Organic Mass Spectrometry, 1975, Vol. 10, pp. 263 to 272. © Heyden & Son Limited. Printed in Northern Ireland

MASS SPECTROMETRY OF ORGANIC COMPOUNDS

X†—FRAGMENTATION OF 2-BUTEN-1-ol ON ELECTRON-IMPACT

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(*Received* 11 *December* 1974; *accepted* (*revised*) 24 *December* 1974)

Abstract—The mass spectra of variously deuterated 2-buten-1-ols (both Z and E) have been examined. Evidence is presented for the formation of the $[M - H_2O]^{+\cdot}$ ion via a 6-membered transition state, and for the occurrence of two distinct reaction pathways for formation of the major ions at *m/e* 57 and 43.

ALTHOUGH the mass spectra of aliphatic and alicyclic alcohols have been investigated in considerable detail in recent years,[2] correspondingly detailed studies on unsaturated alcohols have been rare. A study of this class of compounds is of interest because it presents the possibility for the observation of reactions involving the interaction of two functional groups.

Early work on unsaturated alcohols included studies of some isomeric hexenols,[3] allylic alcohols,[4] and stereoisomeric β-ethylenic and β-aromatic alcohols,[5] together with miscellaneous reports on other unsaturated alcohols.[6] More recently studies have appeared on various $\alpha\beta$-unsaturated secondary alcohols[7–10] and on allyl alcohol,[11] together with an ion cyclotron resonance (i.c.r.) study of 1-hepten-3-ol.[12] In their study of various alcohols of the general structure $RCH(OH)CH{=}CH_2$, Kraft and Spiteller[9] suggested that quantitative rearrangement of the molecular ion of vinyl carbinol to that of an ethyl ketone occurs before fragmentation at 70 eV. In a separate study Willhalm and Thomas[8] reported that allylic alcohols of the general structure $RCH{=}CHCH(OH)CH_3$ give similar mass spectra to the corresponding saturated ketones, but suggested on the basis of metastable data that the ions are formed by different routes. The mechanism of isomerization of 1-hepten-3-ol has been shown by i.c.r. studies[12] not to involve a simple ketonization.

In view of this detailed information on the mechanism of fragmentation of unsaturated secondary alcohols, it is of interest to examine the fragmentation pathways available to unsaturated primary alcohols. It might be anticipated that these compounds would show significant differences in their fragmentation behavior from the secondary alcohols studied, in particular because isomerization as described earlier[12] should not be possible for such compounds. A study of the fragmentation pathways of the 2-buten-1-ols thus forms the subject of this paper. The compounds investigated in this work are listed in Table 1 and the mass spectrum of compound IZ

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† For Part IX, see Ref. 1.

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TABLE 1. 2-BUTEN-1-OLS INVESTIGATED

Number and configuration	Compound	Deuterium content
(I) Z, E	$CH_3CH{=}CHCH_2OH$	
(II) Z, E	$CD_3CH{=}CHCH_2OH$	89·9% d_3, 7·6% d_2, 1·7% d_1, 0·8% d_0
(III) Z, E	$CH_3CH{=}CDCH_2OH$	77·8% d_1, 22·2% d_0
(IV) Z, E	$CH_3CH{=}CHCD_2OH$	93·5% d_2, 4·2% d_1, 2·3% d_0
(V) Z, E	$CH_3CH{=}CHCH_2OD$	Z 75·5% d_1, 24·5% d_0 E 71·1% d_1, 28·9% d_0

is shown in Fig. 1. In general, the mass spectra of the E and Z isomers are very similar, and so with the exception of the *m/e* 54 ion we will discuss the fragmentations of the two isomers together.[13]

The major fragmentation pathways of 2-buten-1-ol were determined by an analysis of its metastable peaks (both first and second field free regions) and by exact mass measurements, and are summarized in Scheme 1. The fragmentation pathways investigated in this study are the major pathways, indicated by double arrows in Scheme 1.

