filtered, and evaporation of the filtrate gave a white solid residue. This crude material was slurried in two 15-ml portions of cold water and dried. The product weighed 10.3 g (74%), mp 73–76°. Recrystallization from diethyl ether raised the melting point to 81–82°. An admixture melting point with material prepared by method A was undepressed. Infrared and nmr spectra were also identical with those obtained by Method A.

N-(2-Chloroethyl)-S-(p-chlorophenyl)thiocarbamate (12). Method A.—A solution of p-chlorophenyl thiochloroformate (0.5 mol) in 200 ml of chloroform was stirred at 5–10° while a solution of 0.5 mol of aziridine in 20 ml of chloroform was added dropwise over a period of 40 min. The reaction temperature was maintained at 10–17° during the addition period. The solution was stirred for 1 hr at room temperature and then re-fluxed for 3 hr, and the solvent was evaporated to give a 96% yield of white crystalline product. Recrystallization from diethyl ether gave glittering white needles melting at 98–99°.

Anal. Calcd for $C_9H_9Cl_2NOS$: C, 67.49; H, 5.66; N, 8.75. Found: C, 67.41; H, 5.55; N, 8.63.

N-(2-chloroethyl)-S-phenylthiocarbamate was also prepared by the above method in 95% yield as white needles from diethyl ether; it had mp 82–83.5°.

Method B.—A 0.015-mol quantity of either **1** or **3** was added in one portion, with stirring, to 25 ml of concentrated (36%) hydrochloric acid. The suspension was allowed to stir for 20 min at room temperature and then warmed on a steam bath for 10 min. A white precipitate remained; after the suspension had cooled, it was filtered. The infrared spectra of these products were identical with those obtained for carbamates prepared by method A.

Kinetic Measurements.—Stock solutions of **1** and potassium thiophenolate were made up with a solvent consisting of 90% acetonitrile–10% methanol (v/v). Under anhydrous conditions and in a nitrogen atmosphere, various quantities of each stock solution and solvent were mixed to obtain desired concentrations. The "zero" time was recorded as the time at mixing. These reaction mixtures were placed in a vial equipped with a rubber serum cap and kept in a constant-temperature bath at 28 ± 0.5°. Samples were withdrawn at various time intervals with a needle syringe and charged into a fixed-volume NaCl cell. Times were recorded during the scan at the peak of the 11.75-μ band. The same cell was used for all the kinetic runs. The temperature of the sample in the infrared beam did not vary significantly from the reaction bath temperature. At 100% conversion the base line is completely flat in the 11.75-μ region. Completely clear, homogeneous solutions were obtained after 100% conversion.

"Cross-Over" Reaction.—To 25 ml of sodium-dried and re-distilled p-xylene was added 300 mg of aziridine **1**, 300 mg of aziridine **5**, and 15 μl of anhydrous triethylamine. This reaction mixture was refluxed under anhydrous conditions for 1 hr. A 15-μl sample of this reaction mixture was injected onto a 10-ft silicone gum rubber column under the following conditions: flow rate, 60 ml/min; inlet pressure, 35 lb/in.²; detector temperature, 350°; injection port temperature, 200°. The column temperature was programmed from 200 to 275° at a rate of 11°/min. The chromatogram consisted of four peaks, in addition to the solvent peak, with retention times of 6.7, 7.0, 8.9, and 9.1 min. These peaks were identified as isocyanates 2, 6, 14, and 7, respectively, by comparison with the chromatogram obtained for a synthetic mixture containing authentic samples of each of the above isocyanates.

Mass Spectrometric Studies. I. The Fragmentation of Methyl Cyclohexyl Ether[1]

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The electron impact induced mass spectra of methyl cyclohexyl ether (**1a**) and six deuterated analogs have been obtained. With the aid of high-resolution techniques, the range of available deuteriated analogs has permitted a very thorough understanding of the spectrum of **1a**. The major decomposition modes of the molecular ion of **1a** have been found to parallel closely the reported fragmentations of cyclohexyl alcohol and methyl cyclobutyl ether, and, just as was found for these compounds, it is initial β cleavage which accounts for the major portion of ions in the spectrum of **1a** and renders this spectrum, too, substantially different from the spectra of acyclic ethers. The base peak in the spectrum, found at m/e 71 $(CH_3O=CHCH=CH_2)^+$, arises via β cleavage of the molecular ion followed by hydrogen transfer and carbon–carbon bond homolysis. One of the features common to the spectra of cyclic and acyclic ethers, 1,3 and 1,4 elimination of the elements of ROH, is discussed as a potentially powerful analytical technique for the measurement of the stereochemistry of deuterium incorporation reactions in ring compounds. The synthetic procedures by which the deuteriated analogs of **1a** have been prepared are described in detail.

