(65) For further discussion pro and con the occurrence of bridged radicals see (a) P. S. Skell, R. D. Woodworth, and J. H. McNamara, *J. Amer. Chem. Soc.*, **79**, 1253 (1957); (b) P. I. Abell and L. H. Piette, *ibid.*, **84**, 916 (1962); (c) N. P. Neureiter and F. G. Bordwell, *ibid.*, **82**, 5354 (1960); (d) B. A. Bohm and P. I. Abell, *Chem. Rev.*, **62**, 599 (1962). (e) L. Kaplan, "Bridged Free Radicals," Marcel Dekker, New York, N. Y., 1972, p 305.

(66) H. Kwart and E. R. Evans, *J. Org. Chem.*, **31**, 410 (1966).

(67) R. Adams and R. E. Rindfusz, *J. Amer. Chem. Soc.*, **41**, 648 (1919).

(68) The sole basis for assigning the trans configuration to this compound was that it represented the predominant isomer; the trans would be expected to be favored sterically over the cis owing to lesser steric interactions of the methyl groups.

(69) The absorption of the protons in CH_3Cl occurs at 3.05 ppm. The absorption of protons in CH_3Br occurs at 2.68 ppm: J. Dyer, "Applications of Adsorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 75.

(70) (a) Trichloromethyl and *o*-thioanisole are considered the "large" groups. (b) The major component of the mixture was designated as the threo diastereoisomer based on the coupling constant for the methine protons (2.8 Hz). In the case where the spatial requirements of "large" and "small" groups are very different, the coupling constant for methine protons is greater than 10 Hz in the erythro isomer and less than 5 Hz in the threo isomer: C. A. Kingsbury and W. B. Thornton, *J. Org. Chem.*, **31**, 1000 (1966); L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, pp 163, 291-292. (c) This nmr was determined from the nmr of the mixture by cancelling the contribution made by *erythro*-**29**.

(71) N. Kharasch and M. M. Weld, *Anal. Chem.*, **27**, 966 (1955).

A Stereochemical Approach toward the Structure of Gas-Phase Ions[1a]

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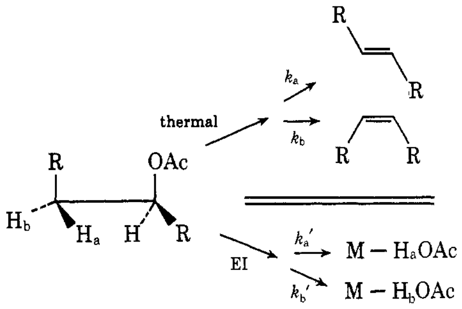
The stereoselectivities for hydrogen abstraction in the electron impact induced loss of acetic acid from three 1,2-disubstituted ethyl acetates as well as the loss of water from three acyclic secondary alcohols have been determined. This information was sought in an attempt to (1) help define the general limits for conformational analysis in the study of gas-phase ions and (2) determine the structural relationships, fundamental to conformation, among the various gas-phase ions and accessible phase molecules studied. In each case, *i.e.*, elimination of acetic acid and loss of water, the results are stereochemically comparable to the analogous thermal reactions, *i.e.*, formation of olefins from the pyrolysis of the subject acetates and 1,4-hydrogen abstraction by the alkoxy radicals derived from the alcohols studied. The overall results may be seen as a stereochemical extension of the historical structure-reactivity approach to ion structure in inaccessible gas-phase molecular radical cations. The success of these stereochemical experiments, along with the results of others in related studies, clearly recommends this type of approach to the elucidation of the nonbonded features of gas-phase ion structure unavailable by present methodology.

The molecular radical cations produced by electron impact and studied in mass spectrometers are now recognized as effective models for understanding the behavior of numerous intermediates in condensed phase.[2] The study of such condensed-phase intermediates is one of the central themes of modern organic chemical research and therefore work on the structure of their mass spectral potential counterparts is important. While interest in such questions in gaseous ion chemistry has led to various methods for structure correlation and elucidation,[3] there is a continuing need for information on the relationship between accessible molecules subject to conventional probes and those encountered in mass spectrometry. In the present work we have chosen two different electron impact induced hydrogen abstracting elimination reactions which appear superficially analogous to certain thermal reactions. For each of these reactions we have compared the stereochemical prerequisites in the transition state of hydrogen abstraction (*i.e.*, thermal *vs.* electron impact) by determining the relative transfer of competitive diastereotopic hydrogens. For both electron-impact reactions the stereochemical course measured in this way is exactly parallel to the compared thermal reactions. These results strongly suggest that the compared reacting molecules are closely corresponding in structure.

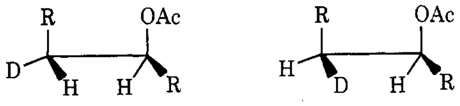
Electron Impact Induced Elimination of Acetic Acid. Earlier work on the electron impact induced (EI) elimination of acetic acid from acetates[4] showed, in analogy to the situation in pyrolysis,[5] that hydrogen is abstracted primarily from the β carbon. Since the detailed stereochemistry of the pyrolysis is known,[5,6] the corresponding sets of β-eliminations suggest looking at the mass spectral counterpart stereochemically to determine the depth of analogy (Scheme I).

Scheme I



As outlined in Scheme I, our objective is the kinetic discrimination between the diastereotopic hydrogens,[7,8] H_a and H_b. This necessitates preparation of the deuterated diastereomers of the subject acetates (Scheme II).

Scheme II



1, R = CH_3 **2**, R = CH_3
3, R = C_6H_5 **4**, R = C_6H_5
5, R = α-naphthyl **6**, R = α-naphthyl

While the labeled acetates **1-4** were prepared following the literature,[6] **5** and **6** were both synthesized from *trans*-1,2-di-α-naphthylethene *via* lithium aluminum deuteride opening of the epoxide and deuterioboration, respectively.[9]

Table I exhibits the mass spectral data for loss of acetic acid from these deuterated materials.

