A Study of Water Elimination as a Function of Ion Lifetime in the Mass Spectrum of Cyclohexanol

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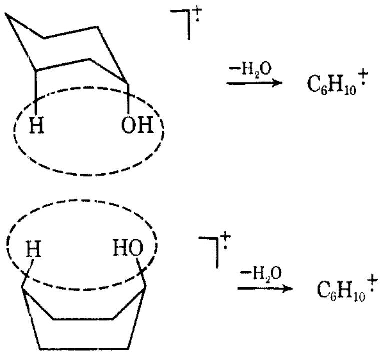
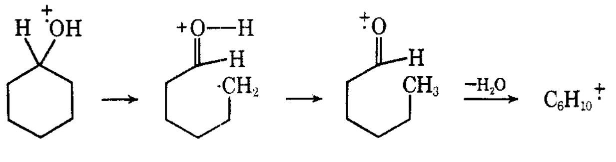
The eliminations of H_2O, HDO, and D_2O from the molecular ions of O-d_1-, 1-d_1-, 2,2,6,6-d_4-, 3,3,5,5-d_4-, and 4,4-d_2-cyclohexanols have been studied in daughter ions generated in 70-, 12-, and 10-eV spectra, and in metastable transitions occurring in the first and second field-free regions of a double-focusing mass spectrometer. It is concluded that *cis* 1,4 elimination of water does occur in the mass spectrum of cyclohexanol. Although 1,2 and 1,3 elimination *apparently* occur as competing unimolecular reactions, no definite conclusions as to their occurrence are possible, since H/H rearrangements probably occur prior to water elimination. In particular, a case can be made to support exchange between the hydroxyl hydrogen and hydrogen attached to C-3(C-5). The $M^+ - H_2O$ ion from cyclohexanol loses a methyl radical. In the spectra of the deuterated derivatives, this further loss of a methyl radical, occurring either in the source or the field-free regions, appears to be preceded by almost complete randomization of H and D.

Several workers have studied the elimination of water from the molecular ion of cyclohexanol.[1-3] From comparison of daughter ion intensities in the mass spectra of deuterated cyclohexanols, they concluded that two major specific processes were involved, 1,3 and 1,4 elimination.



For example, it was found[2] that of the $C_6H_{10}^{+\cdot}$ daughter ions formed, 42% had lost the hydroxyl group and a hydrogen atom from the 4 position, and 42% had lost the hydroxyl group and a hydrogen atom from the 3 or 5 positions. After correcting for the statistical excess of 3 and 5 hydrogens, this implies that the probability of abstracting a C-4 hydrogen atom is twice that of abstracting a C-3 or C-5 hydrogen atom. In order to account for the remaining (16%) $C_6H_{10}^{+\cdot}$ daughter ions, whose formation did not involve loss of the hydroxyl hydrogen but only loss of hydrogens from the 3 and 5 positions, a third minor process was suggested.[2]



Green, *et al.*,[3] have produced evidence to support the proposed mechanism of 1,4 elimination by demonstrating that the 1,4 loss is largely stereospecific (80% *cis*). This result implies that the six-membered ring is "substantially intact."[3] Further support for the proposed 1,4 elimination has been drawn from the behavior of cyclohexane-1,4-diols.[1] Thus, the *trans*-diol eliminates water to a greater extent that the *cis* isomer, and almost completely (90%) by necessarily *cis* 1,4 elimination.[1]

Similarly, both *trans*-4- and *trans*-3-*t*-butylcyclohexanols lose water to a greater extent than their *cis* isomers,[4,5] although the ease of cleavage of the tertiary C–H bond is here recognized as being a significant factor.[5]