A considerable body of data has been amassed from the electron impact induced mass spectra of aliphatic ethers and alcohols.[3] From these data the more significant fragmentation processes undergone by aliphatic ethers and alcohols have been determined and are found to be similar in many ways. The usefulness of the data compiled on these and other classes of compounds in the elucidation of organic structures is great and needs no discussion here. However, owing to the lack of analogy between cyclic and acyclic spectra, difficulties are encountered when attempts are made to use mass spectrometric data from acyclic compounds in structure proofs of ring-containing compounds. The differences between the spectra of these classes of compounds may arise because of higher symmetry and uniquely restricted intramolecular interactions imposed by the rings. The resulting spectra, more often than not, possess few of the features of acyclic analogs. For example, the mass spectra of two cyclic methyl ethers, cyclobutyl and cyclopropyl carbinyl, have recently been reported,[4] and both show base peaks at m/e 58, an ion not found to be of significance for acyclic ethers and quite obviously an ion arising as a consequence of the presence

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(3) For general discussions and leading references, see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, Chapters 2 and 6.

(4) W. G. Dauben, J. H. Smith, and J. Saltiel, *J. Org. Chem.*, **34**, 261 (1969).

of a ring in each structure. Analogously, cyclohexyl alcohol, the spectrum of which has been investigated in considerable detail,[5-8] also shows fragmentations uniquely associated with its ring. Such spectral changes are to be expected with the inclusion of a ring, and many examples of the mass-spectral changes caused by rings are available.[3]

In a study of the effects of deuterium on the conformational equilibria of substituted cyclohexanes,[9] a series of deuteriated methyl cyclohexyl ethers became available. These compounds have permitted a detailed study of the fragmentation of this simple cyclic methyl ether. In Table I the low-resolution mass spectrometric data for methyl cyclohexyl ether (1a) and its deuteriated analogs (1d–1g) are summarized.

1b, OCD_3
c, 1-d_1
d, 2,2,6,6-d_4
e, 3,3,5,5-d_4
f, 3,3,4,4,5,5-d_6
g, 4,4-d_2
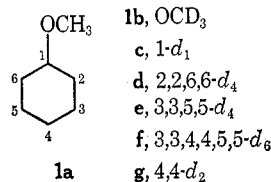
For methyl-saturated alkyl ethers it is observed that α cleavages (carbon–oxygen bonds) and β cleavages (carbon–hydrogen and/or carbon–carbon bonds) are favored mass spectrometric decomposition modes, particularly when the alkyl groups are not too large.[10,11] Limited data available from a recent investigation[4] and data from this work show that, when rings are present in aliphatic ethers, neither α nor β cleavages lead directly to the most abundant ions.

In our work 1a was found to show minor amounts of α cleavage, giving ions at m/e 15 (CH_3^+) as 2.6% and 83 ($C_6H_{11}^+$) as 1.9% of the base peak. β cleavage of 1a can give rise to three different ions, two at m/e 113, as the result of a loss of a proton from either of the α carbons, and one at m/e 114, the identical mass of the parent ion, as a result of cleavage of the C-1–C-2 bond. The first two processes contribute ions totaling only 0.7% of the base spectral peak, whereas the contribution of the latter process can be measured only in terms of those ions which appear to be derived from this initial β cleavage of the C-1–C-2 bond.

In fact, results from deuterium labeling suggest that β cleavage is the initial step of the decompositions of the molecular ion of cyclohexyl alcohol responsible for the production of the base spectral peak.[5,6] By way of analogy, a similar first step might well be expected for the production of the base peak of 1a; Scheme I shows this decomposition. Interestingly enough, this sequence is capable of explaining the production of only 87% of the m/e 71 ions in the spectrum of 1a. Labeling unmistakably shows that the remaining ions are formed from the methyl, oxygen, methinyl, and methylenes of C-3 and C-5 less one hydrogen. Scheme II represents what is intended to be a vague attempt at depicting this process. No

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

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

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

(8) M. M. Green and R. J. Cook, *J. Amer. Chem. Soc.*, 91, 2129 (1969).

(9) G. W. Klein and V. F. Smith, Jr., unpublished results.

(10) F. W. McLafferty, *Anal. Chem.*, 29, 1782 (1957).

(11) C. Djerassi and C. Fenselau, *J. Amer. Chem. Soc.*, 87, 5747 (1965).

