two conformations and the difficulties involved in slowing the hydroxyl proton exchange in many solvents.[16] The former difficulty is illustrated by the data in Table I, which lists a slightly smaller J_{CHOH} value for *trans*-4-*t*-butylcyclohexanol than for *trans*-4-methylcyclohexanol. The two values are, however, nearly within the combined experimental uncertainty of each. If *trans*-4-*t*-butylcyclohexanol had been used as the model system in place of *trans*-4-methylcyclohexanol, the calculated $-\Delta G$ values for equilibria 1 and 2 would have been 0.54 and 1.35 instead of 0.61 and 0.98 kcal/mole, respectively.

Experimental Section

All nmr spectra were obtained on a Varian A-60 nmr spectrometer equipped with a variable-temperature probe. The reported spectral data are the result of several independent measurements, using different batches of solvent and sample. The water concentration in the DMSO varied from about 1% to less than 0.3%. The reported error limits for the ΔG values are the standard deviations obtained using the quoted average deviation (Table I) in the measured parameters. The probe temperature was 35°.

DMSO was dried by heating over calcium hydride and distilling from calcium hydride under reduced pressure (bp *ca.* 80°). It was found that solvent which had been dried by heating over extended periods of time or which was distilled at higher temperatures gave unreliable results.

4-*t*-Butylcyclohexanol was obtained both from a commercial source (Aldrich Chemical Co., Milwaukee, Wis.) and by lithium aluminum hydride reduction of 4-*t*-butylcyclohexanone. Individual samples of each isomer were obtained by preparative gas chromatography of mixtures on a Carbowax 20M column. 4-*t*-Butylcyclohexanol-2,2,6,6-d_4 was obtained through exchange of the ketone in 50% D_2O–dioxane using sodium carbonate, followed by lithium aluminum hydride reduction.

4-Methylcyclohexanol was obtained from a commercial source (Eastman Kodak). Individual samples of each isomer were obtained by preparative gas chromatography on a Carbowax 20M column.

Acknowledgment.—The Varian A-60 spectrometer was made available by Grant G 22718 from the National Science Foundation.

[16] O. L. Chapman and R. W. King, *J. Am. Chem. Soc.*, **86**, 1256 (1964); (b) D. E. McGreer and M. M. Mocek, *J. Chem. Educ.*, **40**, 358 (1963); (c) J. M. Bruce and P. Knowles, *Proc. Chem. Soc.*, 294 (1964); (d) J. G. Traynham and G. A. Knesel, *J. Am. Chem. Soc.*, **87**, 4220 (1965).

Behavior of Some Halogenated Alcohols upon Electron Impact

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The fragmentation patterns of lower molecular weight aliphatic alcohols have been exhaustively tabulated[1] and more recently elucidated.[2] With the exception of the cracking pattern of 2,2,2-trifluoroethanol[3] and a brief discussion of the mass spectrum of 2-chloroethanol,[4] there is no other information available on the mass spectra of low molecular weight halogenated alcohols. Because these compounds are an interesting class in themselves and because of our interest in the broader problem of the effects of halogen incorporation upon electron-impact decomposition modes, we have undertaken a study of some of the simpler members of this series. We present here some data relating to six primary alcohols, seven secondary alcohols, and two tertiary alcohols. To provide a direct comparison, data for some representative nonhalogenated alcohols that have been examined with our instrument are presented in Table I. The fragmentation patterns of these compounds are in essential agreement with those listed by Friedel.[1] All spectra were obtained using a CEC 21-103 (modified) mass spectrometer equipped with a stainless steel inlet which was maintained at 150°. The source temperature was 250°, and 70-ev ionizing electrons were used.