The electron impact induced loss of water from cyclohexanol (*m/e* 100 → *m/e* 82) is accompanied by a "metastable peak" (*m/e* 67.2). For two reasons, we considered it desirable to study the "metastable peaks" for loss of H_2O, HDO, and D_2O from the molecular ions of deuterated cyclohexanols. First, there is a peak at *m/e* 81 in the mass spectrum of cyclohexanol, 10% of the abundance of *m/e* 82 at 70 eV. Conclusions based on daughter-ion intensities at 70 eV are obviously restricted by the presence of ions, analogous to *m/e* 81, in the spectra of the deuterated cyclohexanols. Examination of the metastable transitions in the first field-free region[6] shows that the sole process for formation of *m/e* 82 is loss of water from the cyclohexanol molecular ion, and that the *major* process for formation of *m/e* 81 is loss of water from the $(M^+ - 1)$ ion. Although it is known[2] that the $(M^+ - 1)$ ion is formed in the source by loss of the C-1 hydrogen atom, it is impossible to correct for the $(M^+ - H_3O)$ and $(M^+ - H_2OD)$ ions in the spectra of all but the simplest deuterated cyclohexanols. At nominal 10–12-eV beam energies, the abundance of *m/e* 81 in the spectrum of cyclohexanol is negligible. Second, by looking at the reactions of molecular ions of long lifetime and low internal energy, it was hoped to evaluate the importance of internal hydrogen rearrangement prior to fragmentation. Since hydrogen-scrambling processes in aliphatic compounds frequently have low activation energies and low frequency factors, they compete most effectively with fragmentation reactions having similar *k vs. E* curves.[7] The loss of water from the cyclohexanol molecular ion seems to occur

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(1) C. G. Macdonald, J. S. Shannon, and G. Sugowdz, *Tetrahedron Lett.*, 807 (1963).

(2) H. Budzikiewicz, Z. Pelah, and C. Djerassi, *Monatsh.*, **95**, 158 (1964).

(3) M. M. Green and J. Schwab, *Tetrahedron Lett.*, 2955 (1968).

(4) C. E. Brion and L. D. Hall, *J. Amer. Chem. Soc.*, **88**, 3661 (1966).

(5) L. Dolejš and V. Hanuš, *Collect. Czech. Chem. Commun.*, **33**, 332 (1968).

(6) M. Barber and R. M. Elliot, ASTM E-14 Conference on Mass Spectrometry, Montreal, Canada, June 1964; K. R. Jennings in "Some Newre Physical Methods in Structural Chemistry," R. Bonnett and J. G. Davis, Ed., United Trade Press, London, 1967, p 105; T. W. Shannon, T. E. Mead, C. G. Warner, and F. W. McLafferty, *Anal. Chem.*, **39**, 1748 (1967).

(7) A. N. H. Yeo, R. G. Cooks, and D. H. Williams, *Chem. Commun.*, 1269 (1968); A. N. H. Yeo and D. H. Williams, *J. Amer. Chem. Soc.*, in press.