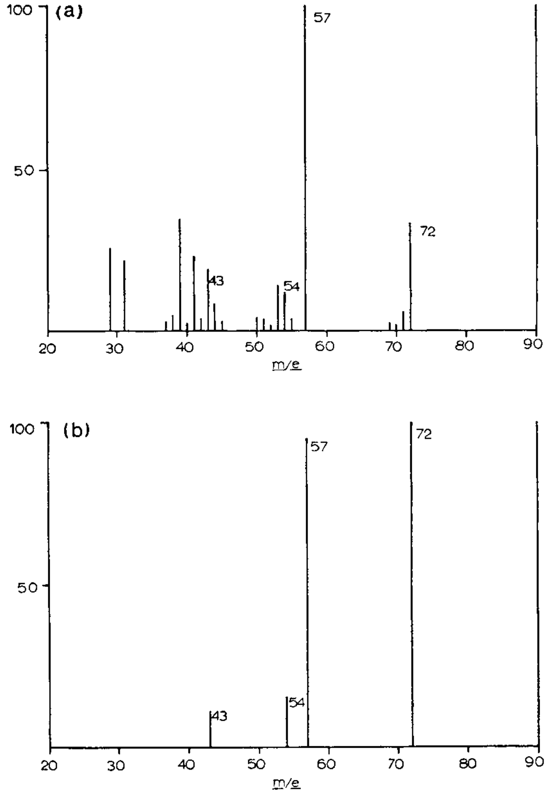
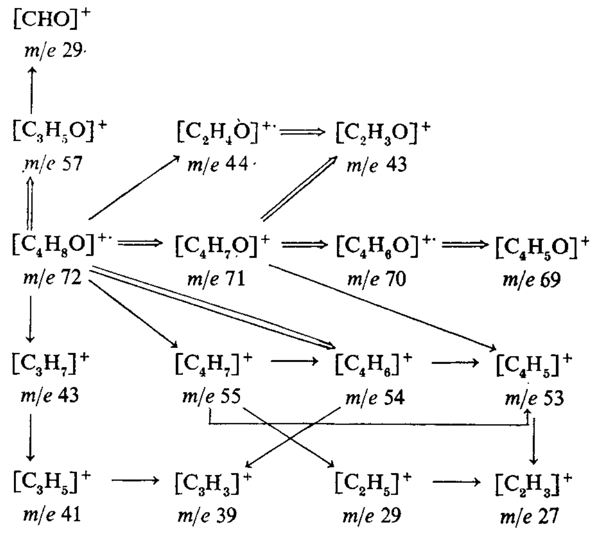


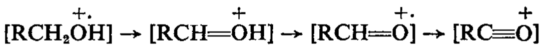
FIG. 1. Mass spectrum of Z 2-buten-1-ol, corrected for natural abundance carbon-13. (a) 70 eV, (b) 10 eV.



SCHEME 1. Fragmentation pathways of 2-buten-1-ol.

$[M - H]^+$ *ions*

At 70 eV both Z and E isomers of 2-buten-1-ol show significant peaks at *m/e* 71, 70, 69, corresponding to the loss of 1, 2 and 3 hydrogen atoms, respectively. A similar loss of hydrogen atoms occurs in saturated alcohols and it has been shown in these cases that the loss occurs by the pathway of Scheme 2.[14] A similar pathway was also originally proposed to account for the loss of hydrogen from unsaturated alcohols,[2] but later results showed that in the case of allyl alcohol at least loss of



$$[\mathrm{RCH_2\overset{+\cdot}{O}H}] \rightarrow [\mathrm{RCH{=}\overset{+}{O}H}] \rightarrow [\mathrm{RCH{=}\overset{+\cdot}{O}}] \rightarrow [\mathrm{RC{\equiv}\overset{+}{O}}]$$

SCHEME 2

hydrogen was a random process and was not confined to loss from the C-1 carbon.[11]

