Dehydration of βγ-Unsaturated Alcohols in Dimethyl Sulphoxide †

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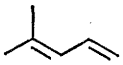
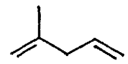
The dehydration of 2-methylpent-4-en-2-ol (V) by heating in dimethyl sulphoxide produced mixtures of the isomeric 2-methylpentadienes (I)—(IV), (I) and (II) being primary dehydration products and (III) and (IV) resulting from an acid-catalysed rearrangement of (I). Deuterium labelling experiments have shown that the acidic protons originate from the alcohol and not from dimethyl sulphoxide, and that the kinetic isotope effect for the formation of (II) is 2.4. Similar dehydration of 4-methylpent-4-en-2-ol (VI) produced the dienes (I), (III), and (IV), but not (II). The results suggest that an *E*2 rather than an *E*1 dehydration process is involved.

A CONVENIENT method for the preparation of 4-methylpenta-1,3-diene (I) involves acid-catalysed dehydration of the commercially available 2-methylpentane-2,4-diol.[1-3] The dehydration product consists of a mixture of 2-methylpenta-1,3-diene (III) (80%) and 4-methylpenta-1,3-diene (I) (20%), and the latter is isolated *via* formation of the Diels–Alder adduct of the former with maleic anhydride.[2,3] Aniline hydrobromide has been commonly used as the dehydrating agent,[1,3] but more recently the same reaction was effected simply by heating the diol in dimethyl sulphoxide at 190 °C,[4] a fairly mild, convenient, dehydration procedure which has been shown to be applicable to secondary and tertiary benzylic alcohols, and tertiary aliphatic alcohols.[5] Both of the above dehydration conditions lead to preliminary elimination of the tertiary alcohol forming 4-methylpent-4-en-2-ol (VI), and probably 4-methylpent-3-en-2-ol also, followed by further dehydration to give the dienes.[1,4]


(I)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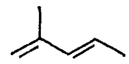
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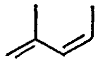
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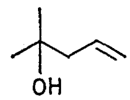
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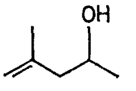
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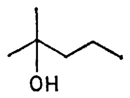
(VII)

However, in order to prepare samples of 4-methylpenta-1,3-diene labelled with deuterium ($^{2}H_{3}$ and $^{2}H_{6}$) in the methyl groups, which were required for n.m.r. spectroscopic analysis,[6] we chose to dehydrate the appropriately labelled 2-methylpent-4-en-2-ol (V) using the dimethyl sulphoxide procedure,[4,5] for two reasons: (i) the alcohols could be prepared from labelled acetone and allylmagnesium bromide, (ii) the dimethyl sulphoxide procedure was considered to be sufficiently mild to prevent exchange or scrambling of the deuterium in the resulting diene, either by an acid-catalysed process or by a thermal 1,5-migration of hydrogen.[3,6] While this approach did provide the labelled 4-methylpenta-1,3-dienes without significant loss or scrambling of deuterium,[6] the formation of *cis*- and *trans*-2-methylpenta-1,3-diene [(IV) and (III), respectively], the latter in significant amounts, together with the expected dehydration products, 2-methylpenta-1,4-diene (II) and 4-methylpenta-1,3-diene (I), was surprising, and was investigated further. The results of this study are reported here.

The distribution of products (I)—(IV) during the course of dehydration of alcohol (V) is given in the Table. The total peak area for the g.l.c. analysis indicated that dehydration was complete after 2—3 h and that the changes in the composition of the product mixture after that period were due solely to rearrangement of the dienes. Clearly, dienes (I) and (II) are the primary dehydration products, and dienes (III) and (IV) are formed by rearrangement of (I), the percentage of (II) remaining constant. However, when the dienes (I) and (II) were individually subjected to heating in dimethyl sulphoxide, neither rearranged to any of the other dienes. This suggested that perhaps the conditions present during these control experiments were not the same as those present during a dehydration. To check this, diene (I) was added to a solution of 2-methylpentan-2-ol (VII) in dimethyl sulphoxide at 170 °C, and under these conditions (I) was found to rearrange to (III) and (IV), but not to (II). Thus the dehydration process appears to produce species which catalyse the diene rearrangement.

Dehydration of 2-methylpent-4-en-2-ol (V)

t/h	1	2	16
Products (%)			
(I)	64	62	54
(II)	26	27	26.5
(III)	5.5	9	19
(IV)	4.5	2	0.5

Dehydration of 4-methylpent-4-en-2-ol (VI)

t/h	1	2	16
Products (%)			
(I)	9	15	41.5
(II)	0	0	0
(III)	69	77	57.5
(IV)	21.5	8	1

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† No reprints available.