Table I[a,b]

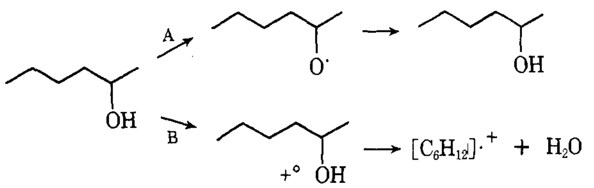
Compd		70 eV (50°)	15 eV (50°)	15 eV (135°)
$CH_3CHDCHCH_3OAc$	**1**	16/84	18/82	24/76
	2	25/75	27/73	32/68
PhCHDCHPhOAc	**3**	24/76	24/76	32/68
	4	49/51	50/50	48/52
αNpCHDCHαNpOAc[c]	**5**			21/79
	6			40/60

[a] The spectra were taken on an MS-902 mass spectrometer (8 kV accelerating voltage) fitted with a cooled inlet system to control the temperature. Some of the runs (135°) were made on a CEC-103 as well and the results were almost identical. **1** and **2** were introduced by heated inlet lines and **3** through **6** *via* direct inlet. [b] The numbers represent averages of numerous determinations (at least ten). In each case the reproducibility (precision) was less than ±1 intensity unit (*e.g.*, 16 ± 1/84 ± 1) over these many determinations and in no case was there a crossover or overlap of the ratios for compared diastereomers. All voltages are nominal and 15 eV was close to threshold for the loss of acetic acid. [c] **5** and **6** were were too involatile to be measured at 50°.

Since both M − DOAc and M − HOAc derive by unimolecular competitive fragmentation from a common parent ion, their ion intensities are related as the ratio of the relative rates of their formation.[10] This fact demands the following relationships (refer to Schemes I and II). In series **1**, **3**, and **5** (M − DOAc)/(M − HOAc) equals $Ik_b/(k_a + k_i)$ where $I = k_H/k_D$ and k_i = loss of HOAc from other positions than the β carbon. Likewise, in series **2**, **4**, and **6**, this ratio is $Ik_a/(k_b + k_i)$. In the absence of k_i (phenyl and α-naphthyl series)[11] (M − DOAc)/(M − HOAc) equals Ik_b/k_a in **3** and **5** and Ik_a/k_b in **4** and **6** and thus simple arithmetic yields k_a/k_b and I for each series.[12] In the *sec*-butyl system the presence of abstraction from the methyl groups (k_i, see above) leaves two choices for obtaining the requisite numbers. The ratio of ion intensities (M − DOAc)/(M − DOAc + M − HOAc) equals $Ik_b/(Ik_b + k_a + k_i)$ in **1** and $Ik_a/(Ik_a + k_b + k_i)$ in **2**. If the isotope effect were one or nearly one, these ratios would reduce to $k_b/(k_a + k_b + k_i)$ and $k_a/(k_a + k_b + k_i)$ and thus simple division would yield k_a/k_b. The upper line under R = CH_3 in Table II was calculated in this manner assuming (see below) that $k_H/k_D = 1$.

An alternative procedure would be to measure the ion intensities for M − DOAc in **1** and **2** on the same scale (*i.e.*, from the same number of molecular ions), thereby obtaining (M − DOAc) (**1**)/(M − DOAc) (**2**), which is Ik_b/Ik_a or k_b/k_a. As well, (M − DOAc) (**1**) − (M − DOAc) (**2**) is $Ik_b - Ik_a$ or $I(k_b - k_a)$ and (M − HOAc) (**1**) − (M − HOAc) (**2**) is $(k_a + k_i) - (k_b + k_i)$ or $k_a - k_b$. In this way k_H/k_D may be obtained as well. In the *sec*-butyl series **1** and **2** the ion intensities of higher *m/e* than the acetic acid loss are related by an essentially constant factor (that is, these ions are formed independent of the stereochemical differences) and this factor could be used to correct for the relative intensity between the spectra of the two diastereomers. The results of these calculations also appear in Table II and independently demonstrated the k_H/k_D of nearly one for this reaction.

Scheme III[a]



[a] Step A may be effected by various reagents and lead to various final products,[17] while step B follows from electron impact at energies above the ionization potential.

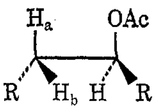
The data in Table II demonstrate that there is a substantial stereochemical dependence for loss of the β hydrogen in forming acetic acid in all three systems. In detail, the stereoselectivity increases steadily from methyl to phenyl to α-naphthyl as does the isotope effect (k_H/k_D). The consistent preference for H_a ($k_a > k_b$) is in line with pyrolytic expectations for an anti relationship for the R groups during the elimination and subsequent production of trans olefin in the thermal reactions.[5,6]

The only reasonable interpretation for such a twofold correspondence between the electron-impact loss of acetic acid and the pyrolytic reaction (*i.e.*, $k_a > k_b$ and the stereoselectivity increasing as $CH_3 < C_6H_5 <$ α-naphthyl) is that the structures of the reacting molecular ions are constitutionally equivalent to those of their neutral precursors (*i.e.*, unrearranged and substantially undistorted) and further that the factors upon which the conformational requirements of the pyrolysis[5,6] depend are the same as in the subject molecular ions. As well, the increase in k_H/k_D going from methyl to the larger groups is consistent with recent predictions[13] of the relationship of restricted degrees of freedom in the transition state to the isotope effects observed in electron-impact fragmentations.[14]

Electron Impact Induced Elimination of Water from Alcohols. The electron impact induced elimination of water from noncyclic aliphatic alcohols is highly regioselective for 1,4-hydrogen (six-membered ring) abstraction.[15,16] The intramolecular hydrogen abstractions observed in alkoxy radicals[17] in similar molecules is regioanalogous to this EI loss of water described above (Scheme III).