The loss of hydrogen observed from the 2-buten-1-ols (I to V) is summarized in Table 2. The data is presented for the E isomer, but identical results were also obtained for the Z isomer. The observed intensities for hydrogen loss from each of the deuterium labeled alcohols II to V are compared with values calculated on the basis of three different mechanisms of hydrogen loss. The first set of values was calculated on the assumption that hydrogen loss follows the pathway of Scheme 2, with specific loss of the C-1 hydrogen followed by the hydroxyl hydrogen. The second set of values was calculated on the assumption that hydrogen loss from the butenols is a completely random process.

Inspection of Table 2 indicates that neither of the above mechanisms gives results which are in complete agreement with the data. The assumption of specific hydrogen loss by the pathway of Scheme 2 gives rather poor agreement in the crucial case of compound IV, while the assumption of complete scrambling gives results which are only in marginally better agreement. Somewhat better agreement is obtained by assuming partial hydrogen scrambling with some specific loss by the pathway of

TABLE 2. EXPERIMENTAL AND CALCULATED INTENSITIES OF IONS FORMED BY LOSS OF HYDROGEN FROM (E)-2-BUTEN-1-OL[a]

	m/e						
Compound	75	74	73	72	71	70	69
(I) $CH_3CH{=}CHCH_2OH$				732	160	044	064
(II) $CD_3CH{=}CHCH_2OH$ obs.	683	176	057	055	020	008	
calc. 1[b]	657	200	064	069	006	001	
calc. 2[c]	657	146	089	046	038	019	
calc. 3[d]	657	164	080	054	027	013	
(III) $CH_3CH{=}CDCH_2OH$ obs.			554	262	092	062	030
calc. 1[b]			570	286	070	060	014
calc. 2[c]			570	271	077	049	033
calc. 3[d]			570	276	075	053	027
(IV) $CH_3CH{=}CHCD_2OH$ obs.		704	106	081	036	019	054
calc. 1[b]		685	031	170	049	003	068
calc. 2[c]		685	143	083	046	038	009
calc. 3[d]		685	106	119	047	026	029
(V) $CH_3CH{=}CHCH_2OD$ obs.			605	283	042	050	020
calc. 1[b]			553	300	039	044	064
calc. 2[c]			553	285	087	052	034
calc. 3[d]			553	290	071	049	044

[a] Peak intensities corrected for ^{13}C and normalized to 1000 in the region of interest.

[b] Calculated assuming specific hydrogen loss according to Scheme 2.

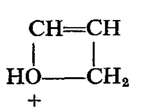
[c] Calculated assuming complete scrambling of hydrogens prior to hydrogen loss.

[d] Calculated assuming 67 % of hydrogen loss from a scrambled ion and 33 % of specific hydrogen loss by the pathway of Scheme 2.

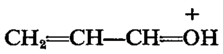
Scheme 2 (calculation 3), but the agreement is not perfect. It may reasonably be concluded, however, that significant hydrogen randomization must precede or accompany hydrogen loss from the 2-butenols and thus the pathway of Scheme 2 is excluded as the sole pathway for the hydrogen loss.

$[M - CH_3]^+$ *ion*

The loss of a CH_3 group from 2-buten-1-ol yields the base peak in the spectrum at *m/e* 57. In the spectrum of compound II this peak still appears largely at *m/e* 57, indicating that the major pathway for its formation involves the loss of the terminal CD_3 group from this compound. A similar ion at *m/e* 57 is formed by the loss of hydrogen from allyl alcohol and labeling studies in this case suggested (but did not require) that the ion have the cyclic oxonium ion structure *a*. Plausible alternative structures for the ion are also possible, however, and structure *b* (which could be formed either by simple ring-opening of *a* or by another pathway) is one attractive possibility because of its potentialities for resonance stabilization.



