-methyl doublet (J_{H-H} = 7.0 Hz) at −1.85 ppm, and the γ-methyl doublet (J_{H-H} = 7.0 Hz) at 1.25 ppm.


$$CH_3\underset{{}^{+}OH_2}{\underset{|}{CH}}\text{——}\underset{CH_3}{\underset{|}{CH}}\text{——}\underset{{}^{+}OH_2}{\underset{|}{CH}}CH_3$$

1,6-Hexanediol, $(^{+}H_2OCH_2CH_2CH_2)_2$, shows the OH_2^+ protons as a triplet (J_{H-H} = 3.5 Hz) at −9.2 ppm, the α protons as a multiplet at −4.8 ppm, and the β- and γ-methylene protons as a complex multiplet between −2.8 and −1.8 ppm.

2,5-Hexanediol (Figure 5) shows the OH_2^+ proton as a doublet (J_{H-H} = 3.5 Hz) at −9.5 ppm, the methine protons as a multiplet at −5.5 ppm, the methylene protons as a multiplet at −2.3 ppm, and the methyl doublet (J_{H-H} = 6.0 Hz) at −1.8 ppm.


$$CH_3\underset{{}^{+}OH_2}{\underset{|}{CH}}CH_2CH_2\underset{{}^{+}OH_2}{\underset{|}{CH}}CH_3$$

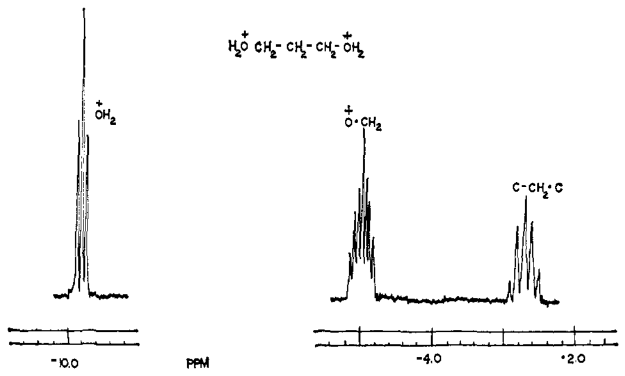


Figure 3.

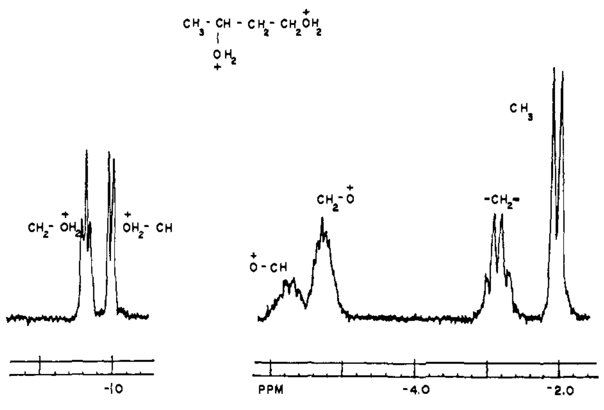


Figure 4.

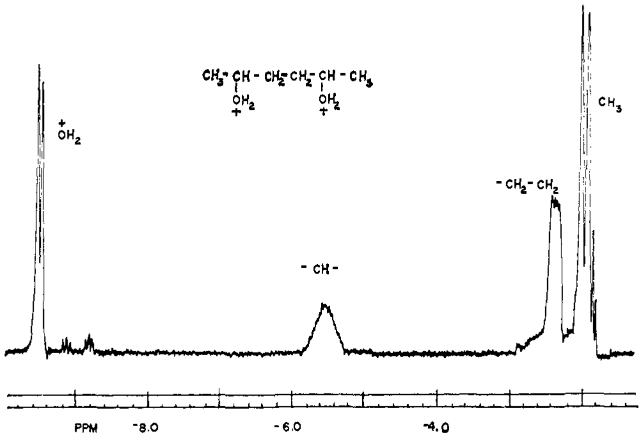
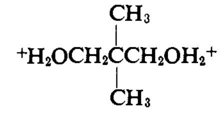


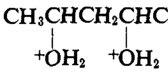
Figure 5.