Such an apparently superficial correspondence of abstraction site makes these reactions (Scheme III) likely

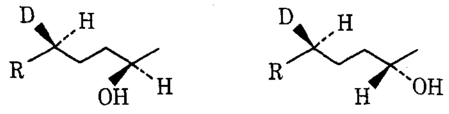
Table II[a,b]



R (registry no.)	k_a/k_b (k_H/k_D) 70 (eV (50°)	15 eV (50°)	15 eV (135°)
CH_3[c] (105-46-4)	1.6 ± 0.1 (1.0) 1.6 ± 0.15 (1.2 ± 0.2)	1.5 ± 0.1 (1.0) 1.4 ± 0.05 (0.8 ± 0.3)	1.2 ± 0.1 (1.0)
C_6H_5 (24295-35-0)	1.7 ± 0.1 (1.8 ± 0.1)	1.8 ± 0.1 (1.8 ± 0.1)	1.4 ± 0.1 (1.5 ± 0.1)
α-Naphthyl (51271-18-2)			1.6 ± 0.1 (2.4 ± 0.3)

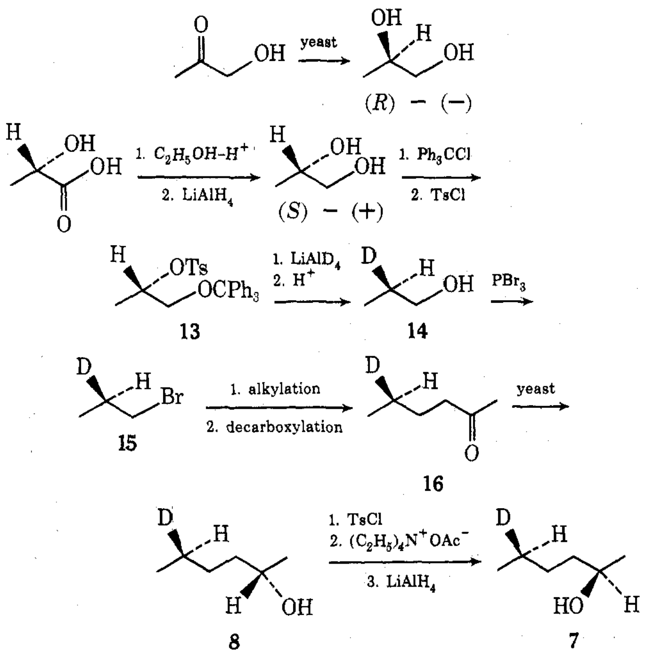
[a] Calculated from data in Table I. [b] Estimated accuracy (±) based on uncertainty in making measurements of ion intensities. The precision of the measurements was better than this. See Table I, footnote *b*. [c] Upper line calculated assuming k_H/k_D 1.0; lower line by comparing spectra of diastereomers on same scale as discussed in text.

Scheme IV



7, R = CH_3 8, R = CH_3
9, R = cyclohexyl 10, R = cyclohexyl
11, R = phenyl 12, R = phenyl

Scheme V[a]



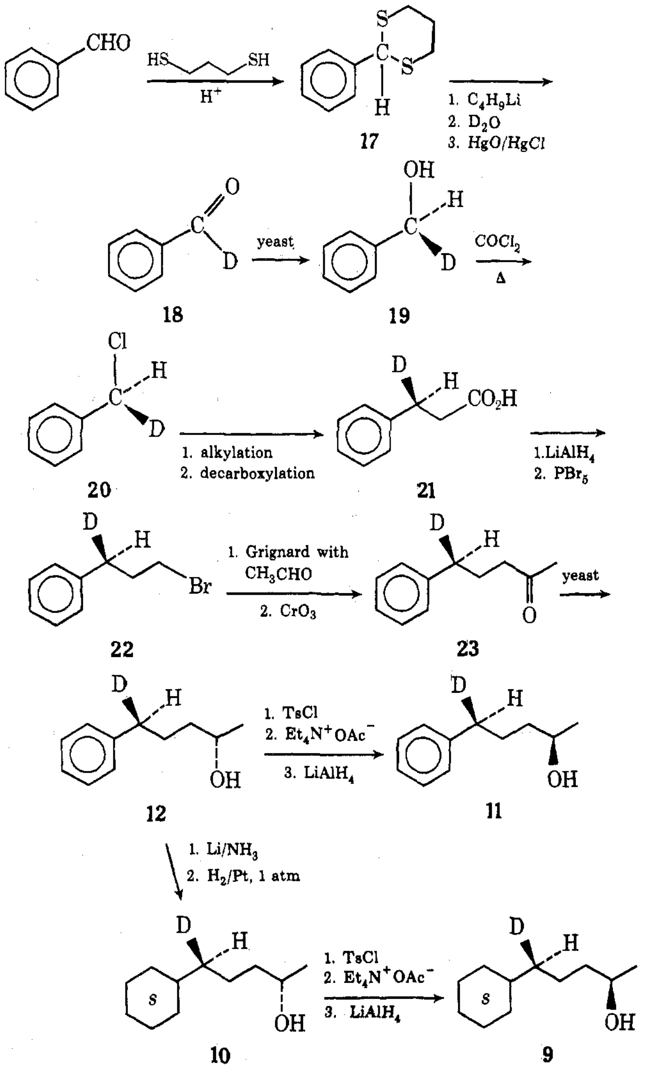
[a] Reference 9.

candidates for a comparison of the stereochemistry of the abstraction step and thereby for comparison of the conformational and structural parameters attendant to these steps. Since, in contrast to the acetates, the detailed stereochemistry of the accessible phase reactions is not known, we carried out both investigations in the present work. The structures appearing in Scheme IV constitute the molecular prerequisites chosen for such a comparative endeavor. The necessary synthetic work appears in Schemes V and VI. Scheme VII outlines the sought kinetic parameters.

We have subjected the molecules in Scheme IV to electron bombardment and, as well, reaction with two reagents, lead tetraacetate and silver oxide–bromine, known to give rise to tetrahydrofuran formation *via* 1,4-hydrogen abstraction. In the EI fragmentation the relative loss of water and deuterated water were measured at 70 eV and *ca.* 100°, while in the accessible phase reactions the relative production of deuterated and undeuterated tetrahydrofuran derivatives was determined. These data are compiled in Table III.