(*a*)



$$CH_2{=}CH{-}CH{=}\overset{+}{O}H$$

(*b*)

In an attempt to distinguish between the cyclic oxonium structure for the *m/e* 57 ion and alternative structures such as *a*, the further decompositions of this ion and its deuterated analogs were investigated. The only important fragmentation for which metastable peaks could be detected was that giving the ion $[CHO]^+$ at *m/e* 29 (Scheme 1). In the spectrum of compound IV this ion appears to the extent of 35% as CHO and 65% as CDO, indicating substantial but not complete hydrogen scrambling prior to its formation. Such hydrogen scrambling could reasonably be accommodated by either structure *a* or *b* for the *m/e* 57 ion, and thus it is not possible to draw a firm conclusion on the question from this evidence.

In spite of this uncertainty about the structure(s) of this ion, it is possible to state categorically that it must be formed by at least two different pathways. This becomes clear from a study of the spectra of the deuterated alcohols, summarized in Table 3.†

TABLE 3. INTENSITIES OF OXYGEN-CONTAINING IONS FORMED BY LOSS OF A METHYL GROUP FROM (E)-2-BUTEN-1-OL AT 13 eV[a]

		m/e				
Compound	60	59	58	57	56	55
$CH_3CH{=}CHCH_2OH$				1000		
$CD_3CH{=}CHCH_2OH$ obs.	141	031	040	788		
calc.[b]				1000		
calc.[c]	140	012	003	848		
$CH_3CH{=}CDCH_2OH$ obs.			690	310		
calc.[b]			778	222		
calc.[c]			673	327		
$CH_3CH{=}CHCD_2OH$ obs.			730	270		
calc.[b]			711	289		
calc.[c]			711	289		

[a] Peak intensities corrected for ^{13}C and normalized to 1000.

[b] Calculated assuming specific loss of the C-4 CH_3 group.

[c] Calculated assuming 82% specific loss of the C-4 group and 18% loss of a CH_3 group made up from a carbon and the hydrogens of C-1 to C-3 in a statistical manner.

It can be seen from this Table that while the bulk of fragmentations leading to the $[M - CH_3]^+$ ion proceed with the loss of the terminal methyl group, about 18% of these ions are formed with the random loss of three of the four hydrogens situated on C-1, C-2 and C-3. The hydroxylic hydrogen is not lost in this process, however. In view of the random nature of this rearrangement, any attempt to write a specific mechanism is likely to be futile, but it is clear that at least two mechanisms must be operating in the formation of the $[M - CH_3]^+$ ion.

$[M - H_2O]^{+\cdot}$ *ion*

The loss of water from the molecular ion and the $[M - 1]^+$ ion of 2-buten-1-ol was observed for both the Z and E isomers, and yields ions at *m/e* 54 and 53. The intensity of these ions was found to vary slightly with the temperature of the ion source, but a study of their intensity as a function of ion chamber temperature showed that they were independent of temperature and reproducible at temperatures below 75 °C (Table 4). At temperatures above 75 °C their intensity increased, presumably

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† The data of Table 3 are presented for measurements at 13 eV, but similar results are obtained for measurements at 70 eV.

TABLE 4. WATER LOSS FROM 2-BUTEN-1-OL AS A FUNCTION OF TEMPERATURE

	Temperature (°C)				
	50	75	100	125	150
$\frac{[M - H_2O]^{+\cdot}}{[M - CH_3]^{+}}$	11·3	11·5	12·2	14·4	14·7

due to the occurrence of thermal dehydration prior to ionization in addition to the electron-impact-induced elimination of water observed at lower temperatures. Because of this temperature effect, all the spectra recorded in this paper were run at an ion source and inlet temperature of 55 °C, which was the lowest conveniently attainable on the spectrometer used. Metastable peaks were observed for the transitions 72 → 54, 71 → 53 and 54 → 53, indicating that the formation of these ions is (at least in part) electron-impact-induced.