TABLE I
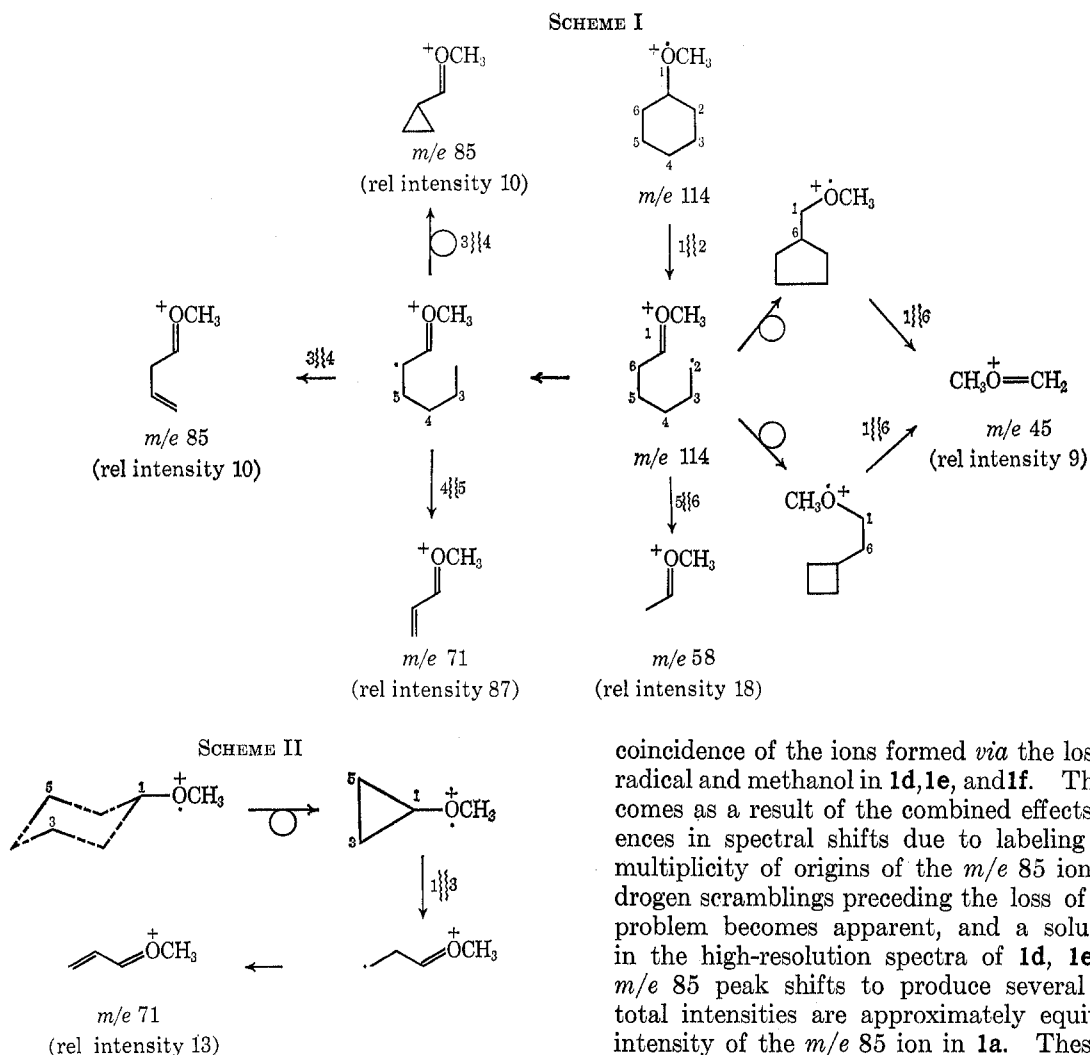MASS SPECTRAL PEAKS FOR METHYL CYCLOHEXYL ETHER AND DEUTERATED ANALOGS AT 70 eV[a,b]

m/e	1a	1b	1c	1d	1e	1f	1g
120						16.5	
119						0.7	
118				17.1	15.7		
117		15.0		0.8	0.7		
116		0.7					15.1
115			15.4				0.7
114	15.6						
113	0.7						
89						4.6	
88		9.3		6.8	0.6	3.4	
87				3.2	4.0	14.0	10.4
86	0.5		9.3	17.0	6.0	1.5	
85	9.7		0.7	4.0	13.8	0.5	2.0
84			1.8	1.0	0.9		8.5
83	1.9	1.5	13.4	0.5	0.6	0.5	3.5
82	12.3	12.2	2.0	0.6	0.7		0.8
81	2.6	2.4	0.7				0.6
80			0.7				0.5
79	0.7	1.0					
78							
77	0.6						
76							
75		1.2				1.8	
74		100.0			13.9	14.1	
73			1.0	3.9	100.0	100.0	1.2
72	1.4		100.0	100.0	2.8	5.0	2.4
71	100.0			12.2	3.1	5.2	100.0
70				3.8	3.6	2.4	
69				3.1	2.7		2.8
68			5.5				3.1
67	6.4	6.5	2.7				0.9
61		17.4					
60				14.8		4.2	
59	1.4		18.0	7.6	6.3	9.0	1.7
58	17.6			6.3	19.7	17.4	14.6
57		1.6		7.4	7.0	4.3	5.8
56		1.8	6.4	6.6	4.1	3.1	5.8
55	10.2	7.0	7.1	3.0	3.1	3.9	5.1
54	4.5	4.2	4.7				2.8
53	4.1	3.4	2.5				2.0
48		9.8					
47			1.9				
46			7.5	5.5	4.6	6.3	0.9
45	9.3		2.4	9.6	8.6	10.1	9.5
44		2.4	4.7	7.0	2.9	8.9	2.3
43	6.6	5.9	2.7	11.1	25.7	21.0	9.2
42	3.4	14.4	21.5	17.7	6.9	8.1	8.3
41	27.3	12.9	10.4	7.3	7.3	8.9	19.7
40	1.8	1.7	5.2	7.1	7.0	6.3	5.9
39	14.0	11.5	10.1	3.9	4.5	6.4	7.5

[a] All intensities have been corrected for isotopic contaminants and contributions due to natural isotopic abundances. [b] Intensities under 0.5% of the base spectral peak have been deleted.

evidence exists for the assignment of intermediate structures or the m/e 71 ion structure, the structure of which may or may not be similar to the ion formed by the major pathway. Nevertheless, the rationale offered for a competitive pathway for the formation of the m/e 71 ion is consistent with the highly specific multiple bond breaking–multiple bond forming process dictated by the results from the deuteriated analogs of 1a.