2,2-Dimethyl-1,3-propanediol shows the OH_2^+ protons as a triplet (J_{H-H} = 3.5 Hz) at −10.2 ppm, the methylene triplet at −4.7 ppm, and the methyl singlet at −1.2 ppm.



$$^{+}H_2OCH_2\underset{CH_3}{\overset{CH_3}{C}}CH_2OH_2^{+}$$

2,4-Pentanediol shows the OH_2^+ protons as a doublet (J_{H-H} = 4.0 Hz) at −10.5 ppm, the methine protons as a multiplet at −5.5 ppm, the methylene protons as a multiplet at −2.7 ppm, and the methyl as a doublet (J_{H-H} = 7.0 Hz) at −2.0 ppm



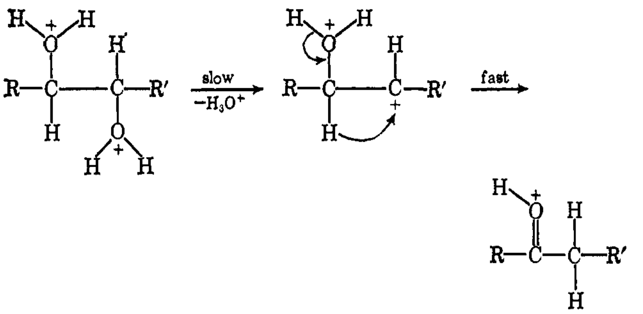
$$CH_3\underset{^{+}OH_2}{CH}CH_2\underset{^{+}OH_2}{CH}CH_3$$

Triprotonated Glycerol. In $HSO_3F-SbF_5-SO_2$ solution at −60° glycerol gave two absorption resonance lines at −5.15 and −5.70 ppm which integrated 4:1, respectively. The acid peak at −11.2 is broader due to exchange with the protons on oxygen. The integration ratio as well as the chemical shifts lead us to suppose that even in this case we may have complete protonation of the hydroxyl groups. The lines observed are the two methylene protons at −5.1 ppm and the methine proton at −5.15 ppm. However, temperature change did not affect the spectra between −90 and +20°, and we need more data to prove the exact nature of this polyol in $FSO_3H-SbF_5-SO_2$.

Diprimary Glycols. In Table I, we may note that the deshielding of the OH_2^+ protons in the diprimary glycols is greater than the deshielding in the corresponding primary aliphatic alcohols[2] (−9.3 ppm in the same conditions). This additional deshielding effect which is reversely proportional to the distance of the two oxygen atoms may be attributed to the repulsion between the two charges on oxygen and is negligible when the two oxygens are separated by more than five carbon atoms (1,6-hexanediol).

Rearrangement of Diprotonated Glycols. When the $FSO_3H-SbF_5-SO_2$ solutions of diprotonated glycols are allowed to warm up, we observe dehydration followed by a rearrangement which depends on the nature of the glycol.

α- and β-glycols undergo specifie pinacolic rearrangements with hydride shifts.



R, R' = H, alkyl

γ-, δ-, and ε-diprimary glycols are very stable and no rearrangement was observed.

Disecondary γ-glycols were observed to undergo cyclization to tetrahydrofuran derivatives.

Ethylene Glycol. Diprotonated ethylene glycol is very stable below 0° but undergoes pinacolic rearrangement to protonated acetaldehyde at higher temperature. The half-life of this reaction is about 24 hr at room temperature.