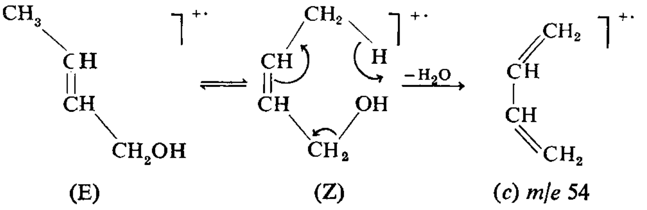
The relative intensity of the $[M - H_2O]^{+\cdot}$ ion was found to be significantly greater for the Z isomer than for the E isomer of the variously deuterated 2-buten-1-ols; for compounds I to V the ratio of the relative intensity of $[M - H_2O]^{+\cdot}$ or $[M - HDO]^{+\cdot}$ loss from the Z isomer to that from the E isomer averaged 2·0. This result suggests that elimination of water is occurring in these compounds at a rate significantly greater than that of the isomerization of the alcohols.

In spite of the lack of stereospecificity in loss of H_2O from the molecular ion, this fragmentation does proceed with substantial site specificity. Table 5 lists the results of our investigation of this water loss at low ionizing energy. Loss of H_2O occurs specifically from compounds IVE and IVZ, while loss of HOD occurs specifically from compounds VE and VZ. Surprisingly, however, water loss is not specific in the case of compounds II and III, with both isomers showing loss of species other than those predicted on the basis of a 6-membered transition state. As a check on the reliability of the method used to calculate the H_2O vs HOD loss from these compounds, the spectrum of compound IVE was obtained at a resolution of 40000. It was found that there was no detectable ion at *m/e* 55 corresponding to $[M - HDO]^{+\cdot}$ in this spectrum; the small peak observed at *m/e* 55 is due entirely to $[M - H_3O]^{+}$.

TABLE 5. WATER LOSS FROM 2-BUTEN-1-OLS

Compound	Ionizing voltage, eV	% Water lost as H_2O	HDO	D_2O
(II) (E)—$CD_3CH{=}CHCH_2OH$	13	24	67	9
(Z)—$CD_3CH{=}CHCH_2OH$	13	15	82	3
(III) (E)—$CH_3CH{=}CDCH_2OH$	13	95	5	—
(IV) (E)—$CH_3OH{=}CHCD_2OH$	13	100	<2	<2
(E)—$CH_3CH{=}CHCD_2OH$	18	100	<2	<2
(Z)—$CH_3CH{=}CHCD_2OH$	18	100	<2	<2
(V) (E)—$CH_3CH{=}CHCH_2OD$	18	<2	100	—
(Z)—$CH_3CH{=}CHCH_2OD$	18	<2	100	—

On the basis of these results, we conclude that the loss of water from the 2-buten-1-ols occurs largely by the pathway of Scheme 3, with limited intervention of hydrogen randomization and/or alternate pathways in some cases.



SCHEME 3

m/e 43

The peak at *m/e* 43 in the unlabeled alcohol is a doublet with the major component having the composition C_2H_3O. At beam energies below 20 eV this component is the only significant ion in this region of the spectrum. The relative intensities of the oxygenated ions in the region *m/e* 41 to 47 are given in Table 6 for the alcohols I to IV. Inspection of Table 6 indicates that at 70 eV there must be at least *two* major pathways for the formation of the ion $[C_2H_3O]^+$. This is seen most clearly in the case of compound II, where there are substantial intensities corresponding to the ions $[C_2H_3O]^+$ (*m/e* 43) and $[C_2D_3O]^+$ (*m/e* 46), with smaller (albeit still appreciable) intensities for ions intermediate in deuterium content between these two. The calculated values shown in Table 6 are for an equal contribution of two reaction pathways, A and B. Pathway A is postulated to involve retention of the intact terminal methyl group in the ion $[C_2H_3O]^+$, while pathway B is proposed to involve retention of the three hydrogens on C-1 and C-2 in this ion. Although the observed and calculated values in Table 6