Primary Alcohols.—The primary alcohols are listed in Table II. The predominant mode of fragmentation is similar to that of the nonhalogenated primary alcohols. For these latter compounds it has been postulated that fragmentation proceeds *via* removal of a nonbonding electron on the oxygen atom followed by α cleavage to form the oxonium ion $CH_2{=}\overset{+}{O}H$ (*m/e* 31).[2] In the present case, *m/e* 31 is the most abundant fragment and accounts for at least 50% of the total ionization in five of the six compounds studied. For the alcohol HCF_2CF_2—CH_2OH *m/e* 31 has a value of 41%. This decrease may be explainable in terms of the appearance of an intense peak at *m/e* 82 corresponding to $C_2F_3H^+$. This ion could arise from the above-mentioned α cleavage followed by some charge retention by the halogenated alkyl portion of the molecule. Subsequent loss of F would yield $C_2F_3H^+$. This ion, however, does not correspond to an intermediate trifluoroethylene molecule ion. Trifluoroethylene[5] when run under similar conditions was found to be characterized by an abundant *m/e* 63 ($C_2F_2H^+$) and this ion is absent in the spectrum of the alcohol. This would indicate that F is being lost from the β-carbon atom of the molecule. Since CF^+ will make some contribution to the *m/e* 31 ion intensity, we have examined *m/e* 31 in the spectrum of $CF_3CF_2CF_2$—CH_2OH obtained under high-resolution conditions.[6] It was found that 95% of *m/e* 31 was due to CH_2OH^+. The second most intense ion in all of the spectra was the formyl ion $CH{\equiv}O^+$ (*m/e* 29). A broad characteristic metastable peak centered at about *m/e* 27.5 (calcd *m/e* 27.1) suggests that this ion may form from CH_2OH^+ by elimination of H_2. An interesting fragment that was found in all spectra was a rearrangement ion of composition CH_2FO^+ which may correspond to the fluoro analog of CH_2OH^+. Although α-fluoro alcohols are extremely unstable,[7] it may be that such

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[1] R. A. Friedel, J. L. Schultz, and A. J. Sharkey, *Anal. Chem.*, **28**, 926 (1956).

[2] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 2.

[3] Mass Spectral Data, Manufacturing Chemists Association Research Project, Serial No. 142.

[4] K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 87, 88.

[5] Trifluoroethylene was obtained from Peninsular Chemresearch, Inc., Gainesville, Fla.

[6] A Hitachi RMU-6D mass spectrometer with double-focusing attachment was used. We are indebted to A. H. Struck of Perkin-Elmer Corp. for this result.

[7] W. J. Middleton and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **86**, 4948 (1964).

TABLE I

NONHALOGENATED ALCOHOLS,[a] PER CENT OF TOTAL IONIZATION (% Σ_{15}) OF SELECTED FRAGMENTS

Fragment[b]	CH_3CH_2OH	$CH_3(CH_2)_2OH$	$CH_3(CH_2)_3OH$	$(CH_3)CHOH(CH_3)$	$(CH_3)_3COH$
Mol ion	7.7	4.3	0.3	0.4	
M—H[c]	13.4	4.5	0.3	1.7	
$M—CH_3$	*38.3*[d]	1.6		*47.5*	*40.0*
$M—H_2O$	2.4	3.7	*17.8*	2.1	0.8
$M—CH_3OH$		2.9	5.8	0.7	1.5
$CH_3COCH_2^+$				0.1	4.0
$C_3H_7^+$ CH_3CO^+	3.2	1.6	10.5	8.8	6.2
$C_3H_5^+$	0.4	3.1	11.5	3.2	8.6
$C_3H_3^+$		2.3	3.4	3.0	3.7
CH_2OH^+	(*38.3*)[e]	*49.2*	16.9	2.8	12.6
COH^+ $C_2H_5^+$	9.5	7.5	6.0	5.1	4.8
CO^+ $C_2H_4^+$	(2.4)	(2.9)	3.5	(0.7)	1.0
$C_2H_3^+$	9.1	7.9	9.5	7.4	4.2
$C_2H_2^+$	3.6	2.5	1.5	1.3	1.0
H_3O^+	1.3	0.4	0.6	3.0	0.2
CH_3^+	4.1	2.1	2.0	5.7	5.5
Max %[f]	2.3	1.1	1.5	2.2	1.4

[a] All alcohols were obtained from the Allied Chemical Corp. [b] Designations are not meant to define mechanisms in all cases. [c] Ion formed by loss of a hydrogen atom. [d] Italic percentages correspond to base peaks. [e] Parentheses indicate that the percentage is also listed using another designation. [f] Largest per cent of total ionization of any m/e whose percentage has not been incorporated into the above table.