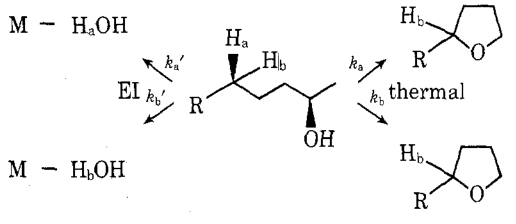
In the formation of the tetrahydrofurans, application of the exact analysis used for the 1,2-diphenyl and 1,2-di-α-napthyl ethyl acetates (see above) will serve to yield both k_a/k_b and k_H/k_D. This is so since the products exclude the intervention of a k_i term just as isolation of the olefins in Curtin's work did.[6] It is likely in the EI loss of water that abstraction is not regiospecific from C-4, and therefore one must evaluate the k_i term or alternatively know k_H/k_D. In numerous studies on closely related molecules it has been shown that the isotope effects for loss of H_2O, and HCl as well, are close to unity.[16] We have made this assumption in the present work in order to obtain k_a'/k_b'.

Scheme VI[a]



[a] Reference 9.

Scheme VII

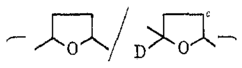
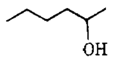
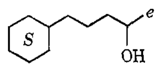
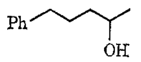


For example, in 7 and 8 for the 2-hexanol EI elimination of water, the rate ratio (k_a'/k_b') is

$$\frac{k_a'/(k_a' + k_b' + k_i)}{k_b'/(k_b' + k_a' + k_i)} = \frac{(M - DOH)/(M - DOH + M - HOH)\ (\text{all for } 7)}{(M - DOH)/(M - DOH + M - HOH)\ (\text{all for } 8)}$$

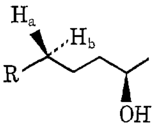
In the 5-cyclohexyl-2-pentanol diastereomers, 9 and 10, we were able to check our calculations and independently determine the isotope effect since measurement of 5,5-dideuterio-5-cyclohexyl-2-pentanol (24)[9] gave a minimum value of 51% 1,4 abstraction, and thus for this system k_i is at most 49% of $k_a' + k_b'$. Correction for k_i gave values of k_a'/k_b' within experimental error of the values obtained assuming $k_H/k_D = 1$. As well, calculated values of k_H/k_D of nearly 1 were obtained after correction for k_i, confirm-

Table III[a]

		70 eV[b] M − DOH/ M − HOH	 Pb(OAc)$_4$	Ag$_2$O/Br$_2$
	**7**	43/57	21/79	20/80[d]
	8	39/61	15/85	15/85[d]
	**9**	25/75	26/74	27/73
	10	21/79	16/84	18/82
	**11**	31/69	23/77	25/75
	12	31/69	14/86	16/84

[a] The numbers are the average of numerous determinations for different experiments carried out over many months. The deviation is ±0.5 absolute. [b] The EI results were obtained on an MS-902 mass spectrometer at *ca.* 100° and 8 kV accelerating voltage. In the case of **7** and **8** the enantiomers were available and gave, as required by symmetry, the same results. In both series (**7**, **8**; **9**, **10**) the results near threshold voltage showed reduced but still real differences between the diastereomers with loss of DOH favored **7** and **9**. These data suggest a scrambling mechanism. See I. Howe and F. W. McLafferty, *J. Amer. Chem. Soc.*, **92**, 3797 (1970). [c] In each case the cis and trans 2,5-substituted tetrahydrofurans were separated by vpc. The deuterium incorporation was independent of the stereochemistry of the tetrahydrofuran. [d] Carried out heterogeneously in hydrocarbon solvent at 25°. All other experiments on Pb(OAc)$_4$ and Ag$_2$O/Br$_2$ were carried out similarly except at 81°. [e] Determinations of the M − DOH/M − HOH ratios as a function of temperature showed a steady increase with decreased temperature. This observation, corresponding to increased values of k_a/k_b (Scheme VII) with decreasing temperature, is in line with the thermal behavior of the electron-impacted acetates.[14]

Table IV[a]



R (registry no.)	k_a/k_b (k_H/k_D) M − H$_2$O 70 eV[b]	Pb(OAc)$_4$[d]	Ag$_2$O/Br$_2$[d]
Methyl (626-93-7)	1.10 (1.0)	1.23 (4.60)	1.19 (4.75)
Cyclohexyl (43142-30-9)	1.19 (1.0) 1.21 (1.2)[c]	1.32 (3.84)	1.29 (3.55)
Phenyl (2344-71-0)	1.00	1.35 (4.47)	1.32 (3.95)

[a] See footnotes to Table III. [b] Accuracy ±0.03 with precision ±0.01. [c] Obtained by independently determining k_1 (see text). Accuracy for this k_H/k_D is ±0.3. [d] Accuracy for stereoselectivity ±0.03; isotope effect ±0.5. In all cases the precision or reproducibility of the measurements is much higher.

ing our original supposition and in line with the literature.[15,16]

Inspection of the results of these calculations (Table IV) shows first that the hydrogen abstraction is stereosensitive in all cases except the EI loss of water from 5-phenyl-2-pentanol. In the latter case we have measured 5-phenyl-2-pentanol-*O-d* at 70 eV and found that H_2O and DHO are eliminated equally. At lower voltages the H_2O loss exceeds DHO loss by 1.35/1 as expected for the longer lifetime ions. Such goings on, since the C-4 hydrogens are likely involved, would stereochemically scramble the label and preclude measurement of the stereoselectivity. The lowered stereoselectivities (k_a/k_b) at threshold voltages observed for 2-hexanol and 5-cyclohexyl-2-pentanol (Table III, footnote *b*) suggest that these k_a/k_b ratios are minimum values.