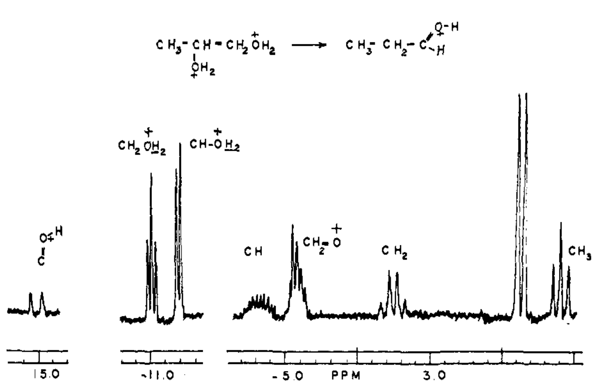
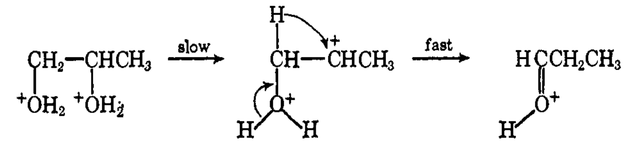
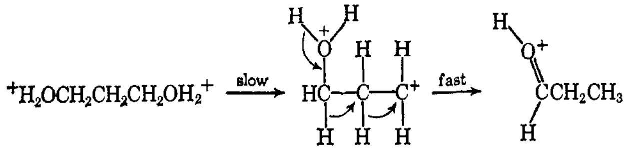


Figure 6.

1,2-Propanediol. As expected from our earlier studies on protonated alcohols, the secondary hydroxyl cleaves first and the following rearrangement yields only protonated propionaldehyde. Figure 6 shows the spectra during the first half-life.



1,3-Propanediol. Dehydration of diprotonated 1,3-propanediol produces a primary carbonium ion which rearranges very fast (1,2-hydride shift) to the secondary cation which undergoes pinacolic rearrangement to protonated propionaldehyde (Figure 7).



The kinetics of this reaction have been measured between 26 and 37° by following the decrease of the α-CH_2 triplet[14] of the diprotonated glycol and the increase of the methyl triplet of protonated propionaldehyde.

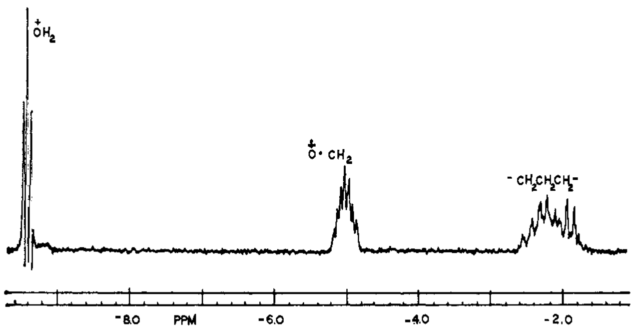


Figure 7.

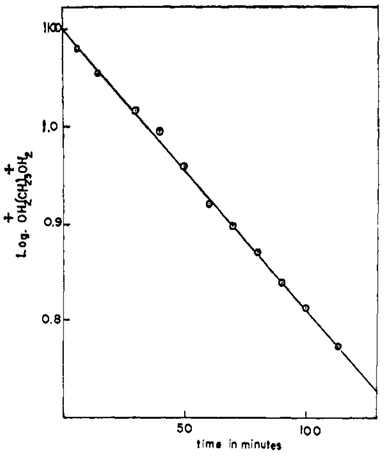
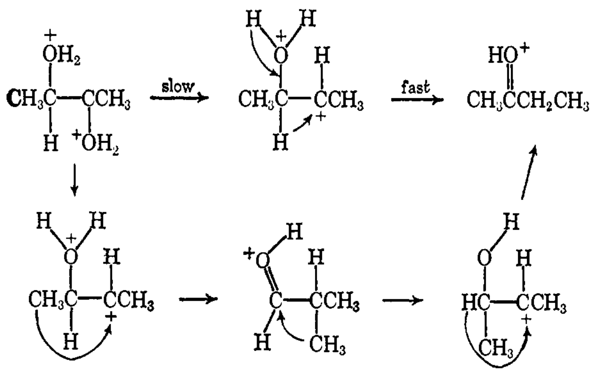


Figure 8.