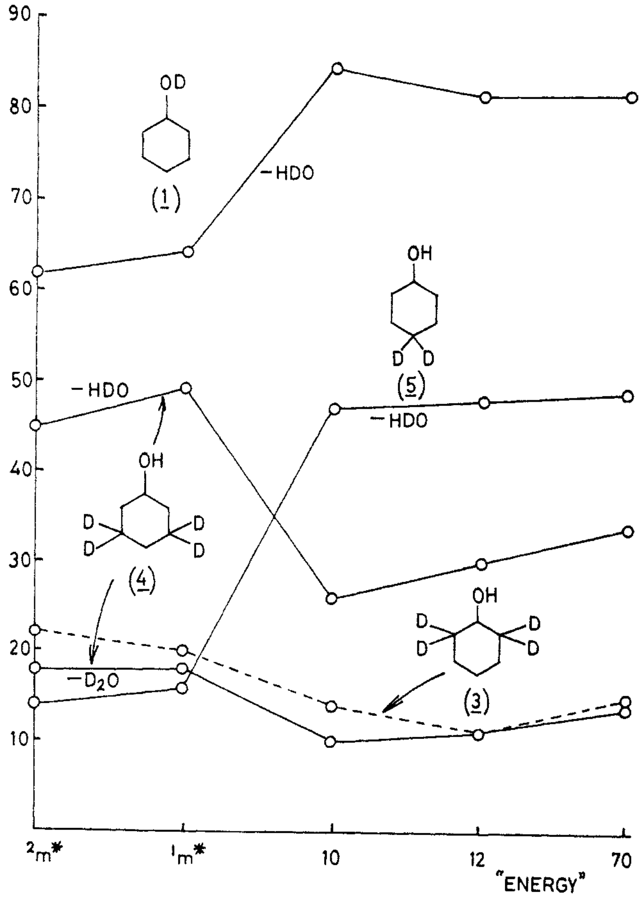


Figure 1.—Percentages of HDO and D_2O lost by **1** and **3**–**5** as a function of parent ion "energies."

Table I

Ionization and Appearance Potentials of Some Ions in the Mass Spectrum of Cyclohexanol

Quantity	Ion, *m/e*	Assignment	Value, eV	AP of m*
IP	100	M^+	10.0	...
AP	82	$M^+ - H_2O$	10.1	10.05
AP	67	$M^+ - H_2O - CH_3$	10.9	10.6
AP	57	$C_3H_5O^+$	11.5	...

with a relatively low activation energy (see Table I) and low frequency factor. Further, hydrogen/deuterium scrambling will probably be most advanced in ions of long lifetime and might therefore be most evident in ions formed in the first and second field-free regions. An additional important advantage of using a metastable defocuser is that metastable transitions can be detected with a very high sensitivity, and, since the precursor and daughter ions are unambiguously identified in each case, no complications arise because of the presence of isotopic impurities.

Discussion

The ionization potential (IP) of cyclohexanol and the appearance potentials (AP) of some of its fragment ions are given in Table I. Also shown in Table I are the appearance potentials of the first field-free region "metastable peaks" (m*) for formation of *m/e* 82 and 67. As expected, these values are somewhat less than the appearance potentials of the corresponding daughter ions, due to the extra energy needed to raise the rate constants slightly in the region of 10^5–10^6 sec^{-1}.

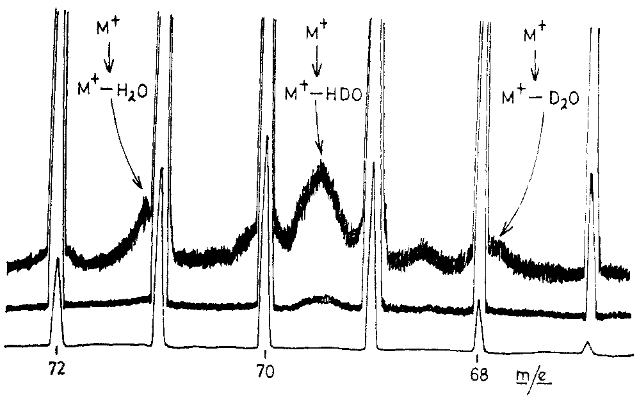
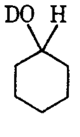


Figure 2.—"Metastable peaks" for loss of H_2O, HDO, and D_2O from 3,3,5,5-d_4-cyclohexanol.

Deuterated, cyclohexanols **1**–**5** were synthesized and studied.



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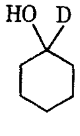

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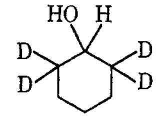

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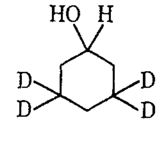

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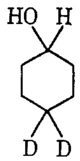


5

Loss of Water from the Cyclohexanol Molecular Ion.—Table II gives the percentages of HDO and D_2O lost by **1**–**5** as measured from daughter ion intensities at nominal 70-, 12-, and 10-eV beam energies (after correction for ^{13}C-containing ions and incompletely deuterated species) and metastable ion intensities (first and second field-free regions) at 70 eV.