TABLE II

R_1CH_2OH, PER CENT OF TOTAL IONIZATION (%Σ_{27}) OF SELECTED FRAGMENTS

Fragment[c]	HCF_2[a]	CF_3[b]	HCF_2CF_2[a]	CF_3CF_2[a]	$CF_3(CF_2)_2$[a]	$HCF_2(CF_2)_3$[a]
Mol ion	1.5	0.2				
M—H[d]	0.1	0.2	0.1			
$M—H_2O$	1.0	0.1				
M—F	0.8	0.9	0.2			
M—HF	0.3	0.2	3.1	0.1		
M—HF—F	6.0	5.8	0.2	0.1	0.5	
R_1^+	2.9	2.6	0.3	0.3	0.2	
$C_2F_3H^+$		(0.1)	8.9	0.4	0.2	1.2
CF_3^+		(2.6)	0.5	4.3	7.3	3.3
HCF_2^+	(2.9)[e]	5.2	9.3	2.7	3.4	7.2
$FCHOH^+$	0.1	1.6	2.9	4.7	2.3	0.3
FCH_2^+	5.4	9.9	4.0	2.6	3.0	2.4
CH_3OH^+ FCH^+	3.0	1.8	1.9	1.4	1.1	1.3
CH_2OH^+ CF^+	*56.9*[f]	*51.5*	*41.0*	*54.9*	*51.7*	*51.1*
COH^+	10.7	11.5	10.8	12.8	11.8	7.1
Max %[g]	2.2	1.6	1.5	1.8	2.2	2.3

[a] Obtained from the Peninsular Chemresearch Inc., Gainesville, Fla. [b] Obtained from the Allied Chemical Corp. [c] See footnote *b*, Table I. [d] Ion formed by loss of a hydrogen atom. [e] See footnote *e*, Table I. [f] Italic percentages correspond to base peaks. [g] See footnote *f*, Table I.

an ionic species is resonance stabilized *via* structures such as $FCH{=}\overset{+}{O}H \longleftrightarrow F\overset{+}{C}H{-}OH$. Only 2,2-difluoroethanol showed an abundant molecule ion and a fragment of significant intensity corresponding to loss of H_2O from the molecule ion. The halogenated alcohols thus differ from their hydrogen counterparts where loss of H_2O from the molecule ion occurs with significant intensity in all cases.[1] The rearrangement ion CFH_2^+ (m/e 33) was formed from all of the alcohols, accounting for as much as 10% of the total ionization in the case of $CF_3—CH_2OH$. HCF_2^+ (m/e 51) also occurs with significant intensity in these compounds although it accounts for a larger per cent when it is not necessary to postulate its formation *via* a rearrangement process (*i.e.*, $HCF_2CF_2—CH_2OH$).

Secondary Alcohols.—The seven secondary alcohols are listed in Table III. All of the alcohols have the hydroxyl group located on the second carbon atom. For nonhalogenated secondary alcohols of general formula $CH_3—CHOH—R$, Friedel[1] has found that the base peak occurs at m/e 45, corresponding to α cleavage with loss of R. In the case of $CH_3—CHOH—CH_3$ (Table I), the ion resulting from loss of CH_3 represents 47.5% of the total ionization. For the alcohols examined here, of formula $R_1—CHOH—R_2$, where R_2 either equals R_1 or has a mass greater than R_1, R_1CHOH^+ is either the base peak or at least 70% of the base. However, in no case does this ion account for more than 28% of the total ionization. For $CF_2Cl—CHOH—CFCl_2$, it represents only 9%. The fluoro-