The results show first-order rate for cleavage (Figure 8) and a quantitative formation of the protonated aldehyde. The rate-determining step is the formation of the hydroxyethylcarbonium ion. The following hydride shifts and pinacolic rearrangement are too fast to be followed by the slow nmr method used and do not allow the determination whether the two steps are concerted or consecutive. The activation energy was determined from the Arrhenius equation $K = \Delta e^{E_a/RT}$ and by measuring the reaction rates at +26 and +37°. The Arrhenius plot is shown in Figure 9. The activation energy value found is $E_a = 16.2 \pm 1$ kcal/mole (four experiments).

2,3-Butanediol. Diprotonated 2,3-butanediol rearranges quantitatively to protonated methyl ethyl ketone, a small part of it through protonated isobutyraldehyde.



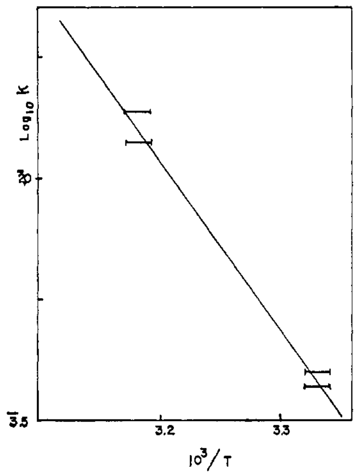


Figure 9.

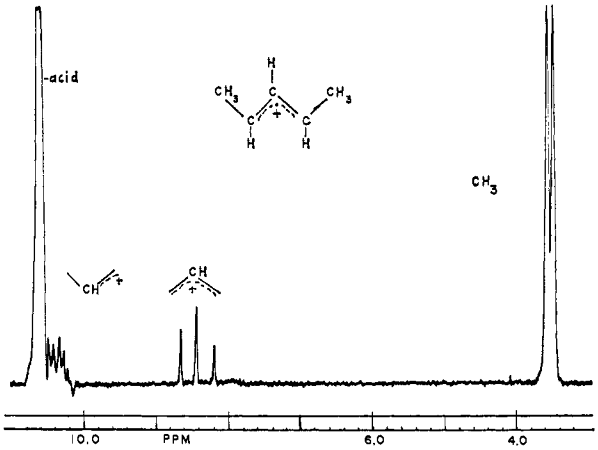
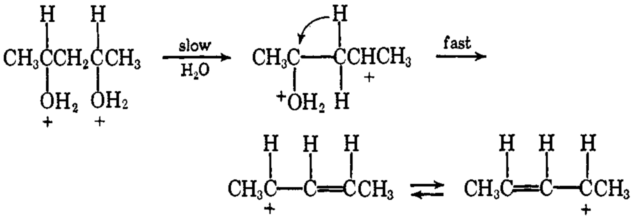


Figure 10.

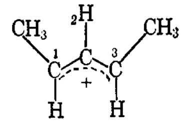
The half-life of this rearrangement is about 7 hr at +30°.

1,3-Butanediol. The diprotonated species is stable below −20°. Above this temperature complex reactions take place which could not be followed.

2,4-Pentanediol. Diprotonated 2,4-pentanediol is very stable below −40°. Above this temperature it dehydrates first to a protonated hydroxyalkylcarbonium ion which further dehydrates with formation of the allylic carbonium ion



which may also be written



The CH_3 groups appear as a doublet ($J_{H-H} = 7.0$ Hz) at −3.45 ppm. The H(2) proton appears as a triplet ($J_{H-H} = 14.0$ Hz) at −8.30 ppm and the H(1) and -(3) protons appear as a multiplet at −10.10 ppm. The spectrum is displayed in Figure 10. The half-life of this rearrangement is about 1 hr at −35°.

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(14) Above 10° the OH_2^+ proton exchange with the acid solvent and the spectra of diprotonated 1,3-propanediol show the α-CH_2 as a triplet ($J_{H-H} = 7.0$ Hz) and the β-CH_2 as a quintuplet.