Table II

Percentage Composition of (M^+ – Water) Ions from 1–5[a]

Compd	Loss	Daughter ions 70 eV	Daughter ions 12 eV	Metastable ions[b] 10 eV	Metastable ions[b] $_1m^*$	Metastable ions[b] $_2m^*$
1	HOD	82	82	85	64	62
2	HOD	6	3	3	*b*	*b*
3	HOD	15[c]	11	14	20	22
	D_2O	3[c]	1	*b*	*b*	*b*
4	HOD	34[c]	30	26	49	45
	D_2O	14[c]	11	10	18	18
5	HOD	49[c]	48	47	16	14
	D_2O	5[c]	4	3	2	*b*

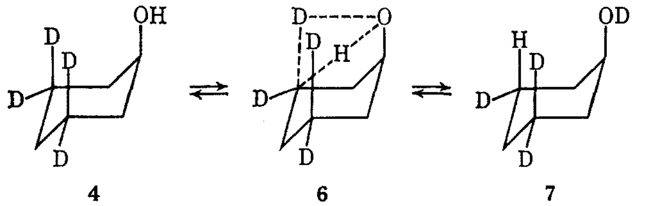
[a] The estimated accuracy for the daughter ion data at 12 and 70 eV is ±1%; at 10 ev, and for metastable transitions, it is ±2%. [b] Too small to measure (<2%). [c] Uncorrected for contributions from ($M^+ - H_3O$) and ($M^+ - H_2OD$) ions.

The data for daughter ions accord well with previous figures,[2] except that we find a significant loss (11–15%) of HDO from the 2,2,6,6-d_4 derivative **3**; this loss of HDO becomes more pronounced (20–22%) in the field-free regions (Table II). The major significant processes (>10%) at all energies are loss of HDO from **1**, **3**, **4**, and **5** and of D_2O from **4**, and the results for these processes are summarized graphically in Figure 1 (the energy scale is of course arbitrary, but it is convenient for clarity of exposition). Perhaps the most important point to emphasize is that the 3,3,5,5-d_4 derivative (**4**) undergoes competing metastable transitions in both field-free regions for loss of H_2O, HDO, and D_2O (Figure 2; the additional "metastable peaks" at *m/e* 70.1 and

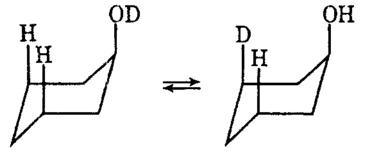
68.5 correspond to loss of H_2O and HDO from $M^+ - 1$ and from the $d_3 - M^+$ impurity). Since competing metastable transitions are to be expected only if the processes have very similar activation energies (within *ca.* 50%),[8] and since the activation energies in question are very low (Table I), it may reasonably be concluded that some measure of H/D rearrangement precedes the loss of D_2O from **4**; such H/D rearrangement is by no means unexpected[9] (see also ref 7 and references cited therein).

If it is accepted that H/D rearrangement can occur in the specifically deuterated derivatives prior to water loss, then the earlier conclusions that competitive 1,3 and 1,4 eliminations are involved in the water loss[1-3] may or may not be correct. For example, it is conceivable that exchange of H and D could occur to some extent between C-3 (C-5) and C-4 prior to the water elimination. In any event, an interpretation of the data (Table II and Figure 1), which (probably incorrectly) ignores H/D exchange reactions, would now have to include a significant competing 1,2 elimination (especially important in ions of low internal energy—see dotted line in Figure 1). It is noteworthy that, if it is *assumed* that there is no H/D scrambling, the necessary 1,2 elimination cannot be thermally induced, since it is most important in metastable transitions, *i.e.* occurs from the molecular ion and not the neutral molecule. Thus, it is possible to interpret the results in terms of competing 1,2, 1,3, and 1,4 eliminations of water (involving four-, five-, and six-membered transitions states), assuming H/D exchange reactions to be very minor, or to assume at the other extreme that H/D exchange is extensive and that the actual elimination process may even involve only a single transition state (*e.g.*, *cis* 1,4 elimination in the boat form). Some picture inbetween these extremes is also possible.