[1] M. G. Dupont and M. Darman, *Bull. Soc. chim. France*, 1939, 1208.

[2] G. B. Bachman and C. G. Goebel, *J. Amer. Chem. Soc.*, 1942, **64**, 787.

[3] H. M. Frey and R. J. Ellis, *J. Chem. Soc.*, 1965, 4770.

[4] V. J. Traynelis, W. L. Hergenrother, H. T. Hanson, and J. A. Valicenti, *J. Org. Chem.*, 1964, **29**, 123.

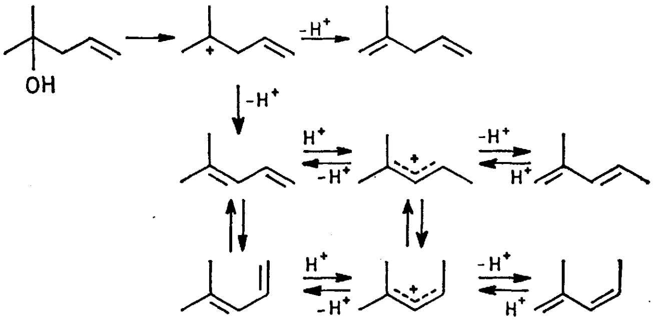
[5] V. J. Treynelis, W. L. Hergenrother, J. R. Livingston, and J. A. Valicenti, *J. Org. Chem.*, 1962, **27**, 2377.

[6] A. J. Bellamy and W. Crilly, *J.C.S. Perkin II*, 1972, 395; 1973, 122.

Recently Santosusso and Swern[7] have shown that when dimethyl sulphoxide is heated in the presence of air, small quantities of strong acids are produced, and that the dehydration of tertiary aliphatic alcohols is catalysed by these acidic components. When aniline was added to such a dehydration, the reaction still proceeded, albeit more slowly, but when freshly prepared sodium n-octoxide was added no dehydration occurred; both potassium t-butoxide and sodium carbonate also prevented dehydration. It had previously been reported that the addition of aniline and sodium n-octoxide had no appreciable effect upon the dehydration,[4] and it was therefore concluded[4] that the dehydration could not be acid catalysed. However the positive identification of sulphuric acid amongst the dehydration products,[7] and the complete inhibition of dehydration when freshly prepared sodium n-octoxide was added[7] argues strongly in favour of an acid-catalysed dehydration process. The presence of strong acids in a dehydration mixture would readily account for the isomerisation of (I) to (III) and (IV), by a simple protonation–deprotonation mechanism. When a solution of alcohol (V) in dimethyl sulphoxide over molecular sieve (4A) was heated at 170 °C no dehydration had occurred after 16 h, but when the molecular sieve was removed the dehydration proceeded normally. It thus appears that the molecular sieve can absorb those species which are necessary for catalysing the dehydration. When a small quantity of aniline was added to a solution of (V) in dimethyl sulphoxide, very little dehydration had occurred after 16 h at 170 °C; the small amount of diene which had formed was almost entirely a mixture of (I) and (II) (3 : 1). The formation of anilinium salts would be expected to reduce the rate of dehydration of (V) and also the rearrangement of (I) if these processes were catalysed by strong acids.

In order to determine which component(s) in a dehydration mixture was responsible for the production of protons and to shed further light upon the dehydration–rearrangement mechanism, several deuterium-labelled experiments were performed. These were (i) dehydration of (V) in [$^{2}H_{6}$]dimethyl sulphoxide, (ii) dehydration of 1,1,1-trideuterio-2-trideuteriomethylpent-4-en-2-ol {[$^{2}H_{6}$](V); from [$^{2}H_{6}$]acetone and allylmagnesium bromide} in dimethyl sulphoxide, and (iii) dehydration of *O*-deuterio-2-methylpent-4-en-2-ol {[^{2}H](V)} in dimethyl sulphoxide. The dehydrations were performed under normal conditions (170 °C; 16 h) and the dienes produced were analysed by g.l.c.–m.s. None of the dienes produced in experiment (i) showed deuterium incorporation. From experiment (ii), diene (I) was predominantly $^{2}H_{6}$, with smaller amounts of $^{2}H_{5}$ and $^{2}H_{4}$, diene (II) was $^{2}H_{5}$ only, while dienes (III) and (IV) both showed a considerable degree of deuterium loss by exchange, being largely $^{2}H_{2}$—$^{2}H_{5}$. Finally experiment (iii) gave (I) which was largely $^{2}H_{0}$ with increasingly smaller amounts of $^{2}H_{1}$—$^{2}H_{5}$, (II) with no deuterium incorporation, and (III) and (IV) with considerably more deuterium incorporation than (I), $^{2}H_{0}$—$^{2}H_{5}$. The difference in product distribution in experiment (ii) compared with that from undeuteriated (V) reflects the slower rate of cleavage of C–D relative to C–H bonds, leading to less (II) (16.5 *versus* 32%)[6] (see later).