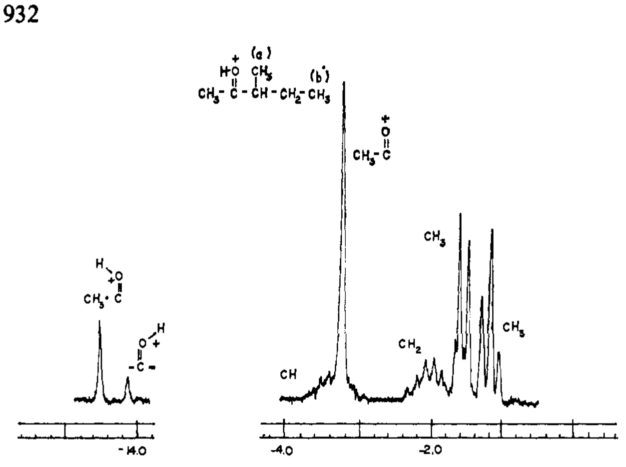


Figure 11.

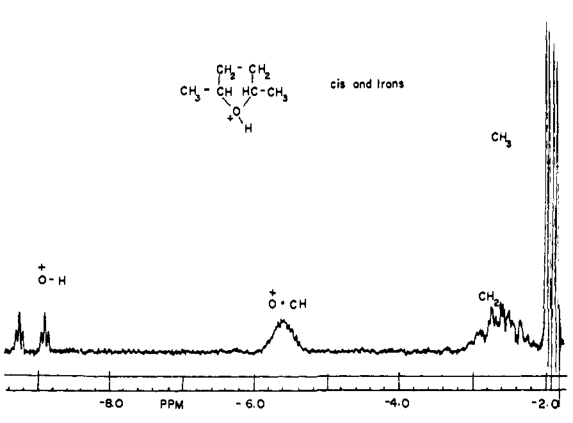
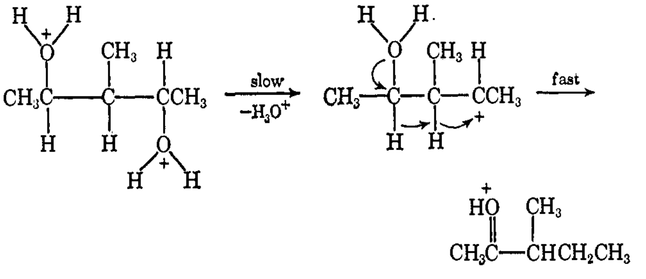
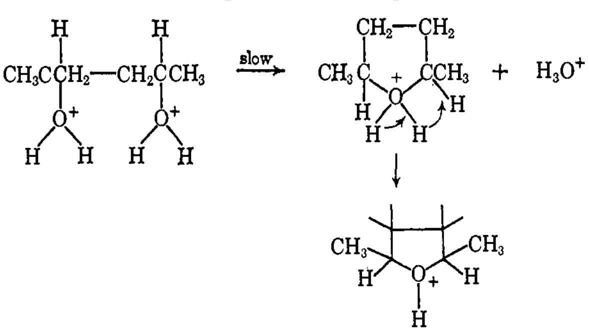


Figure 12.

3-Methyl-2,4-pentanediol. Diprotonated 3-methyl-2,4-pentanediol rearranges to protonated methyl *sec*-butyl ketone. The half-life of the reaction is about 1 hr at −50° (Figure 11).



2,5-Hexanediol. The diprotonated glycol is very stable at −60° but undergoes at about −30° rearrangement to protonated *cis*- and *trans*-α,α′-dimethyltetrahydrofurans. In Figure 5 we can already see some of the lines of this compound and Figure 12 shows the spectrum after completion of the reaction. The half-life of this reaction is about 1 hr at −30°. Protonated α,α′-dimethyltetrahydrofuran (*cis* and *trans*) shows the OH^+ proton as a triplet (J_{H-H} = 3.0 Hz) at −9.3 and 8.9 ppm, the methine protons at −5.6 ppm, the methylene proton multiplet around −2.5 ppm, and the methyl doublet (J_{H-H} = 6.0 Hz) at −1.98 and 1.85 ppm.