TABLE III

$(R_1)CHOH(R_2)$, PER CENT OF TOTAL IONIZATION ($\%\Sigma_{27}$) OF SELECTED FRAGMENTS[a,b]

Fragment[e]	$R_1 = CH_3$[c]	CH_3[c]	CF_2H[d]	CF_3[d]	CF_2Cl[d]	CF_2Cl[d]	$CFCl_2$[d]
	$R_2 = CF_3$	CF_2CF_3	CF_2H	CF_3	CF_2Cl	$CFCl_2$	$CFCl_2$
Mol ion			0.2				
M—H[f]	1.0						
M—H_2O	0.1		0.1				
M—F	0.6		0.4	0.7			
M—Cl					0.2	0.3	0.1
M—R_2	*24.3*[g]	*27.5*	*18.6*	12.5	9.6	*9.0*	11.2
M—R_1	2.1	0.8				3.2	
M—R_2—HCl					4.8	2.7	11.3
M—R_2—HF			11.8	7.5	6.4	7.7	3.2
M—R_2—H_2	8.1	8.4		0.3			
M—R_1—HCl						(7.7)[h]	
M—R_1—HF	2.0	0.9				1.3	
M—HCl—F					4.6	1.5	
M—HF—F	1.0		0.7	4.6			
R_1^+	4.7	4.1	12.7	9.4	9.7	6.5	*12.9*
R_2^+	2.6	0.5				6.7	
$C_2Cl_2F_2H^+$						3.2	2.2
$C_2F_2H_3^+$	0.4	0.5	4.3				
$C_2ClF_3H^+$					7.9	2.9	
$C_2F_4H^+$		0.7		3.8			
CF_3^+	(2.6)	3.4	0.4	(9.4)		1.8	
$CHFCl^+$					7.1	6.9	6.9
$ClCHOH^+$					1.6	1.9	3.9
HCF_2^+[i]	3.8	2.7	(12.7)	*18.0*	6.8	2.4	
$FCHOH^+$[j]	1.4	2.3	3.8	10.3	5.0	5.4	2.4
FCH_2^+	0.4	0.5	15.6	0.2	0.3	0.4	0.4
FCH^+	2.7	0.4	2.0	1.6	2.5	2.2	1.9
CF^+	2.7	3.5	7.0	4.2	5.0	4.4	4.5
CH_2OH^+							
COH^+	8.0	9.7	7.3	14.7	*10.1*	6.7	4.5
$C_2H_3^+$	8.1	7.7	0.3				
F^+	4.4	4.3					
H_3O^+							
Max %[k]	3.8	2.5	1.7	2.5	2.0	2.0	2.3

[a] When $R_1 = CH_3$, per cent based on Σ_{13}. [b] Per cent for Cl-containing ions include contributions from all isotopic species. [c] See footnote *a*, Table II. [d] See footnote *b*, Table II. [e] See footnote *b*, Table I. [f] Ion formed by loss of a hydrogen atom. [g] Italic percentages correspond to base peak. [h] See footnote *e*, Table I. [i] Possible contribution from CH_2Cl^{37}. [j] Possible contributions from CH_2Cl^{35}, CCl^{37}. [k] See footnote *f*, Table I.