The results from experiments (i) and (iii) indicate that the protons involved in the interconversion of (I), (III), and (IV) originate from the OH group of the alcohol and not from dimethyl sulphoxide, while the results from experiments (ii) and (iii) confirm that (II) is formed irreversibly and that (I) alone is involved in a protonation–deprotonation interconversion with (III) and (IV) (Scheme 1). Protonation at C(1) in (I) would produce two, possibly interconverting, isomeric allylic cations, which on elimination of a proton from one of the geminal dimethyl groups would produce (III) and (IV). The stability of (II) is presumably related to the higher energy carbenium ions which would be formed on protonation of either double bond. Although the first step in the dehydration is represented as the formation of a tertiary carbenium ion,[4,5] an *E*2-type elimination is also a possibility;[8a] an α′β elimination from an *S*-alkoxysulphonium ylide would be unlikely in view of the results from experiment (i) (*cf.* the Kornblum reaction).[8b]



SCHEME 1

Two other alternative mechanisms for the formation of (III) and (IV) were considered. Diene (I) is known to undergo a unimolecular, thermal isomerisation to (IV) *via* a suprafacial 1,5-migration of hydrogen.[3,6] However, although the known rate constant for this isomerisation (gas phase)[3] could accommodate the rate at which (I) is isomerised if the temperature of the dienes was maintained at 170 °C, the necessary accompanying thermal isomerisation of (IV) to (III) is too slow[3,9] to account for the observed distribution of products after 16 h. In any case, once generated, the dienes tend to accumulate in the condenser (b.p. <80 °C) so that the mean temperature experienced by the dienes would be considerably below 170 °C. Furthermore, such a process would have to be accompanied by a protonation–deprotonation reaction in order to accommodate the

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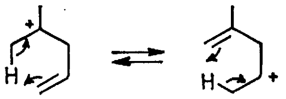
[7] T. M. Santosusso and D. Swern, *J. Org. Chem.*, 1976, **41**, 2762.

[8] ' Organic Chemistry of Sulphur,' ed. S. Oae, Plenum, New York, 1977 (*a*) p. 424; (*b*) pp. 419 and 502.

[9] H. M. Frey, A. M. Lamont, and R. Walsh, *Chem. Comm.*, 1970, 1583.

deuterium distribution in (III) and (IV) from experiments (ii) and (iii).

The second alternative mechanism for generating (III) and (IV) involves rearrangement of a tertiary carbenium ion generated in the dehydration process (Scheme 2). The less stable secondary carbenium ion thus formed could eliminate a proton to give (II)—(IV). This mechanism could be rejected on the basis of experiment (ii) since if (II) were formed by this route to any extent then some $^2H_6$ species should be formed; the results clearly showed that $^2H_5$ was the only species formed. However, we thought it worthwhile to study the dehydration of 4-methylpent-4-en-2-ol (VI), since this alcohol is an intermediate in the dehydration of 2-methylpentane-2,4-diol,[1,4] and (VI) might lead directly to the secondary carbenium ion and indirectly to the tertiary carbenium ion (Scheme 2).

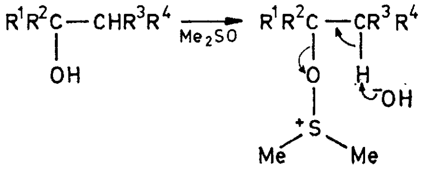


SCHEME 2

As shown in the Table, dehydration of alcohol (VI) gave (III) and (IV) as primary products, and (I) by subsequent rearrangement of (III) and (IV). Surprisingly, but in agreement with previous work,[4] no (II), the other expected primary product, was formed. If the process shown in Scheme 2 were operating, the same products, particularly (II), would be formed, and we therefore conclude that Scheme 2 is not important in the dehydration of either alcohol. As in the dehydration of alcohol (V), the dehydration of alcohol (VI) appeared, from the peak area of the g.l.c. analysis, to be complete after 2—3 h.