TABLE 6. RELATIVE INTENSITIES OF OXYGEN-CONTAINING IONS IN THE RANDE *m/e* 41 TO 48 FOR THE (E)-2-BUTEN-1-OLS I TO IV[a]

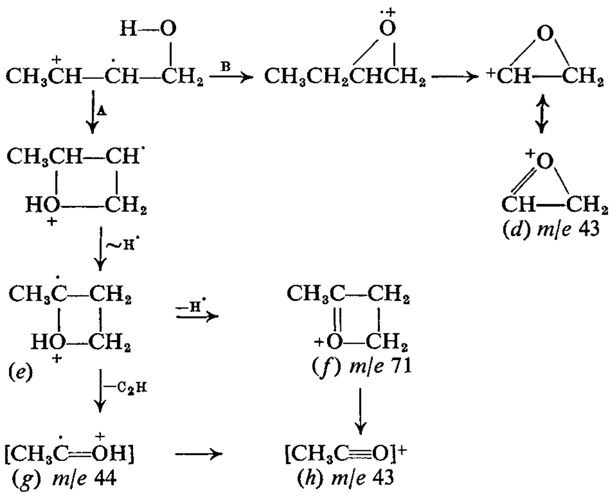
Compound		*m/e*							
		48	47	46	45	44	43	42	41
(I) $CH_3CH{=}CHCH_2OH$	70 eV				086	152	703	051	008
	13 eV					098	898	007	
(II) $CD_3CH{=}CHCH_2OH$									
70 eV obs.			011	328	151	171	296	036	007
calc.[b]		036	068	322	050	088	355	026	004
13 eV obs.				620	159	050	171		
calc.[c]			066	609	057	037	230	002	
(III) $CH_3CH{=}CDCH_2OH$									
70 eV obs.					198	343	414	036	004
calc.[b]				033	111	366	449	034	005
13 eV obs.				025	150	200	625		
calc[c]					019	253	723	005	
(IV) $CH_3CH{=}CHCD_2OH$									
70 eV obs.				165	338	170	308	019	
calc.[b]			040	072	373	116	363	026	003
13 eV observed				068	124	124	684		
calc.[c]				023	211	084	673	004	

[a] Peak intensities corrected for ^{13}C and normalized to 1000 in the region of interest.

[b] Calculated for 50% contribution by pathways A and B: see text for details.

[c] Calculated for 75% contribution by pathway A and 25% contribution by pathway B.

are not in perfect agreement, their general correspondence is close enough to suggest that the two pathways must both contribute substantially to the overall fragmentation. Whether the deviations between the observed and calculated values are due to partial hydrogen randomization during fragmentation or to contributions from other pathways cannot be determined on the basis of the available evidence.



SCHEME 4

Mechanisms which satisfy the available labeling evidence are indicated in Scheme 4 (I → *d* and I → *h*). Evidence for the two subpathways of pathway A (I → *e* → *f* → *h* and I → *e* → *g* → *h*) as well as the direct pathway B is found in the observation of metastable peaks for the transitions *m*/*e* 72 → 43, 71 → 43 and 44 → 43 in the spectrum of the unlabeled alcohol. Although other pathways are not excluded by the available evidence, we believe that the two mechanisms proposed offer a consistent interpretation of the fragmentations leading to the $[C_2H_3O]^+$ ions.

At lower beam energies pathway A increases in importance relative to pathway B. The calculated values in Table 6 at 13 eV are for a 75% contribution by pathway A and 25% by B; although the agreement is again not perfect, it nevertheless serves to indicate that the major fragmentation of the alcohols at low beam energies must involve pathway A.