It is difficult to reach reliable conclusions. Certainly, if competing 1,2, 1,3, and 1,4 eliminations are involved, they must have similar activation energies, since all give competing metastable transitions. While such a situation is not inconceivable, it seems somewhat unlikely. The evidence in favor of hydrogen exchange between the hydroxyl hydrogen and those attached to C-3 (C-5) is strong. Thus, if the reaction **4** → **7** *via* the transition state **6** has a lower activation energy and lower frequency factor than water loss, then, for ions losing water in the field-free regions, the concentration of **7** in relation to **4** will be higher than for ions losing water in the source.



4 **6** **7**



1 **8**

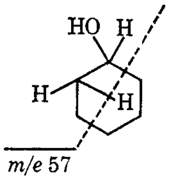
It follows that in the field-free regions (a) the OD derivative **1** will lose more H_2O (*via* **8**) than when reacting in the source; (b) **4** will lose more D_2O (*via* **7**) than when reacting in the source; and (c) HDO loss from **4** (*via* **7**) will increase relative to reaction in the source, since **7** cannot lose H_2O. These are the experimental observations (Figure 1).

It is also true that a good case can be made to support the occurrence of a direct 1,4 elimination, since this occurs with a high *cis* stereospecificity (80%) in 70-eV spectra.[3] In addition, if it were assumed that only a 1,3 elimination were involved following randomization of the 4,4 deuteriums of **5** among C-3, C-4, and C-5 prior to the formation of the majority of the M^+ − water daughter ions at 70 eV, then it becomes impossible to explain the large loss (49%, larger than the statistical value of 33%) of HDO from the 4,4-d_2 derivative **5** at 70 eV and the smaller loss (34%) of HDO from the 3,3,5,5-d_4 derivative **4** at 70 eV. Thus, the case for a direct *cis* 1,4 elimination in ions of relatively high internal energy seems established beyond reasonable doubt.

A concrete case for a competing direct 1,2 and 1,3 elimination is less easy to make. Indeed, the data (Table II and Figure 1) are also perfectly consistent with solely a direct *cis* 1,4 elimination with C-3 (C-5) and C-2 (C-4) deuteriums (of **4** and **3**, respectively), scrambling into the hydroxyl and *cis* C-4 positions, and increasingly so in ions of longer lifetime (Figure 1).

In summary, direct *cis* 1,4 elimination of water from the molecular ion of cyclohexanol seems to be established. A reasonable case can be made in support of H/H exchange between the hydroxyl hydrogen and those attached to C-3 (C-5). Direct 1,2 and 1,3 eliminations of water may occur as competing unimolecular decompositions, but owing to the possibility of H/H scrambling, their occurrence is not proved in the present case.

Formation of *m/e* 57.—The ion at *m/e* 57 gives rise to the base peak in the mass spectrum of cyclohexanol at 70 eV, but at 12 eV *m/e* 82 ($M^+ - H_2O$) is the base peak. This fact, along with the observation that formation of *m/e* 57 is not accompanied by an abundant "metastable peak," establishes that the reaction leading to *m/e* 57 is one of higher activation energy and higher frequency factor than that leading to *m/e* 82 (assuming that the reactions are truly competing).[10] The measured appearance potentials (Table I) of *m/e* 82 and 57 confirm the former conclusion. The *m/e* 57 peak is formed in the source without any significant hydrogen scrambling even at low electron-volt values. The shift in *m/e* 57 in **1**-**5** indicates cleavage as shown, as previously described.[1,2] Since *m/e* 57 is formed



m/e 57

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(8) H. M. Rosenstock and M. Krauss in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, p 36.

(9) F. W. McLafferty in "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, Chapter 2, p 131.

(10) D. H. Williams and R. G. Cooks, *Chem. Commun.*, 663 (1968); F. W. McLafferty and R. B. Fairweather, *J. Amer. Chem. Soc.*, **90**, 5915 (1968).