The *cis* and *trans* isomers have been separated by vpc and could be obtained chromatographically pure. Identification was done by comparing the physical properties and the nmr spectra with those described by Mihailovic, *et al.*[15] In FSO_3–SbF_5–SO_2 solution the OH^+ proton of the *trans* isomer is more deshielded than the corresponding proton of the *cis* isomer. The reverse deshielding effect is observed on the CH_3 protons (δ_{trans} = −1.85 ppm, δ_{cis} = −1.95 ppm).

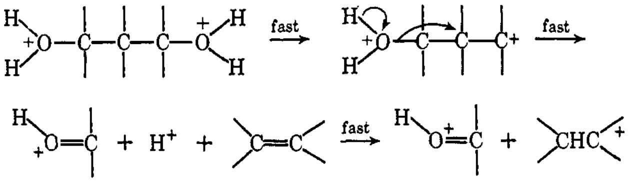
Diprotonated γ-, δ-, and ε-diprimary glycols show exceptional stability. The spectra of the diprotonated 1,4-butanediol, 1,5-pentanediol, and 1,6-hexanediol remain unchanged up to +40°. At higher temperatures lines broaden progressively, and the solutions turn dark and solidify. No rearrangement reaction could be followed under these conditions.

Ditertiary Glycols. Ditertiary glycols could not be observed as protonated species. The cleavage reaction is too fast at −70° and the following rearrangement depends on the carbonium ion formed.

Pinacol, $(CH_3)_2C(OH)C(OH)(CH_3)_2$, at −70° in FSO_3H–SbF_5–SO_2 solution rearranges immediately and the only species observed in solution is protonated pinacolone.[16]

2,5-Dimethyl-2,5-hexanediol, $(CH_3)_2C(OH)CH_2CH_2C(OH)(CH_3)_2$, below −50° dehydrates to give the stable dicarbonium ion $(CH_3)_2C^+CH_2CH_2C^+(CH_3)_2$.[17] We observe the methylene multiplet at −4.2 ppm and the methyl triplet at −5.0 ppm. At −70° this dication is stable but above −50° different decomposition reactions take place which could not be followed.

2,3,3,4-Tetramethyl-2,4-pentanediol, $(CH_3)_2C(OH)C(CH_3)_2C(OH)(CH_3)_2$, at −70° in FSO_3H–SbF_5–SO_2 solution cleaves immediately and quantitatively to protonated acetone and dimethylisopropylcarbonium ion. These two species are very stable[16,18] and no competitive reaction is occurring at −60°.



Experimental Section

Materials. 2,2,5,5-Tetramethyl-3,4-hexanediol was prepared by acyloin condensation of methyl pivalate[19] and lithium aluminum hydride reduction of the acyloin and the diketone obtained.[20] After recrystallization in hexane the melting point was 120°. All

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[16] G. A. Olah, M. Calin, and D. H. O'Brien, *J. Amer. Chem. Soc.*, **89**, 3586 (1967).

[17] J. M. Bollinger, C. A. Cupas, K. J. Friday, M. L. Wolfe, and G. A. Olah, *ibid.*, **89**, 156 (1967).

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other glycols were reagent grade commercial materials used without further purification.

Nmr Spectra, Preparation of Diprotonated Glycols, and Study of Their Cleavage. A Varian Associates Model A-56-60A spectrometer with variable-temperature probe was used for all spectra. The preparation of the samples and the procedure for the kinetic study were described in an earlier paper for alcohols.[2]

Acknowledgment. Support of this work by grants of the National Science Foundation and the National Institutes of Health is gratefully acknowledged. The award of a postdoctoral fellowship by the North Atlantic Treaty Organization is also acknowledged (J. S.).