In conclusion, this study demonstrates the common occurrence of fragmentation processes involving multiple reaction pathways. In two of the fragmentations discussed, those leading to the ions at *m*/*e* 57 and 43, the occurrence of multiple pathways was demonstrated by deuterium labeling evidence, and while the detailed mechanisms proposed may be subject to revision, there is no doubt that multiple pathways are an important feature of the fragmentation of even a simple molecule like 2-buten-1-ol. Further corroboration of this conclusion is obtained from a study of Scheme 1, which clearly shows the importance of multiple pathways in the genesis of most of the ions formed from this molecule.

EXPERIMENTAL

All mass spectra were determined on an AEI MS-902 double focusing mass spectrometer, with sample insertion via an all glass heated inlet system. Spectra were run at a resolution of 5000, sufficient to resolve hydrocarbon ions from oxygenated ions and exact mass measurements were obtained on all the ions discussed in this paper. Metastable peaks were observed for all the transitions discussed.

Unlabeled 2-buten-1-ol was obtained from Eastman Organic Chemicals as a 25:75 mixture of Z and E alcohols. Separation of these isomers and of the isomeric deuterated alcohols was achieved by preparative gas liquid chromatography (g.l.p.c.) on a $\frac{3}{8}$ in × 12 ft 1:1 carbowax: $\beta\beta'$-oxydipropionitrile column at 90 °C.

4-d$_3$-2-*Buten*-1-*ols* (II). 2-d_3-Acetaldehyde in 98·8% isotopic purity (by n.m.r.) was prepared by the method of Baldwin and Pudussery.[18] A mixture of carbomethoxymethylenetriphenylphosphorane[19] (0·0387 mol) and 2-d_3-acetaldehyde (0·0387 mol) in 50 ml of ethylene glycol was stirred for 12 h, during which time the temperature reached 40 °C. Distillation of the reaction mixture afforded a mixture (b.p. 80 to 115 °C) of 73% E and 27% Z methyl crotonates, as indicated by g.l.p.c. on a $\frac{1}{8}$ in, 10% carbowax column. Reduction of the esters was achieved by the method described by Fieser,[20] to yield a mixture of Z and E 4-d_3-2-buten-1-ols. The isomers were separated by preparative g.l.p.c. The n.m.r. spectra of the deuterated alcohols indicated the absence of the absorption due to the methyl protons (at 1·63 ppm in the unlabeled alcohol). Low electron energy (10 eV) mass spectra of the alcohols indicated deuterium incorporation to be as follows: 89·9% d_3, 7·6% d_2, 1·7% d_1, 0·8% d_0.

2-d$_1$-2-*Buten*-1-*ols* (III). The procedure used was similar to that described above for 4-d_3-2-buten-1-ol, except that unlabeled acetaldehyde was used and the carbomethoxymethylenetriphenylphosphorane used was pre-exchanged with deuterium oxide (3 ×) and recrystallized prior to use; *O*-d_2-ethylene glycol was used as the solvent. The 2-d_1-methyl crotonate obtained was reduced to yield a mixture of Z and E 2-d_1-2-buten-1-ols, which were shown by low electron energy (10 eV) mass spectra to have a deuterium incorporation of 77·8% d_1, 22·2% d_0.

1-d$_2$-2-*Buten*-1-*ols* (IV). Reduction of a mixture of Z and E methyl crotonates with lithium aluminum deuteride gave a mixture of Z and E 1-d_2-2-buten-1-ols, which was separated by g.l.p.c. and shown by low electron energy mass spectra (10 eV) to have a deuterium incorporation of 93·5% d_2, 4·2% d_1, 2·3% d_0.

1-O-d$_1$-2-*Buten*-1-*ols* (V). The *O*-deuterated alcohols were prepared by exchange of the pure Z or E isomers with deuterium oxide in the inlet system and source of the mass spectrometer. The alcohol was admitted to the source via an all glass heated inlet system, followed by deuterium oxide. Repeated scans were taken until the *m/e* 73: *m/e* 72 ratio became constant. Low electron energy (10 eV) runs indicated deuterium incorporation of 75·7% d_1 for the Z alcohol and 71·1% d_1 for the E alcohol.

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