The accessible phase hydrogen abstraction steps for the alkoxy radicals produced by lead tetraacetate and silver oxide–bromine are stereoidentical (Table IV). All six reactions show preference for H_a over H_b and also the isotope effects are comparable and in line with expectations from the photochemical hydrogen abstraction of ketones and the intermolecular transfers in *tert*-butoxy radicals.[18] Moreover, the stereoselectivities are sensible for the relative known steric requirements of methyl, cyclohexyl, and phenyl groups in six-membered rings,[19] and by inspection of models for various possible transfer-step geometries. Without unnecessary (for our present purpose) comment on the molecular disposition during the hydrogen transfer step, we may see that whatever may be inferred,[20] the data (Table IV) for the *thermal reactions necessitate a consistent mechanism*.[21] This conclusion requires for the two thermal reactions that the structure of the alkoxy radical and hydrocarbon chain are unrearranged and that all of those parameters of molecular geometry attendant to conformational analysis be consistently applied in the various thermal reactions. There is no reason why the latter statement should not be identically applied to the comparison of stereoselectivity between the thermal reactions and the electron-impact eliminations of water. Here as well (EI results, Table IV) the H_a diastereotopic hydrogen *is abstracted preferentially over* H_b and also this preference is greater for cyclohexyl over methyl. We have further determined the stereoselectivity (k_a/k_b), Scheme VII (Cl for OH), for 2-hexyl chloride (EI loss of HCl). This elimination from alkyl chlorides has been proposed to occur by a stereoanalogous mechanism to water loss from alcohols when involving 1,4-hydrogen abstraction.[16] In corroboration of this hypothesis and also extending and confirming the correspondence between EI and thermal 1,4-hydrogen abstractions in 2-hexyl-X (X = O·, OH·$^+$, Cl·$^+$)[22] we find a value of 1.28 at 70 eV (8 kV accelerating voltage) and *ca.* 100° on the MS-902 mass spectrometer.

With regard to the lack of quantitative equivalence among the thermal and EI stereoselectivities and isotope effects, there is no reason to expect exact correspondence of rate constants, since the rate expressions, as a function of energy and temperature, are entirely different for an array of molecules in thermal equilibrium[23] [Pb(OAc)$_4$ and Ag_2O/Br_2 reactions] and single isolated molecules (EI loss of H_2O or HCl).[24] Indeed, just as the values of k_H/k_D for the thermal reactions are within reason for such hydrogen abstractions,[18] so the hydrogen *vs.* deuterium discrimination for EI loss of water in 2-hexanol and 2-cyclohexyl-5-pentanol is predicted to be very low ($k_H/k_D \rightarrow 1$).[13]

The insensitivity of the stereoselectivities to beam energy and the contrasting sensitivity to temperature (Table II)[14] suggests to us that there is not a quasi-equilibrium distribution of energy into the rotational modes of the reacting molecular ions. This view that there is a disproportionate share of vibrational excitation is supported by the low sensitivity to isotopic substitution ($k_H/k_D \rightarrow 1.0$), a vibrational phenomenon, and the high sensitivity to stereochemistry, a rotational phenomenon.

Conclusion

Since studies of the nature of stereochemical events which distinguish diastereotopic hydrogens are the most

EXPERIMENTAL SECTION

Optical rotations were taken on a Bendix ETL-NPL automatic polarimeter (α,±.001°) and NMR spectra on a Varian A-60 or T-60 spectrometer with 100 MHz data obtained from a Varian HA-100. Melting points were determined on a Thomas-Hoover apparatus and microanalysis were carried out by Spang Laboratories, Ann Arbor. The mass spectral data come from an MS-902, AEI mass spectrometer[28] with conditions specified in the various tables in the text. In all cases deuterated materials were shown to be identical to authentic hydrogen compounds by vpc and tlc. (Scheme 2).

The deuterated diastereomeric acetates, 1, 2, 3, 4 (2-butyl and 1,2-diphenylethylacetates) were prepared as described.[5,6] The preparations of 5 and 6 follows.

Preparation of trans-1,2-Di(1-napthyl)-ethene oxide. Trans-1,2-Di-(1-napthyl)-ethene[29] (.013 moles) as a slurry in 15 ml methylene chloride was reacted slowly (15 minutes) with solid m-chloroperbenzoic acid[30] (.015 moles) causing solution of the alkene and refluxing. After two hours of stirring a voluminous precipitate was present. Dilution with benzene:ether (1:1) and extraction with $KHCO_3$ and water yielded an orange solid. This material on recrystallization (ethanol) gave a white solid (45% yield) mp 139-142°. NMR: multiplet δ 7.10-8.15 (7H) and singlet δ 4.28 (1H).

Anal. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44.
Found: C, 89.24; H, 5.26.

Erythro-2-Deutero-1,2-Di-(1-napthyl)-ethanol. To lithium aluminum deuteride (0.6 g) was added 125 ml of tetrahydrofuran (anhydrous, distilled from lithium aluminum hydride) and 3.5 g of trans-1,2-di-(1-napthyl)-ethene oxide. After a 16 hr reflux the bright green solution was treated with saturated Na_2SO_4 to remove excess lithium aluminum deuteride. There was thus obtained 2.4 g of a white solid, mp 161-164° (identical to authentic hydrogen compound.

Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08
Found: C, 88.54; H, 6.16.

Threo-2-deutero-1,2-di-(1-napthyl)-ethanol. In an apparatus consisting of two connected (for gas transfer) flasks with magnetic stirring and a N_2 purge was added anhydrous diglyme (50 ml) containing 1.0 g of $NaBD_4$. To this was added 25 ml of anhydrous diglyme with 6.0 g of $BF_3O(C_2H_5)_2$. A nitrogen stream carried the gas produced to the second flask containing 5.0 g of trans-1,2-di-(1-napthyl)-ethene in 100 ml of anhydrous tetrahydrofuran. After five hrs the yellow fluorescent

reaction flask solution was added to 50 ml of 3N NaOH in an ice-salt bath. At -15°, 5 ml of 30% H_2O_2 was added and the solution stirred overnight. The aqueous layer on extraction yielded a beige solid which was boiled with 25 ml of ether and subsequently kept at 0° for 2 hrs. The resulting crystals weighed 4.3 g, mp 162-166°. They were identical to authentic hydrogen compound. See Erythro preparation above.

Erythro and Threo-2-Deutero-1,2-di(1-napthyl)-ethyl acetates (5 and 6). The acetates were prepared in each case from their alcohol precursors (1.2 g) (see above) in dry pyridine (5 ml) (distilled from barium oxide) with acetyl chloride (.4 g). Appropriate work-up followed by chromatography on 50 g of silica-gel (hexane, methylene chloride 1:1) yielded a clear honey like-oil which crystallized from ether to give 1.0 g of a white solid, mp 85-87°. Both acetates were identical to authentic hydrogen material, mp 85-87°.