Another ion arising from an initial β cleavage and subsequent decomposition is found at m/e 58. High-resolution studies show that this ion contains oxygen.

SCHEME I

m/e 85
(rel intensity 10)

m/e 85
(rel intensity 10)

m/e 71
(rel intensity 87)

m/e 114

m/e 114

m/e 45
(rel intensity 9)

m/e 58
(rel intensity 18)

SCHEME II

m/e 71
(rel intensity 13)

The mechanism of its formation, consistent with deuterium labeling, is shown in Scheme I. The process put forth for the production of the base peak of methyl cyclobutyl ether,[4] m/e 58, is directly analogous. For 1a the m/e 58 ion, formed in competition with other ions derived from initial β cleavage, contributes 17% of the base peak. Similarly, cyclohexyl alcohol gives an m/e 44 ion (CH_2=$CHOH^+$) as about 70% of the base peak.[6]

One of the most interesting of the mass spectrometric decompositions of 1a is the loss of the elements of methanol, leading to the m/e 82 ion. This sort of decomposition is well documented for acyclic ethers,[10,11] and thorough studies have been made of the analogous loss of water in cyclohexanol.[5-8] From these previous investigations it was expected that 1a would lose the elements of methanol from the methoxyl and a hydrogen from carbons 3, 4, or 5. These eliminations for cyclohexyl alcohol were initially thought to be highly specific cis eliminations,[5,6] but more detailed studies indicate that a pathway by which nonspecific elimination takes place is important.[7,8]

Although the series of labeled methyl cyclohexyl ethers available in this investigation should be quite sufficient to confirm the positions of origin of the elements of methanol, a complication arises as a result of the loss of a fragment, shown by high resolution to be C_2H_5, giving rise to an m/e 85 ion. This causes a

coincidence of the ions formed via the loss of the ethyl radical and methanol in 1d,1e, and1f. This coincidence comes as a result of the combined effects of the differences in spectral shifts due to labeling and either a multiplicity of origins of the m/e 85 ion of 1a or hydrogen scramblings preceding the loss of ethyl.[12] The problem becomes apparent, and a solution is found in the high-resolution spectra of 1d, 1e, and 1f; the m/e 85 peak shifts to produce several peaks whose total intensities are approximately equivalent to the intensity of the m/e 85 ion in 1a. These high-resolution spectra conveniently permit the ratios of oxygen-containing to hydrocarbon ions to be determined. The reduced data are summarized in Tables II and III. The ratios of M − CH_3OH to M − CH_3OD ions are then calculated: 1d, 14.7:1.3, 1e, 4.5:8.6. 1f, 1.7:8.9; 1g, 8.5:3.5. From these ratios it is a simple matter to obtain the sources of hydrogen as percentages from the various ring positions. The results are:

TABLE II

HYDROCARBON IONS IN THE m/e 77–89 REGION OF THE 70-eV MASS SPECTRA OF METHYL CYCLOHEXYL ETHER AND DEUTERATED ANALOGS[a,b]

| Ion	1a	1b	1c	1d	1e	1f	1g
M − 31	1.9		1.8	1.1	1.5	1.6	1.7
M − 32	12.3		13.4	14.7	4.5	1.7	8.5
M − 33	2.6		2.0	3.7	9.7	9.2	3.5
M − 34	0.1	1.5	0.7	1.0	0.9	1.3	0.8
M − 35	0.7	12.2	0.7	0.5	0.6	0.5	0.6
M − 36	0.2	2.4	0.4	0.6	0.7	0.3	0.5
M − 37	0.6	0.2	0.4	0.3	0.4	0.5	0.3
M − 38		1.0	0.2	0.3	0.3	0.4	0.3
M − 39		0.2		0.3	0.3	0.3	0.2
M − 40		0.4		0.1	0.1	0.3	
M − 41						0.1	

[a] All intensities have been corrected for isotopic contaminants and contributions due to natural isotopic abundances. [b] Relative to the base spectral peak.

(12) A. N. H. Yeo, R. G. Cooks, and D. H. Williams, *Chem. Commun.*, 1269 (1968).