chloro-2-propanols differ from the fluorochloroacetones[8] in that for the latter compounds ion intensities resulting from α cleavage with charge retention by the oxygen containing fragment are vanishingly small. The spectra of the three chlorinated alcohols do not appear to exhibit any specific mode of fragmentation. The three most abundant ions in each spectrum have values of about 10%. Ionic species formed *via* the loss of HX (X = H, F, Cl) from the intermediate ion $R_1CH{=}\overset{+}{O}H$ could account for about 10% of the total ionization in each of the halogenated alcohols. An ion originating in this way may explain the formation of C_2HClFO^+ in the spectra of the chlorinated alcohols. For the alcohols containing three and four chlorine atoms this fragment is the second most abundant ion in the spectra. For the latter compound this mechanism would require loss of HCl from $CFCl_2CH{=}\overset{+}{O}H$. If HCl loss were to occur from adjacent carbon atoms the resulting ion would have the structure $CFCl{=}C{=}\overset{+}{O}H$. If the H that is lost were to come from the hydroxyl group, C_2HClFO^+ could result from a concerted cyclization with elimination of HCl. It is interesting to note that Haszeldine[9] has postulated the formation of the epoxide $\overline{CF_2CFClO}$ from the oxidation of chlorotrifluoroethylene. The *m/e* 31 for the secondary alcohols now accounts for a much smaller percentage of the total ionization. CH_2OH^+ must now be formed by a rearrangement process. High-resolution measurements[6] show that *m/e* 31 from $(CH_3)CHOH(CF_3)$ is composed of equal parts of CF^+ and the oxonium ion. The formyl ion $CH{\equiv}O^+$ was found to have a high relative abundance in all of the spectra. For $(CF_2Cl)CHOH(CF_2Cl)$ it is the base peak and for $(CF_3)CHOH(CF_3)$ it is the second most abundant ion. Rearrangement ions are formed in all of the halogenated alcohols. For $(CF_3)CHOH(CF_3)$ the rearrangement ion, CF_2H^+, is the most abundant in the spectrum.

Tertiary Alcohols.—Friedel[1] has found that for dimethyl tertiary alcohols the base peak results from α cleavage of the heavier alkyl group. For $(CH_3)_3COH$ (Table I) the peak corresponding to loss of CH_3 is the base peak and represents 40% of the total ionization.

(8) J. R. Majer, *Advan. Fluorine Chem.*, **2**, 55 (1961).

(9) R. N. Haszeldine and F. Nyman, *J. Chem. Soc.*, 1084 (1959).

The two fluorinated tertiary alcohols examined in this study, $(CH_3)_2(CF_3)COH$ and $(CF_3)_2(CH_3)COH$, have their fragmentation patterns summarized in Table IV. The base peak for both compounds occurs at *m/e* 43, which would correspond to the acetyl ion $CH_3C{\equiv}O^+$. In the case of $(CH_3)_2(CF_3)COH$ this assignment is not unequivocal because of the possible formation of the rearrangement ion, $C_3H_7^+$. Unfortunately the peak at *m/e* 44 is too high to permit a choice on the basis of isotope ratios. The ions corresponding to loss of CF_3 from the molecule ion are prominent in both spectra. This ion accounts for 11.4% of the total ionization in $(CH_3)_2COH(CF_3)$ and is the second most abundant. For this compound the acetyl ion could form from an intermediate acetone molecule ion. This latter ion could result from α cleavage of CF_3 and simultaneous loss of the hydroxyl H. This seems unlikely as the characteristic acetone molecule ion is missing in the alcohol spectrum. A more probable explanation of acetyl formation would involve loss of CF_3 and CH_4 to form the ion directly. Similar considerations would apply to formation of the acetyl ion in $(CH_3)COH(CF_3)_2$. Here its formation *via* decomposition of an intermediate 1,1,1-trifluoroacetone molecule ion seems unlikely after consideration of the fragmentation pattern[8] of 1,1,1-trifluoroacetone. In both alcohols loss of CF_3 rather than CH_3 predominates, especially in $(CH_3)COH(CF_3)_2$ where the ratio of the corresponding peak heights is about 20:1.