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92
Found: C, 84.50; H, 5.88.

Mass spectral analysis of the deuterated acetates showed 97.0% and 93.9% deuterium incorporation for 5 and 6 respectively. NMR analysis (100 MHz) showed that 6 was > 98% epimerically pure while 5 contained 35.5% of 6. These results were used to correct the mass spectral results on loss of DOAc and HOAc.

Preparation of the Diastereomeric-5-deutero-2-hexanols 7 and 8. Acetol was reduced by actively fermenting yeast to give [R]-propylene glycol $[\alpha]_D^{25}$ -21.7, c.12, H_2O[31] (85% yield). Lithium aluminum hydride reduction of S(-)-ethyl lactate[32] yielded the enantiomeric [S]-propylene glycol, $[\alpha]_D^{25}$ +23.0, c.6.7, H_2O.[33]

The enantiomeric preparations described below (one enantiomer) were identical and differed only for chiral measurement (NMR on appropriate derivatives or $[\alpha]_D$).

[S]-1-Trityloxy-2-propyltosylate 13. Under N_2 at 0° C in 100 ml dry pyridine, [S]-(+)-1,2-propanediol (.507 mole) was added over one hr to (0.52 mole) triphenylmethylchloride in pyridine.[34] After stirring at 50° for four hrs, standard work up yielded an orange oil which crystallized from 30-60 petroleum ether mp 81-83°, $[\alpha]_D$ + 12.7 (c.11, $CHCl_3$); yield 80%. This material (128 g) was dissolved in dry pyridine and at 0° was charged with p-toluene sulfonyl chloride (154.5 g) in pyridine. After stirring for 2 days, appropriate work-up and $CHCl_3$ extraction yielded an orange oil which could be crystallized from 1:1 ether:petroleum, mp 90-91°, $[\alpha]_D^{25}$ -5.5° (c.20, $CHCl_3$), (13) yield 83%.

Anal. Calcd for $C_{29}H_{28}O_4S$: C, 73.71; H, 5.97; O, 13.55; S, 6.77
Found: C, 73.74; H, 5.97; S, 6.80.

The enantiomeric $[\alpha]_D^{25}$ = +5.4 (c.20, $CHCl_3$).

[S]-2-deuteropropanol 14. The tosylate 13 (157 g, 0.33 mole) was reduced (38 hrs with stirring) in ether with lithium aluminum deuteride (14.0 g, 0.33 mole). Standard work-up with saturated Na_2SO_4 followed by continuous $CHCl_3$ extraction yielded 111.0 g of propyl trityl ether identical by tlc to authentic material. This material was left over 96 hrs with 900 ml of n-hexanol and five drops of concentrated HCl. From time to time a few drops more of acid was added. Distillation through a high efficiency column gave 2-deutero-propanol 14, $[\alpha]_D^{25}$ +.06 (neat). The enantiomeric material was $[\alpha]_D^{25}$ -.06 (neat). These compounds were identical to authentic n-propanol by vpc analysis. Attempts to determine the optical purity by esterification with chiral acids failed as the diastereotopic (external) hydrogens could not be distinguished in the two enantiomers. Mass spectral and NMR analysis showed essentially complete monodeuteration.

[S]-3-deutero-2-hexanone 16. The deuterated alcohol 14 was converted to its bromide with the PBr_3 at 0° in γ-collidine and xylene. Appropriate work-up gave the 2-deutero-bromopropane 15 (67% yield) identical to authentic hydrogen compound. $[\alpha]_D^{25}$ -1.5° (neat) enantiomer $[\alpha]_D$ +1.5° (neat). The deuterated bromopropane 15 was alkylated and decarboxylated by standard procedures[35] to yield (51%) [R]-5-deutero-2-hexanone 16, $[\alpha]_D^{25}$ +0.4° (neat); identical by vpc analysis to authentic 2-hexanone.

Fermentation of [R]-5-deutero-2-hexanone to the Alcohol 8.[36] A 5 l. flask fitted with a gas trap to show gas evolution and an overhead stirrer was charged with 1.4 l of distilled water, 450 g of dextrose, and a paste of 450 g bakers yeast (Red Star) in 450 ml of water. Fermentation began immediately and after ten minutes 7.0 g (.007 mole) of [R]-5-deutero-2-hexanone in 10 ml ethanol was added to the stirred mixture. After 22 hrs NaCl (525 g) was added and the brewers mess was steam distilled collecting 1 liter of distillate. Continuous extraction of this distillate (more NaCl added) yielded after distillation, 2.1 g of [R],[S]-5-deutero-2-hexanol (29%) 8, $[\alpha]_D^{25}$ +12.2 (c.1.0, ethanol); diastereomers (antipode of 7) $[\alpha]_D^{25}$ +12.0 (c.2.5, ethanol). Mass spectral analysis showed essentially complete deuteration while the α-methoxy-α-trifluoromethyl phenyl acetate derivatives[37] showed a single resonance for the methyl and trifluoromethyl signals although racemic 2-hexanol gave doublets for each (with 10% added trifluoroacetic acid) separated by 2.5 Hz and 15 Hz, respectively. The fermentation gives the (S) configuration[36] at the alcohol site.

Alcohol 8 was converted to its diastereomer 7 by inversion of configuration at the carbinol centers following Cope;[38] $[\alpha]_D^{25}$ -12.2° (c.1.0, ethanol).

[S]-(+)-3-Deutero-3-Phenyl Propionic Acid. α-Deuterobenzaldehyde was prepared as described[39] and reduced by fermenting yeast following the lit.[40] The chiral benzyl alcohol had $[\alpha]_D^{25}$ +1.38° (neat), lit.[40] $[\alpha]_D^{25}$ +1.58° (neat). NMR analysis of the α-MTPA[37] ester of this alcohol showed > 98% optical purity. [S]-(+)-α-Deuterobenzyl chloride 20 was prepared by reaction of the alcohol 19 with phosgene followed by a 44 hr reflux in dioxane.[41] $[\alpha]_D$ +1.26° (neat), lit.[41] $[\alpha]_D$ +1.51° (neat). The latter was calculated based on optical purity calculated by comparison with Mosher's work. Mass spectral analysis on these materials showed incorporation of > 98% of one deuterium.