TABLE III

OXYGEN-CONTAINING IONS IN THE m/e 84–89 REGION OF
THE 70-eV MASS SPECTRA OF METHYL CYCLOHEXYL
ETHER AND DEUTERATED ANALOGS[a,b]

Ion	1a	1b	1c	1d	1e	1f	1g
M − 29	9.7	9.3	9.3				10.4
M − 30	0.1	0.1	0.6	6.8	0.6		
M − 31				2.1	2.5	2.8	0.3
M − 32				2.3	1.5	1.7	
M − 33				0.4	4.1	4.8	
M − 34						0.2	

[a] All intensities have been corrected for isotopic contaminants and contributions due to natural isotopic abundances. [b] Relative to the base spectral peak.

C-2 and C-6, 8%; C-3 and C-5, 66%; C-4, 23%; C-3, C-4, and C-5, 84%.

The failure of these data to equal 100% by summing the figures of **1d**, **1e**, and **1f** or **1d** and **1g** and the fact that both sums are different are inconsistencies which can be accommodated by the operation of an isotope effect. A value of k_D/k_H of about 0.9 would remove the discrepancies.

The loss of methanol gives rise to hydrocarbon ions at m/e 82 (Scheme III). The spectrum of bicyclo-

SCHEME III
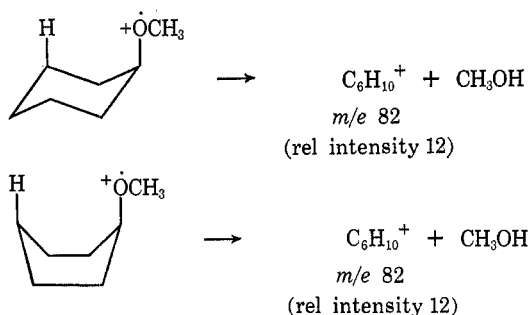
[2.2.0]hexane has been obtained and gives its base peak at m/e 41 and three other principal ions of equal intensity at m/e 67, 54, and 39.[13] Each of these ions is found in the spectrum of **1a** and may in part be attributed to the initial loss of methanol followed by further decompositions.

Turning now to the data on the oxygen-containing ions in the m/e 84–89 region (Table III), it can be seen that the M − 29 ion of **1a** arises from the loss of an ethyl radical. The effects of labeling suggest multiple sources of this ion. Hydrogens from C-2 and C-4 account for one, two, three, or four of the ethyl group's hydrogens, a similar number comes from C-3 and C-5, and some hydrogen has its origin at C-1 and C-4. Simple schemes by which an ethyl group is lost as a combination of C-2 and C-3, their hydrogens, and a hydrogen from either C-5 or C-6 are shown in Scheme I. However, the loss of ethyl fragments which involve hydrogens from four or more carbons is difficultly formulated. The implication to be drawn from such a variety of ion sources is that a prior hydrogen randomization is operative.[12]

Of the principal ions in the spectrum of **1a** not yet discussed, those shown by high resolution to be hydrocarbon ions are found at m/e 55 ($C_4H_7{}^+$), 54 ($C_4H_6{}^+$), 53 ($C_4H_5{}^+$), 41 ($C_3H_5{}^+$), and 39 ($C_3H_3{}^+$). The m/e 43 peak is a doublet with equal contributions

from the ions $C_3H_7{}^+$ and $C_2H_3O{}^+$. The ion at m/e 45 contains oxygen and its formula is $C_2H_5O{}^+$.

The sources of the hydrocarbon ions are obscured by congestion in the spectra of the labeled compounds in these regions. The m/e 54, 41, and 39 ions were observed in the spectrum of bicyclo[2.2.0]hexane,[18] and a portion of these ions may arise *via* the initial loss of methanol from **1a** to give an m/e 82 ion similar to the parent ion of this hydrocarbon. Very little more can be said with certainty concerning the specific sources of these hydrocarbon ions.

On the other hand, the $C_2H_5O{}^+$ ion at m/e 45 is clearly formed from the methoxyl group, most if not all of the hydrogen from C-1, and a hydrogen, or hydrogens, from C-2, C-3, C-5, or C-6. Rationale for the formation of this ion consistent with the effects of labeling are presented in Scheme I.

The lack of similarity between the spectrum of **1a** and the spectra of acyclic methyl ethers generally can be seen to arise from the decompositions involving hydrogen abstractions and bond migrations which could be achieved only through intermolecular reactions for compounds lacking a ring. In contrast, then, the similarity between the decomposition modes of **1a** and those of cyclohexyl alcohol is expected on the basis of the structural similarity of oxygen attached to a six-membered ring.