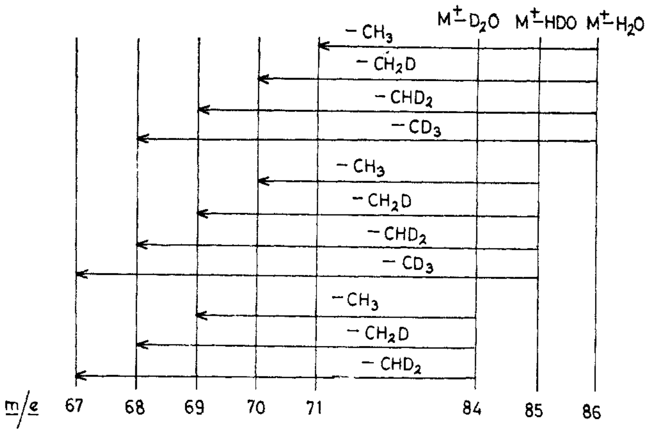

Figure 3.—Routes by which *m/e* 67–71 may arise in the spectra of 2,2,6,6-d_4- and 3,3,5,5-d_4-cyclohexanol.

from ions of relatively high internal energy and short lifetime, it is not surprising that H/D exchange does not precede its formation.[7]

There are *very weak* 1_{m^*} peaks of decreasing intensity for formation of *m/e* 57 from *m/e* 58, 72, and 99 and/or 100. The ion at *m/e* 58 is formed from *m/e* 99 or 100, as again indicated by very weak "metastable peaks."

Formation of *m/e* 67 ($M^+ - H_2O - CH_3\cdot$).—Examination of the metastable transitions in the first field-free region shows that *m/e* 67 is formed *solely* from *m/e* 82 ($M^+ - H_2O$) by loss of a methyl radical. Intensities of "metastable peaks" (in the first field-free region) for corresponding processes from abundant M^+ − water daughter ions from **3**, **4**, and **5** are given in Table III. Also shown are the calculated intensities assuming complete randomization of the hydrogens and deuteriums prior to loss of methyl.

TABLE III

INTENSITIES OF "METASTABLE PEAKS" FOR THE PROCESS M^+ – WATER → M^+ – WATER – $CH_3\cdot$

Compd	M^+ − water	Loss	"Metastable peak" intensity, %[a]	Calculated intensity for random loss, %
3	M − H_2O	CH_3	18	16.7
		CH_2D	45	50.0
		CHD_2	27	30.0
		CD_3	10	3.3
4	M − H_2O	CH_3	24	16.7
		CH_2D	49	50.0
		CHD_2	25	30.0
		CD_3	2	3.3
	M − HOD	CH_3	38	29.2
		CH_2D	48	52.5
		CHD_2	13	17.5
		CD_3	1	0.8
5	M − H_2O	CH_3	51	46.7
		CH_2D	44	46.7
		CHD_2	5	6.6
	M − HOD	CH_3	75	70.0
		CH_2D	25	30.0

[a] Estimated accuracies of ±2%.

The results in Table III demonstrate that in M^+ − water ions of long lifetime the hydrogens and deuteriums are almost completely randomized prior to expulsion of a methyl radical. The "metastable peaks" in the second field-free region show a similar distribution, but their accurate comparison is precluded by the presence of normal peaks in the spectra.

The various routes by which *m/e* 67, 68, 69, 70, and 71 daughter ions may arise in the spectrum of a d_4 cyclohexanol are given in Figure 3. By weighting each M^+ − water daughter ion according to its concentration at the collector, it is possible to calculate what the relative intensities of the M^+ − water − methyl daughter ions in the spectra of **1**–**5** would be if the hydrogens of the M^+ − water ions formed in the source are randomized. These figures are compared with observed values in Table IV. The comparison suggests that there is extensive randomization prior to this reaction even in ions of shorter lifetimes ($\leqslant 10^{-6}$ sec) than those giving rise to metastable transitions.