Diethylmalonate (dried 4A molecular sieves, and distilled) and 50 ml of benzene was added to a 1 liter flask containing 1.55 g (.067 mole Na wire) and 500 ml of benzene (distilled from Na wire). After overnight reflux, 8.4 g of 20 in benzene was slowly added (45 min). After 40 hrs of reflux and stirring, and standard work-up the residue was distilled through a 10 cm Vigreux column at 15 mm of Hg to remove everything boiling over 100°. The remaining oil (13.5 g) (mostly monoalkylated benzyimalonic ester diethyl ester) was decarboxylated following the lit.[42] by 18 hrs reflux with 90 ml of ethanol, 15 ml of water and 12.6 g KOH. After work-up and distillation [123° (.07 mm)] there was obtained 6.0 g (60% yield) of a white solid 21, mp 48-50°, authentic sample (Aldrich) mp 48-49°. $[\alpha]_D^{22}$ +.36° = .003 (acetone).[43]

[S]-(+)-5-Deutero-5-Phenyl-2-Pentanone 23. 21 (5.9 g) was reduced in anhydrous ether (250 ml) with lithium aluminum hydride (1.6 g). After appropriate work-up (saturated Na_2SO_4) there was obtained 5.3 g (99%), 63-68° (0.1 mm), $[\alpha]_D^{21}$ +.56° (neat); NMR ($CDCl_3$): δ 7.2 (s, 5H); 3.6 (t, J = 6 Hz, 2H); 2.7 (triplet of triplets, J = 4 Hz, J = 1.5 Hz, 1H); 2.2 (s, 1H); 1.6-2.1 (m, 2H) ppm. The product was identical by vpc and distillation to authentic proteum compound (available from Aldrich). It was converted to the bromide, 22, at 0° in 15 ml of $CHCl_3$, containing 15.5 g Na_2CO_3 and 14 g of PBr_5. 5.2 g of 23 yielded 5.0 g of 22 (bp 107-111° (15 mm)) pure by vpc on 10% FFAP on 60/80 Chrom W at 180° (identical to authentic hydrogen compound).

The bromide 22 (5.3 g) was reacted in 100 ml of anhydrous ether with 0.65 g of magnesium turnings to form the black Grignard reagent. This solution was cooled to -78° and to it was added via syringe, over 15 min, ice-cold acetaldehyde (13.6 g, freshly distilled and dried over Molecular Sieves). The solution turned colorless and was treated with excess 5% HCl at room temperature.

Extraction and distillation yielded 2.2 g of a clear liquid (0.1 mm 70-80°) which was a mixture (3:1) of alcohol and ketone (23) by vpc on 1/4", 5', 5% QF-1, 60/80 Chrom W. This mixture was oxidized by Jones reagent[44] to the ketone (quantitative conversion by vpc) (23), 1.7 g (44% yield from 22) which was identical to authentic material by vpc and distillation. The hydrogen 5-phenyl-2-pentanone was prepared analogously starting from 3-phenyl-1-propanol (Aldrich). It had: Calcd $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.30, H, 8.61; as well as appropriate mass spectral and NMR characteristics.

Preparation of [S],[S]-(+)-5-Deutero-5-Phenyl-2-Pentanol 12 by Fermentation.[36,45] Glucose (90 g), 380 ml of water, 3 g of 23 and 9 ml of ethanol were charged to a 6 L Erlenmeyer flask with a device to detect gas evolution. With stirring (magnetic), 21.6 g of yeast (Bakers, Red Star) was added. Over the next 82 hrs, 180 g of yeast, 400 g of glucose and 1 liter of water were added in portions from time to time as the CO_2 evolution diminished. Salt was added and the subsequent brew was steam distilled to half-volume. This distillate was fractionated further by distillation to remove H_2O:ethanol azeotrope. Subsequent extraction and bulb to bulb distillation yielded 2.75 g of a liquid shown by vpc to be 90% at 60:40 mixture of alcohol:ketone (1/4", 5', 5% QF-1 on 60/80 Chrom W at 140°). Chromatography on 50 g of Silica gel with methylene chloride at a 1 drop/second separated the ketone from alcohol. For 12, $[\alpha]_D^{22}$ +11.4 (c.9.185, cyclohexane) identical to authentic hydrogen material, $[\alpha]_D^{23}$ +12.0 ± .1° (c.60.3, cyclohexane) by vpc and distillation and tlc. The latter was converted to its acetate derivative which was purified by vpc for analysis.

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80
Found: C, 75.69; H, 8.81.

This material, 12 was shown to be > 98% optical purity by NMR analysis of its α-methoxy-α-trifluoromethylphenyl acetates (MTPA).[37]

The (+)-diastereomer 12 was converted to 11 following Cope.[38] 11 was at least 98% optically pure by NMR. Analysis of its MTPA ester[37] and had $[\alpha]_D^{22}$ -11.3° (cyclohexane).

Preparation of 5,5-Dideutero-5-Phenyl-2-Pentanol 24. α,α-Dideuterobenzyl bromide (4.0 g), obtained via lithium aluminum deuteride reduction of benzoic acid and conversion to the bromide, was added via syringe over 15 min to a refluxing solution of 1.2 g of sodium wire in 50 ml of absolute ethanol (refluxed for 24 hr over magnesium turnings) containing 8.0 g of diethylmalonate. After refluxing for 16 hr, appropriate work-up and removal of all materials boiling above 100° at 15 mm the product was decarboxylated with 10 g of 48% HBr under reflux for 5 hrs. Distillation, bp 125°, 0.25 mm gave a crystalline solid, mp

48-49°; authentic material (see above) mp 48-49°. This material, 3,3-dideutero-3-phenyl propionic acid was converted to 5,5-dideutero-5-phenyl-2-pentanol, 24 exactly as described above for the monodeuterated material. 24 was identical to authentic material by vpc and tlc and mass spectral analysis showed > 98% of two deuterium per molecule.