It is, however, a subtle difference, caused by the ring, in one of the decomposition modes common to acyclic and cyclic ethers, alcohols, halides, and analogous compounds which may be the most practically significant aspect to be derived from an understanding of these spectra. This feature is the elimination of HOR from ethers, HOH from alcohols, HX from halides, and corresponding elements from other classes of compounds. For cyclic compounds the geometric restrictions of the ring dictate that only the *cis* hydrogens on, for example, C-3, C-4, and C-5 of **1a** or cyclohexyl alcohol can participate in this decomposition while the rings are intact. Confirmation of the *cis* geometry in the elimination of water from derivatives of cyclohexyl alcohol has been offered in the study of the mass spectra of *cis*- and *trans*-1,4-dideuteriocyclohexane-1,4-diol and other cyclic and bicyclic alcohols.[5] A further confirmation of the stereospecificity of this elimination has been obtained in studies of labeled 3-hydroxy steroids.[14] However, evidence recently offered indicates that the stereospecificity of electron impact induced 1,3 and 1,4 elimination of water from cyclohexyl alcohol is low, while the corresponding elimination of hydrogen chloride from cyclohexyl chloride is high.[7,8] The interpretation given for these results is that the water loss from cyclohexyl alcohol involves a competing mechanism through which the ring hydrogens become equivalent, probably through β cleavage of the ring.

It is our intention to examine carefully the stereochemistry of the eliminations of methyl alcohol from **1a**, since such decompositions offer unique and practical methods for determining the stereospecificities of deuteride reductions of tosylates and halides, deuteriolyses of alkyl lithiums and Grignards, and any other deuterium-incorporation reactions of cyclic systems which

(13) R. Srinivasan, *J. Amer. Chem. Soc.*, **83**, 4923 (1961).

(14) J. Karliner, H. Budzikiewicz, and C. Djerassi, *J. Org. Chem.*, **31**, 710 (1966).

are not prohibited by the presence of the methoxyl function in a remote position. We have an interest in stereospecifically labeled ring compounds,[9] but, without an effective, practical means of analysis, the interpretation of the results could be rendered meaningless. The results of our further study of the electron impact induced elimination of methyl alcohol from 1a and the application of this masss pectrometric decomposition to the measurement of stereospecificities of deuterium incorporations will be published shortly.

Experimental Section[15]

Trideuteriomethoxycyclohexane (1b).—To a mixture of 100 ml of dry ether and 1.7 g (41 mmol) of a 58% sodium hydride-mineral oil dispersion was added 4.0 g (40 mmol) of cyclohexanol in 25 ml of dry ether. The mixture was stirred at reflux for 24 hr, after which 6.0 g (41 mmol) of trideuteriomethyl iodide in 50 ml of dry ether was added. This mixture was stirred at reflux for 24 hr before the addition of sufficient water to give two homogeneous layers. The ether layer was separated and the aqueous layer was extracted with two portions of ether. The combined ether extracts were washed with water and saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Most of the ether was removed by distillation through a 100 cm × 10 mm Vigreux column, and *ca.* 6 ml of an ether solution containing 1b and mineral oil remained.

Pure samples of the ether were obtained by preparative vpc using a 25 ft × 3/8 in. 20% Carbowax 20M on 60–80 mesh Chromosorb W column at 90°. Mass-spectrometric analysis showed 0.0% d_0, 1.8% d_1, and 2.6% d_2 compounds as contaminants.

Methoxycyclohexane-1-d_1 (1c).—Into a flask containing 0.6 g (14 mmol) of lithium aluminum deuteride was distilled, from lithium aluminum hydride, 100 ml of ether. To this stirred suspension was added, dropwise, 4.9 g (50 mmol) of cyclohexanone in 25 ml of freshly dried ether. Following the addition, the mixture was stirred at reflux for several hours before sufficient water was added to destroy the excess deuteride, hydrolyze the salt, and convert the inorganic salts into a form which settled rapidly on cessation of stirring. The ether solution was decanted from the salts, the salts were washed with additional portions of dry ether, the washings were combined, and the major portion of the ether was removed by distillation through a Vigreux column.

The above solution was treated in a similar fashion to that described for 1b, except that methyl iodide was used in place of the labeled material. A solution of 1c obtained in this manner was purified in the same fashion used for 1b.

Mass spectrometric analysis showed less than 0.5% d_0 compound as a contaminant.

Methoxycyclohexane-2,2,6,6-d_4 (1d).—A mixture of 40 g (410 mmol) of cyclohexanone, 100 g (4.99 mol) of 99.8% deuterium oxide, and 1.0 g of freshly fused, anhydrous potassium carbonate was heated to reflux. After a short period, distillation through a short Vigreux column was begun and continued until two fractions consisting of all the volatile material had been collected. The initial distillate, *ca.* 90 ml, was extracted with two portions of purified pentane and kept for the initial exchange with cyclohexanone in future runs. The second fraction was added to an equal volume of purified pentane, combined with the pentane washings of the initial distillate, dried over anhydrous magnesium sulfate, and distilled through a Vigreux column. This procedure was repeated until mass-spectrometric analysis showed 98.5 or greater atom % deuterium in the cyclohexanone.

The reduction of cyclohexanone-2,2,6,6-d_4 by lithium aluminum hydride was carried out as in the deuteride reduction of cyclohexanone. The resulting alcohol was converted into the methyl ether and purified as described above.

Mass spectrometric analysis showed 0.0% d_0, 0.0% d_1, 0.6% d_2, and 4.2% d_3 compounds as contaminants.