TABLE IV
$(R_1)(R_2)(CH_3)COH$, PER CENT OF TOTAL IONIZATION ($\%\Sigma_{13}$) OF SELECTED FRAGMENTS

Fragment[c]	$R_1 = CH_3$[a] $R_2 = CF_3$	CF_3[b] CF_3
Mol ion		
M—H[d]		
$M—H_2O$	0.1	
M—HF		
$M—CH_3$	5.6	0.4
$M—CF_3$	11.4	7.3
$C_3H_3F_4^+$		2.3
$C_3H_3F_2^+$	0.2	2.2
CF_3^+	1.9	8.0
CHF_2O^+	0.3	3.3
CH_3CFOH^+	4.9	6.4
HCF_2^+	0.7	2.8
CH_3CO^+	*22.7*[e]	*32.1*
$C_3H_7^+$		
$CHCO^+$	4.6	0.3
$C_3H_5^+$		
$C_3H_3^+$	2.5	
CF^+	9.0	2.3
CH_2OH^+		
$C_2H_5^+$	3.1	1.4
COH^+		
$C_2H_3^+$	2.6	1.1
CH_3^+	7.1	4.1
Max %[f]	2.1	2.5

[a] See footnote *a*, Table II. [b] See footnote *b*, Table II. [c] See footnote *b*, Table I. [d] Ion formed by loss of hydrogen atom. [e] Italic percentages correspond to base peaks. [f] See footnote *f*, Table I.

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Hydrogenation of a Benzylic Ether without Hydrogenolysis. 1-β-Cyclohexyl-1,5-D-anhydroglucitol

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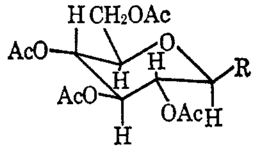
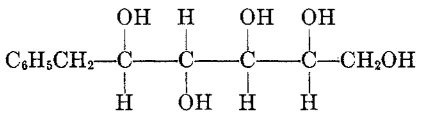
Benzylic groups are frequently characterized by the readiness with which they undergo hydrogenolysis. The topic has been reviewed by W. H. Hartung and R. Simonoff.[1] An example using a cyclic ether in this category is 2-phenyltetrahydropyran, which changes into 5-phenyl-1-pentanol[2] when hydrogenated with a palladium catalyst. A carbohydrate example is the cleavage of methyl 4,6-*O*-benzylidene-α-D-glucoside by hydrogen and platinum into toluene and methyl α-D-glucopyranoside.[3]



Ia, $R = C_6H_5$
b, $R = C_6H_{11}$

In view of this evidence, we expected a rather facile hydrogenolysis of 1-β-phenyl-1,5-D-anhydroglucitol tetraacetate (Ia) into the tetraacetate of L-gulo-6-phenyl-1,2,3,4,5-hexanepentol



$$C_6H_5CH_2-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-CH_2OH$$

Actually, however, none was obtained. With a palladium catalyst there was no reaction. With a platinum catalyst there was hydrogenation to 1-β-cyclohexyl-1,5-D-anhydroglucitol tetraacetate (Ib) in 82% yield. If any hydrogenolysis occurred concurrently, the product was in too small amounts to identify. That hydrogenation of Ia can occur without any significant amount of hydrogenolytic cleavage is a noteworthy observation in view of the benzylic ether structure.

The structure of Ib was supported by elemental analysis and by its infrared spectrum which lacked peaks characteristic of an aromatic ring in the 6.2–6.8-μ region.

An acidic medium was used with the platinum catalyst, namely, acetic acid containing perchloric acid. It is known[4] that acids increase the effectiveness of platinum to hydrogenate the aromatic ring. In the carbohydrate area, it is known also that the hydrogenation and hydrogenolysis reactions are sometimes

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(1) *Org. Reactions*, **7**, 263 (1953).

(2) R. H. Baker, K. Cornell, and M. Cron, *J. Am. Chem. Soc.*, **70**, 1490 (1948).

(3) K. Freudenberg, H. Toepffer, and C. Andersen, *Ber.*, **61**, 1750 (1928).

(4) J. Brown, H. Durand, and C. S. Marvel, *J. Am. Chem. Soc.*, **58**, 1594 (1936).