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MASS SPECTROMETRY IN STRUCTURAL AND STEREOCHEMICAL PROBLEMS CVIII.[1] DEUTERIUM ISOTOPE EFFECTS IN SITE-SPECIFIC MASS SPECTROMETRIC REARRANGEMENT PROCESSES[2]

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Although deuterium labelling is one of the most extensively used methods for delineating mass spectrometric fragmentation pathways, only one previous measurement has been made[3] of the value of the isotope effect in the widely studied and quoted McLafferty rearrangement.[4] The use of this derived value (0.88 for D/H transfer for mono- and di-γ-deuterated methyl butyrate) has led to some quantitative discrepancies in determining the extent of primary vs. secondary hydrogen transfer in McLafferty rearrangements involving aliphatic[5] and alicyclic[6] ketones. Since such discrepancies may be associated with differing isotope effects for closely related rearrangement processes, it was deemed advisable to undertake a comprehensive survey of the range of the deuterium isotope effect in this site-specific sixmembered hydrogen transfer process, especially since this may also be of some mechanistic significance in comparison with similar photochemical reactions. Of those classes of compounds in which exclusive migration of the γ-hydrogen on electron impact has been shown to occur, aliphatic[5,7] and alicyclic[6,8] ketones and aliphatic methyl esters[9] (X=O); alkyl benzenes[10] and alkyl benzyl ethers[11] (X=C<); 1-alkyl isoquinolines[12] (X=N-); and alkyl thion esters[11] (X=S) were chosen for the measurement and study of deuterium vs. hydrogen transfer.

Mono-deuterium labelling of a secondary γ-carbon atom ($R'=CH_3$) rather than a primary one (R'=H) was preferred as it gave a statistical 1:1 probability for hydrogen to deuterium transfer and because of the established ease of transfer of a secondary over a primary hydrogen in certain of these rearrangement processes.[5,6] In general ethanol-1-d_1, prepared by sodium borodeuteride reduction of acetaldehyde, was the starting material for the incorporation of the deuterium label through the intermediacy of n-butyl bromide-3-d_1 or n-propyl bromide (or iodide)-2-d_1.

The isotope effect (I.E.) was defined by previous workers[3] as equal to the "atoms of deuterium per atom of hydrogen transferred for the hypothetical case in which equal numbers of deuterium and hydrogen are available for transfer". As we chose a 1:1 transfer availability, a simple ratio of the respective rearrangement peak heights, corrected for natural isotopic abundances and non-deuterated material, furnished the defined I.E. value. High resolution mass measurements of the rearrangement peaks were carried out where necessary to ensure homogeneity of peak composition.

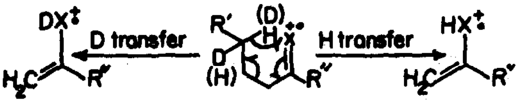
All mass spectra were recorded by Dr. A. M. Duffield with an Atlas CH-4 mass spectrometer at 70 e.v., trap current of 10 μ amps, using a TO-4 ion source with gas cartridge operating at 185°. The gas inlet system was maintained at 70° and the inlet line at 150°. High resolution measurements were performed by Mr. R. Ross on an A.E.I. MS-9 instrument at an ionizing energy of 70 e.v. Compounds were purified for mass spectrometric analysis by vapor phase chromatography.

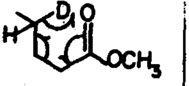
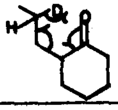
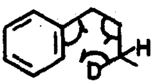
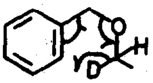
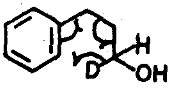
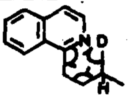
The results (Table 1) clearly indicate the wide range of isotope effects (0.50 to 0.98) exhibited by the particular classes of compounds investigated and justify a reappraisal of previous calculations involving isotope effects which have utilized solely the I.E. value for methyl butyrate (0.88)[3]. Our value for the higher homolog (I) of this ester (0.92) would suggest that there is a consistency within a particular class of compounds although such subtle changes as the interpolation of a heteroatom in the side chain of an alkyl benzene adjacent to the rearrangement site (e.g. IV vs. V, VI and VII) markedly affects the transfer of hydrogen with subsequent I.E. lowering (0.80 to 0.50). The difference between the values for the ketones II and III is probably attributable to stereochemical grounds.

Measurements at low ionizing voltages, down to a nominal 10 e.v., showed no significant change in the isotope effect or specificity for compounds VI, VIII, IX and their γ-d_2 counterparts. The possible mechanistic implication of the results collected in Table 1 will be discussed in our full paper together with other relevant data.

TABLE 1.

Deuterium Isotope Effects in Various γ-Hydrogen Transfers



X		Compound	Isotope Composition	Specificity of γ-H transfer	Rearrangement peaks corrected m/e		Isotope Effect
O	I		98% d_1	>95%[9]	74 75	94.3 86.7	$\frac{86.7}{94.3}=0.92$
	II		97.5% d_1	>95%[5,7]	72 73	95.2 93.5	$\frac{93.5}{95.2}=0.98$
	III		97% d_1	>95%[6]	98 99	94.1 73.4	$\frac{73.4}{94.1}=0.78$
C	IV*		98.9% d_1	95%[10]	92 93	119.4 95.2	$\frac{95.2}{119.4}=0.80$
	V		98% d_1	94%	92 93	50.7 26.0	$\frac{26.0}{50.7}=0.51$
	VI		98% d_1	94%	92 93	27.3 13.6	$\frac{13.6}{27.3}=0.50$
	VII		4% d_o 84% d_1 12% d_2 **	13	92 93	37.5 18.8	$\frac{18.8}{37.5}=0.50$
N-	VIII		98% d_1	>95%[12]	143 144	96.5 72.0	$\frac{72.0}{96.5}=0.75$
S	IX		98% d_1	98%	90 91	96.5 77.0	$\frac{77.0}{96.5}=0.80$

*The mass spectrometric analysis of this compound, performed on a C.E.C. Model 21-102/103 instrument at 70 e.v., was kindly made available to us by Dr. S. Meyerson (see ref. 10).

** Starting material (hydrocinnamaldehyde) was contaminated with its alcohol and acid.

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(11) See Table 1. The γ-d$_2$ derivatives of VI and IX were prepared and their mass spectra measured under conditions identical to those used for the γ-d$_1$ compounds.

(12) Unpublished results from this laboratory.

(13) J. D. McCollum and S. Meyerson, unpublished results quoted in "Mass Spectrometry of Organic Ions," F. W. McLafferty, ed., Academic Press, N.Y. and London, 1963, pp. 510.