Methoxycyclohexane-3,3,5,5-d_4 (1e).—A mixture of 186 g (1.50 mol) of *p*-methoxyphenol, 250 ml of methanol, and 7.5 g of 5% rhodium-on-alumina catalyst was placed in a 500-ml Pyrex

container of a Parr shaker and subjected to 3-atm hydrogen pressure until no further uptake of gas was observed. The methanol was removed on a rotary evaporator and a mixture of *cis*- and *trans*-4-methoxycyclohexanol was isolated by distillation, giving 182 g (1.40 mol, 93%), bp 110–120° (25 mm).

A solution of 155 g (1.19 mol) of 4-methoxycyclohexanol in 300 ml of acetone was cooled and held below 10° while Jones reagent,[16] a solution made from 100 g (1.00 mol) of chromium trioxide, 300 ml of water, and 85 ml of sulfuric acid, was added, dropwise, over a period of 2 hr. The organic layer was separated and dried over anhydrous potassium carbonate, and the acetone was removed on the rotary evaporator. Distillation of the residue gave 121 g (945 mmol, 79%) of 4-methoxycyclohexanone, bp 91–95° (15 mm). The product obtained from this treatment shows no unreacted alcohol by vpc analysis. This procedure represents a marked improvement over the previously reported technique of oxidation with potassium dichromate in aqueous sulfuric acid,[17] which in our hands always produced lower yields of ketone contaminated with alcohol.

The exchange of 4-methoxycyclohexanone with deuterium oxide was carried out in very much the same manner described for cyclohexanone. A complication arose as a result of the tendency of this ketone to form an azeotrope with water. This problem was largely overcome by recycling the spent deuterium oxide and/or extraction of the aqueous forerun with pentane.

The lithium aluminum hydride reduction of 4-methoxycyclohexanone-2,2,6,6-d_4 was carried out in a manner directly analogous with that described for the lithium aluminum deuteride reduction of cyclohexanone. The product was not distilled, but used directly in the formation of 4-methoxycyclohexyl-2,2,6,6-d_4 *p*-toluenesulfonate.

To a solution of 13.4 g (100 mmol) of 4-methoxycyclohexanol-2,2,6,6-d_4 in 250 ml of dry pyridine was added 21.0 g (110 mmol) of *p*-toluenesulfonyl chloride. The resulting solution was allowed to stand at room temperature overnight before being poured over cracked ice and water. The crude product was taken up in ether, washed with 10% hydrochloric acid, saturated sodium bicarbonate solution, and saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The ether was removed on the rotary evaporator, and 21.9 g (79.5 mmol, 80%) of 4-methoxycyclohexyl-2,2,6,6-d_4 *p*-toluenesulfonate was obtained as a crude solid. Recrystallization from hexane gave material of mp 80–81°, between the literature values for the pure *cis*- and *trans*-4-methoxycyclohexyl *p*-toluenesulfonates.[18]

To 1.9 g (50 mmol) of lithium aluminum hydride in 100 ml of dry tetrahydrofuran was added 7.1 g (25 mmol) of 4-methoxycyclohexyl-2,2,6,6-d_4 *p*-toluenesulfonate. The mixture was stirred at reflux for 12 hr, after which sufficient water was added to destroy the excess lithium aluminum hydride and convert the inorganic salts into a form which settled rapidly on cessation of stirring. The THF solution was decanted from the salts and diluted with an equal volume of pentane. The salts were washed with pentane and combined with the THF–pentane solution. The resulting solution was dried over anhydrous magnesium sulfate and the bulk of the THF and pentane was removed by distillation through a 100 cm × 10 mm Vigreux column. The residue, 2.7 g of liquid, was shown by vpc analysis to consist of a 3:1 mixture of methoxycyclohexane-3,3,5,5-d_4 and 4-methoxycyclohexene-2,6,6-d_3 and solvent. The yield of methoxycyclohexane-3,3,5,5-d_4 was calculated to be 1.2 g (10 mmol, 40%). Purification was by vpc as previously described.

Mass spectrometric analysis showed 0.0% d_0, 0.0% d_1, 0.6% d_2, and 6.4% d_3 compounds as contaminants.

Methoxycyclohexane-3,3,4,4,5,5-d_6 (1f).—The lithium aluminum deuteride reduction of 4-methoxycyclohexanone-2,2,6,6-d_4 was carried out as described for the lithium aluminum hydride reduction. Procedures similar to those for 1e were followed for the preparation of 4-methoxycyclohexyl-3,3,4,5,5-d_5 *p*-toluenesulfonate and the reduction of the tosylate to give 1f.

Mass spectrometric analysis showed 0.0% d_0, 0.0% d_1, 0.0% d_2, 0.6% d_3, 1.2% d_4, and 9.6% d_5 compounds as contaminants.

Methoxycyclohexane-4,4-d_2 (1g).—The lithium aluminum deuteride reduction of 4-methoxycyclohexanone to give *cis*- and *trans*-4-methoxycyclohexanol-1-d_1 was carried out as described for the lithium aluminum hydride reduction of 4-methoxycyclo-

(15) Low-resolution mass spectra were measured with a CEC Model 21-103 mass spectrometer. High-resolution mass spectra were measured with a Varian MAT Model CH5 mass spectrometer.