Preparation of 5-Cyclohexyl-2-Pentanol by Catalytic Hydrogenation.[46] 5-Phenyl-2-pentanol (0.5 g) was added to 1 g of rhodium (0.5%) on alumina followed by 12 ml of glacial acetic acid. After 16 hr at 50 psi of H_2 gas in a Parr/shaker and standard work-up, there was obtained 0.4 g of a clear liquid. Vpc showed no starting material and the vpc collected (3/8", 10', 5% QF-1 on 60/80 Chrom W) material showed no NMR signal below δ 4.0 ppm. The mass spectrum showed no $M^{\cdot+}$ but featured ions at M-15 and M-18.

Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02
Found: C, 77.35; H, 12.78.

Catalytic Hydrogenation of 5,5-Dideutero-5-Phenyl-2-Pentanol. 30 μl of the alcohol was added to 0.5 g of 0.5% rhodium on alumina in 5 ml of acetic acid and handled as above. Mass spectral analysis of the product showed ca 50% of the label lost.

5-Cyclohexyl-2-Pentanol via Birch Reduction.[47] In an appropriate cooled (-78°) apparatus, 0.1 g of freshly cut lithium wire (cleaned of mineral oil) was added to 125 ml of liquid ammonia. After one half hour, 1.5 g of 5-phenyl-2-pentanol was added with another 0.1 g of lithium wire and stirred for one hr. Absolute ethanol (20 ml) was added slowly to the beautiful blue solution which yielded its color. Appropriate work-up after the addition of ether and 5% HCl, yielded 1.4 g of a cloudy oil. This oil (0.166 g) was hydrogenated using 5% platinum on carbon in 5-10 ml of ethylacetate at 25° under 1 atm. of hydrogen gas. After three hr 60 ml of H_2 had been taken up. Filtering and flash evaporation and bulb to bulb distillation left an oil (clear, colorless, 0.130 g) which was identical by vpc analysis to authentic 5-cyclohexyl-2-pentanol.

This exact procedure on 5,5-dideutero-5-phenyl-2-pentanol gave 5,5-dideutero-5-cyclohexyl-2-pentanol with 90% of two deuterium per molecule by mass spectral analysis.

This procedure was applied to [S],[S]-5-deutero-5-phenyl-2-pentanol to yield [S],[S]-5-deutero-5-cyclohexyl-2-pentanol identical to authentic hydrogen compound by vpc and tlc (10), with 89% of one deuterium per molecule (mass spectral analysis on the M-15 ion) and optical purity by its MTPA[37] ester of at least 90%. The procedure of Cope[38] converted this material to its epimer 9, exactly as described for the phenyl series above.

subtle mechanistic probes of the geometry of reacting molecules now known,[25] one must allow that we are dealing with a method of ion-structure determination with a low threshold for structural discrimination. It follows that at least in the molecule ions discussed herein, our results strongly suggest structural equivalence between the reacting molecular ions and their accessible phase brethren.

Bentley and Johnstone[26] have pointed out that "all of the methods used to investigate ion structures in organic mass spectrometry involve comparisons amongst ions and except for atoms and a few simple molecules no ion structures have been absolutely determined." This statement, although true for methodology defined as ion-structure determination, leaves out the huge body of work on the attempted application of the accessible phase physical-organic principles (structure–reactivity relationships) to mechanism in electron-impacted organic ions. When these studies involve the effect of stereochemistry on reactivity after electron impact, they become by their nature sensitive probes of ion structure whether called so or not and the success of stereochemical principles in predicting these reactions is heavy evidence for structural correspondence. The present work may be seen as an extension of earlier studies along these lines and our results, among others,[27] clearly recommend a stereochemical approach toward the elucidation of the structure of gas-phase ions.

Registry No.—**1**, 35293-32-4; **2**, 35293-33-5; **3**, 51271-14-8; **4**, 51271-15-9; **5**, 51271-16-0; **6**, 51271-17-1; **7**, 36013-33-9; **8**, 36013-32-8; **9**, 51271-19-3; **10**, 51348-67-5; **11**, 51271-20-6; **12**, 51348-68-6; **13**, 51293-27-7; **14**, 51271-21-7; **15**, 51271-22-8; **16**, 51271-23-9; **19**, 3481-15-0; **20**, 51348-69-7; **21**, 51293-28-8; **22**, 51271-24-0; **23**, 51271-25-1; **24**, 51271-26-2; *trans*-1,2-di(1-naphthyl)ethene, 1233-36-9; *erythro*-2-deuterio-1,2-di(1-naphthyl)ethanol, 51271-27-3; *threo*-2-deuterio-1,2-di(1-naphthyl)ethanol, 51271-28-4; [*S*]-(+)-1,2-propanediol, 4254-15-3; *α,α*-dideuteriobenzyl bromide, 51271-29-5.

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(10) These are average rate constants over the range of accessible excited states. Subsequent fragmentation of the M − H(D)OAc ions are effectively repressed at low voltages and from the invariance of ratio with beam energy (Table I) plays no role at 70 eV either. Metastable peaks are observed for all the M − H(D)OAc fragmentations and this experiment, in addition to the low temperatures used (not capable of pyrolysis in these systems in our hands) and previous comparative observations of acetic acid loss by EI and cold photoionization,[4] precludes the possibility of mass spectral pyrolysis.

(11) The greater average loss of deuterium from the aromatic materials (Table I) is consistent with the expected 1,2 and 1,3 loss of HOAc from the methyl groups in the *sec*-butyl acetates.[4] The mass spectra of 1,2,2-trideuterio- and 2,2-dideuterio-1,2-diphenyl ethyl acetates, determined under identical conditions with those specified in Table I, show sole loss of DOAc requiring a specific 1,2 elimination. We presume that the α-napthyl system is also C-2 specific.[12]

(12) This is identical with Curtin's analysis of the stilbene system.[6]

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