Stable Carbonium Ions. LIV.[1] Protonation of and Hydride Ion Abstraction from Cycloalkanes and Polycycloalkanes in Fluorosulfonic Acid–Antimony Pentafluoride

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received June 12, 1967*

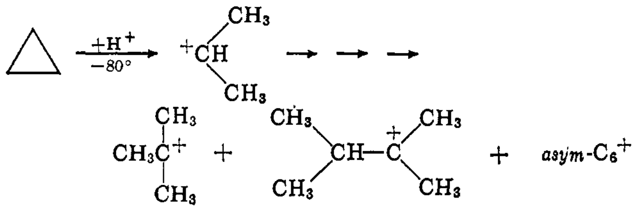
Abstract: The behavior of cycloalkanes and polycycloalkanes in the strong acids $FSO_3H–SbF_5$ and $HF–SbF_5$ with and without SO_2ClF as diluent was investigated. At temperatures above 0° ring cleavage occurs to give acyclic alkylcarbonium ions. At lower temperatures hydride ion is abstracted and cycloalkyl cations are formed.

In previous work,[3,4] we have investigated the formation of carbonium ions from alkanes in the strong acids $FSO_3H–SbF_5$ and $HF–SbF_5$. Hydride ion is abstracted in the decreasing order of reactivity from the tertiary, secondary, and primary positions. Secondary and primary carbonium ions formed under these acidic conditions are stabilized by immediate rearrangement (frequently with fragmentation or dimerization) to tertiary carbonium ions. The methylcyclopentyl cation[5] is the only cycloalkyl cation which has been investigated previously. It was therefore of interest to extend our investigations to the study of the formation of carbonium ions from cycloalkanes and polycycloalkanes in strong acids.

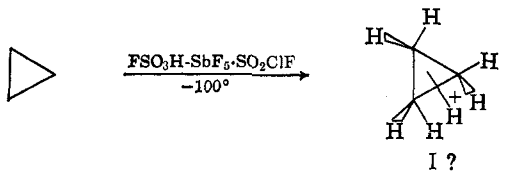
Results and Discussion

Cycloalkanes are protonated in $FSO_3H–SbF_5$ or $HF–SbF_5$ solution with subsequent hydrogen abstraction or cleavage, depending on reaction conditions. Which reaction path is taken depends on (a) the reaction temperature, (b) the acid strength, and (c) the ring size. At low temperatures (generally −60 to −100°) hydride abstraction is favored; at higher temperatures cleavage occurs. Decreasing acid strength tends to favor cleavage.

Cyclopropane is protonated and cleaved in $FSO_3H–SbF_5–SO_2ClF$ or $HF–SbF_5–SO_2ClF$ solution above −80° to give acyclic products. Through various di- and trimerization processes and fragmentations, the products are, in varying amounts, the *t*-butyl and *t*-hexyl cations (the pmr spectra of which are well known from our previous work).[2,3,6] The cyclopropyl cation itself is not stable in these systems, as shown previously.[4]



At −100° cyclopropane behaves differently. In $FSO_3H–SbF_5–SO_2ClF$ solution it forms a species the pmr spectrum of which shows four lines, probably two doublets at −2.30 and −2.10 ppm (J_{H-H} = 6 Hz) and a septuplet at −6.40 ppm (J = 6 Hz) (Figure 1), besides some ring-opened ions. On warming to −80°, the pair of doublets collapses to a single doublet (Figure 2). This transformation is reversible. The pmr spectral observation could indicate that protonated cyclopropane (I) is formed: the single proton (on the face of the cyclopropane ring or in an "edge"-protonated but equilibrating system) gives rise to the septuplet at δ −6.40 coupled to six methylene hydrogens, which in turn appear as a doublet. On comparison of the chemical shifts with those of comparable open-chain ions, such as isopropyl cation,[6] the allyl cation,[7] and cyclopropyl cations,[8] one finds the nmr absorption of the assumed protonated cyclopropane shifted upfield. A large anisotropy effect must be thus responsible for this effect.



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[1] Part LIII: G. A. Olah and J. Sommer, *J. Amer. Chem. Soc.*, **90**, 927 (1968).

[2] National Institutes of Health Postdoctoral Research Investigator, 1965–1967.

[3] G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2227 (1967).

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