TABLE IV

OBSERVED AND CALCULATED INTENSITIES OF M^+ – WATER – METHYL DAUGHTER IONS IN THE MASS SPECTRA OF DEUTERATED CYCLOHEXANOLS 2–5

		Obsd intensity[a]		Calcd intensity[b]	
Compd	*m/e*	70 eV	12 eV	70 eV[c]	12 eV
2	68	66	68	64	69
	67	34	32	36	31
3	71	17	18	13	15
	70	39	38	45	46
	69	29	29	34	33
	68	14	14	7	6
	67	1	1	1	1
4	71	22	25	10	10
	70	35	31	36	35
	69	31	33	38	39
	68	10	10	14	13
	67	2	1	2	1
5	69	30	32	20	21
	68	52	53	55	55
	67	18	15	25	24

[a] Corrected for ^{13}C abundance; estimated accuracy of ±1%. [b] Calculated intensity = M^+ − water daughter ion intensity corrected for ^{13}C only × probability of loss of methyl fragment assuming complete randomization of the hydrogens. [c] Ignores $M^+ - H_3O$ and $M^+ - H_2OD$ contributions to M^+ − water ion intensities.

Experimental Section

All mass spectra were determined on an AEI MS 9 double-focusing instrument operating at a source temperature of 180–200°. Samples were introduced through a heated inlet system. Ionization and appearance potentials were determined by the semilogarithmic plot method.[11] Metastable transitions in the first field-free region of the mass spectrometer were examined by means of a defocusing device.[6]

Preparation of Deuterated Cyclohexanols.—1-d_1-Cyclohexanol (**2**, 98% d_1, 2% d_0) was prepared by lithium aluminum deuteride reduction of cyclohexanone. 2,2,6,6-d_4-Cyclohexanol (**3**) was prepared by lithium aluminium hydride reduction of 2,2,6,6-d_4-cyclohexanone, which in turn was obtained from cyclohexanone by repeated base-catalyzed equilibration with deuterium oxide. Cyclohexanone was refluxed with deuterium oxide in the presence of anhydrous potassium carbonate for 48 hr and the cyclohexanone was reisolated by ether extraction. Five such exchanges gave 2,2,6,6-d_4-cyclohexanone (97% d_4, 3% d_3). 3,3,5,5-d_4- and 4,4-d_2-cyclohexanols (**4** and **5**) were obtained by reduction of the *p*-toluenesulfonylhydrazones of 2,2,6,6-d_4-4-hydroxycyclohexanone and 4-hydroxycyclohexanone with lithium aluminum hydride and deuteride, respectively. The conditions employed were identical with those previously described for the preparation of

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(11) See, for example, C. Lifschitz, E. D. Bergmann, and B. Pullmann, *Tetrahedron Lett.*, 4583 (1967).

4,[12] except that the preparation of **5** was completed by work-up with deuterium oxide containing a small amount of deuterium chloride.

The samples of **2**, **3**, **4**, and **5** were purified by preparative vapor phase chromatography on a 2-ft Apiezon column at 80°. Their percentage isotopic purity was calculated from low-voltage spectra. The low-voltage spectra of the corresponding cyclohexanones were much more amenable to analysis than the low-voltage spectra of the cyclohexanols themselves, owing to the low appearance potential of the $M^+ - 1$ ion of cyclohexanol. Consequently, small amounts of **4** and **5** were oxidized to the corresponding ketones,[12] 3,3,5,5-d_4-cyclohexanone (89% d_4, 11% d_3) and 4,4-d_2-cyclohexanone (86% d_2, 13% d_1, and 1% d_0), respectively.

The mass spectrum of O-d_1-cyclohexanol (**1**, 86% d_1, 14% d_0) was obtained as follows. Cyclohexanol was heated in deuterium oxide to 100° for 1 hr; the resulting cyclohexanol was isolated by ether extraction and introduced into the mass spectrometer after previous exchange of the inlet system with several samples of deuterium oxide.

The isotopic purities of **1**–**5** are summarized in Table V.