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hexanone-2,2,6,6-d_4. Both the preparation of the *p*-toluenesulfonate ester and lithium aluminum deuteride reduction of the ester were accomplished as described above for **1e**.

Mass-spectrometric analysis showed 0.5% d_0 and 3.7% d_1 compounds as contaminants.

Registry No.—**1a**, 931-56-6; **1b**, 14069-88-6; **1c**, 22187-97-9; **1d**, 22187-98-0; **1e**, 22187-99-1; **1f**, 22188-00-7; **1g**, 22188-01-8; *cis*-4-methoxycyclohexa-

nol, 22188-02-9; *trans*-4-methoxycyclohexanol, 22188-03-0.

Thermal Rearrangement of *o*-Methyldiaryl Ethers

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o-Methyldiaryl ethers have been found to rearrange to *o*-benzylphenols at elevated temperatures. For example, 2,6-dimethylphenyl phenyl ether (**1**) cleanly rearranges at 370° under vacuum to 2-benzyl-6-methylphenol (**2**) with 4-methylxanthene (**3**) as a minor side product. The reaction may have general synthetic utility for the production of *o*-benzylphenols. These *o*-benzylphenols appear to be formed by an intramolecular free-radical reaction in which the benzyl methylene group occupies the aryl position originally attached to oxygen. The formation of both *o*-benzylphenols and xanthenes was catalyzed by oxidizing agents such as sulfur. A chain mechanism is proposed for this rearrangement reaction.

The ether linkage of aryl ethers is considered one of the more stable chemical bonds. Phenyl ether is unaffected by hydrogen iodide at 250°[1] and only slowly attacked by sodium hydroxide at 300°.[2] Effective cleavage of the ether bond requires such vigorous reagents as alkali metals in refluxing pyridine[3] or sodium in liquid ammonia.[4] In fact, the extreme stability of phenyl ethers has made them important heat-exchange fluids and high-temperature lubricants.[5]

Recent studies[6-9] indicate that this thermal stability is also characteristic of poly(2,6-dimethyl-1,4-phenylene ether). However, at very high temperatures (>400°), poly(2,6-dimethyl-1,4-phenylene ether) undergoes an exothermic decomposition.[6] In the course of studying this decomposition, changes in the nuclear magnetic resonance spectrum were observed that suggested the formation of diphenyl methylene groups. Since structural characterization of high polymers is notoriously difficult, model compounds were studied.

The model compound initially chosen was 2,6-dimethylphenyl phenyl ether (**1**). When **1** was heated at 370° for 23 hr, changes in the nmr spectrum similar to those observed with polymer occurred. The two products detected by vapor phase chromatography were identified as 2-benzyl-6-methylphenol (**2**) and 4-methylxanthene (**3**) (eq 1). Further investigation

was warranted, since the migration of a phenyl group from oxygen to a saturated carbon had not previously been reported and the study of rearrangement reactions has often been significant in revealing new mechanistic paths.

Results

A series of aryl ethers have been examined to determine the scope of the rearrangement and to obtain information about the mechanism of the reaction. Table I shows the results obtained with six of the aryl ethers that have been examined. This reaction appears to be in a unique class, since prolonged reactions at high temperatures usually produce such a myriad of products that they have no synthetic utility. However, in these cases, the reaction mixture consisted of only three components: starting material, the corresponding phenol from rearrangement, and the xanthene.

The structures of the *o*-benzylphenols reported in Table I were confirmed by infrared, ultraviolet, and nuclear magnetic resonance spectroscopy. These compounds show a characteristic band at 3520–3540 cm^{-1} in their infrared spectra due to a π-bonded phenolic OH, and, except for the major product from **7**, an nmr peak at τ 6.2–6.4 (diaryl methane group). The 2-diphenylmethyl-6-methylphenol (**14**) derived from **7** showed an nmr peak at τ 4.4 (triarylmethyl proton). The products from **5**, **6**, **7**, and **8** are new compounds and their structures were confirmed by comparison with authentic compounds synthesized by alkylation of the appropriate phenols with benzyl chlorides.

1

$$(1)$$

2   3
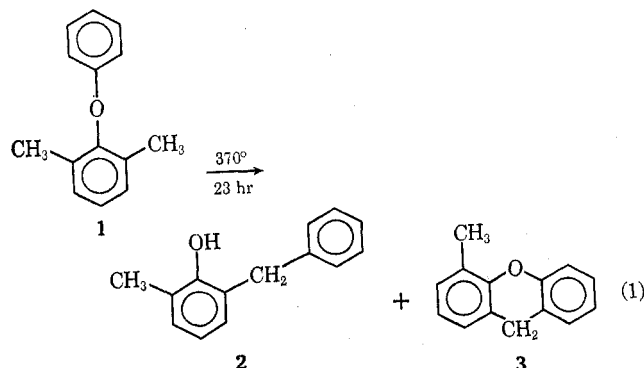
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