Table V

Isotopic Purities of Deuterated Cyclohexanols

Compd	%				
	d_0	d_1	d_2	d_3	d_4
1	14	86	...	...	...
2	2	98	...	...	...
3	...	...	...	3	97
4	...	...	...	11	89
5	1	13	86	...	...

Registry No.—Cyclohexanol, 108-93-0; water, 7732-18-5; **1**, 14848-87-4; **2**, 21273-02-9; **3**, 21273-03-0; **4**, 21273-04-1; **5**, 21273-05-2.

Acknowledgment.—One of us (R. S. W.) would like to acknowledge a Morrell Fund Studentship.

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(12) D. H. Williams, H. Budzikiewicz, Z. Pelah, and C. Djerassi, *Monatsh.*, **95**, 166 (1964).

Some Reactions of Difluoramino Compounds with Bases and Reducing Agents[1]

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Lithium borohydride reacted with ethyl 5,5-bis(difluoramino)hexanoate to give 5,5-bis(difluoramino)hexanol, and with 1,3,3-tris(difluoramino)butane to give 3,3-bis(difluoramino)butylamine, isolated as the trifluoroacetate. Hydrolysis of ethyl 5,5-bis(difluoramino)hexanoate with hot alkali gave 5,5-bis(difluoramino)hexanoic acid. This ester reacted with methanolic hydrazine to give the hydrazide, which was nitrosated to form the azide, which, in turn, was converted into the isocyanate and to 4,4-bis(difluoramino)pentylurea. Reduction of 2,2-bis(difluoramino)-5,5,5-trinitropentane with alkaline peroxide gave 2,2-bis(difluoramino)-5,5-dinitropentane, which was hydrolyzed to 4,4-bis(difluoramino)pentanoic acid. Reduction of cycloalkyl difluoramines with lithium aluminum hydride gave primary and rearranged secondary amines. Dimethyl N-phenyliminocarbonate was obtained from reactions of methoxide with α,α-dichloro-α-difluoraminotoluene, α-bromo-α,α-bis(difluoramino)toluene, and α,α-dibromo-α-difluoraminotoluene. The latter was converted into α-bromo-α-fluoriminotoluene with ammonia or sodium 2-propanenitronate.

The synthesis of *gem*-bis(difluoramino) compounds by the reaction of carbonyl compounds with difluoramine has recently been reported.[2] 1,1-Bis(difluoramino)-1-halo compounds and 1-difluoramino-1,1-dihalo compounds were prepared by replacement reactions of halo, nitro, and nitroso compounds with difluoramine.[3,4] The present paper deals with some chemical properties of these compounds and their ability to withstand reaction conditions encountered in some common chemical transformations of other functional groups.

The effect of reducing agents on difluoramino groups has been studied by several groups. The reduction of tertiary difluoramino compounds by titanous ion gave fragmentation products indicative of nitrene intermediates, *e.g.*, acetone and methylamine from *t*-butyldifluoramine.[5] The formation of fluorimines from α-halodifluoramines has been reported using pyridine,[5] iodide ion,[6] ferrocene,[7] and iron carbonyl.[8] Simple primary and secondary alkyldifluoramines are readily dehydrofluorinated to give nitriles and fluorimines, respectively, although teritary alkyldifluoramines are relatively stable toward base.[5,9]

The reactivity of internal *gem*-bis(difluoramino)alkanes was screened in test-tube experiments using 2,2-bis(difluoramino)octane as a model compound. The starting material was recovered after 20 hr at ambient temperature from methanol solutions of hydrazine, sodium nitrite, and sodium azide, from a slurry with aqueous sodium borohydride, and from an ether solution of the more powerful reducing agent,[10] lithium borohydride. The compound did not react with aqueous potassium iodide, but when acetonitrile containing 10% water was used as the solvent, iodine was liberated slowly (several days for completion). The compound was reduced by lithium aluminum hydride but the products were not determined.

Using conditions under which the difluoramino

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