The absence of (II) from the dehydration products of (VI), and the stability of (II) once it is formed in the dehydration of (V), could be taken as evidence that free localised, carbenium ions are never formed in the dehydration step, particularly in the case of (VI), and that some form of *E*2-elimination is operating. One possible process is shown in Scheme 3,[8a] while a simple acid-catalysed elimination involving the protonated alcohol and a base is a further possibility. Cleavage of the C–O bond in (VI) is expected to be more difficult than in (V); secondary alcohols are reported to be unreactive under the dimethyl sulphoxide dehydration conditions.[5] In this situation it would be more important that C–H bond cleavage assists cleavage of the C–O bond in (VI) than in (V), and an activated C–H bond, *i.e.* allylic, will be better able to perform this function. We therefore feel that elimination from (VI) probably involves concerted C–O and C–H bond cleavage and is unfavourable for the formation of (II), while elimination from (V) is less dependent upon concerted cleavage of the C–H bond.

Since (II) is only formed by the primary dehydration process and is formed irreversibly, the percentages of (II) from (V) (32%) and [$^2H_6$](V) (16.5%) may be used to calculate the kinetic isotope effect favouring C–H *versus* C–D bond cleavage in the dehydration process to give (II). If we assume that the rate of elimination to give (I) [+ (III) and (IV) as secondary products] is unaffected by the isotopic substitution, then k_{CH}/k_{CD} is 2.4. In a similar manner the percentage of 2-methylpent-1-ene formed by dehydration of alcohols (VII) (44%) and [$^2H_6$](VII) (28.5%) *versus* the percentage of the only other product, 2-methylpent-2-ene, gave k_{CH}/k_{CD} for the formation of 2-methylpent-1-ene as 2.0. In the latter case it was assumed, by analogy with (II), that 2-methylpent-1-ene is only formed by the primary dehydration process and is formed irreversibly. The two values are in reasonable agreement, as might be expected since the presence or absence of a βγ-double bond in the alcohol is unlikely to affect elimination into the terminal position. The observation of a kinetic isotope effect, which will be the sum of both primary and secondary effects, does not of course necessarily mean that the cleavage of the C–H and C–O bonds is concerted; an *E*1 elimination would exhibit an isotope effect in the non-rate-determining step and hence also affect the product distribution.



SCHEME 3

EXPERIMENTAL

2-*Methylpent*-4-*en*-2-*ol* (V).—Reaction of allylmagnesium bromide [from allyl bromide (0.5 mol) and magnesium (0.75 g atom)] with acetone (0.38 mol) in ether at 20 °C, gave the alcohol (71%), b.p. 44 °C at 27 mmHg (lit.,[10] 46—46.5 °C at 30 mmHg), which was shown to be pure by g.l.c., δ(CCl_4) 1.15 (s, Me_2), 2.15 (d, *J* 8 Hz, $CH_2{=}CHCH_2$), 2.3 (s, OH), 5.0 (m, $CH_2{=}CH$), and 5.8 (m, $CH_2{=}CH$).

O-Deuterio-2-methylpent-4-en-2-ol was prepared from the parent alcohol by shaking twice with deuterium oxide (2 × 10 mol. equiv.), separating the alcohol and drying over molecular sieve.

1,1,1-Trideuterio-2-trideuteriomethylpent-4-en-2-ol was prepared in the same manner as the parent alcohol using [$^2H_6$]acetone. The n.m.r. spectrum was identical except that the singlet at δ 1.15 was absent.

4-*Methylpent*-4-*en*-2-*ol* (VI).—The alcohol was prepared by treating 2-methylallylmagnesium chloride [from 2-methylallyl chloride (0.25 mol)] with acetaldehyde (0.20 mol) in ether. The product was a mixture of 4-methylpent-4-en-2-ol and 2,5-dimethylhexa-1,5-diene in the ratio 4 : 1. The latter is the by-product of the reaction generating the Grignard reagent, and was identified by g.l.c.–m.s. (*m/e* 110) and n.m.r. spectroscopy. The alcohol had δ 1.15 (d, *J* 6 Hz, CH_3CHOH), 1.7 (m, $CH_2{=}CCH_3$), 2.1 (m, CH_2CHOH), 3.1br (s, OH), 3.9 (m, CHOH), and 4.7 (m, $CH_2{=}CCH_3$); the presence of the diene produced no further absorptions. It was found to be unnecessary to separate the alcohol from the diene for the dehydration studies.

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[10] H. R. Henze, B. B. Allen, and W. B. Leslie, *J. Org. Chem.*, 1942, **7**, 326.

2-*Methylpentan*-2-*ol* (VII).—The alcohol was prepared [11] by reacting propylmagnesium bromide with acetone, and had b.p. 121—123 °C (lit.,[11] 121—124 °C).

1,1,1-Trideuterio-2-trideuteriomethylpentan-2-ol was prepared in a similar manner using [$^2H_6$]acetone.

Dehydration Procedure.—The dimethyl sulphoxide was purified by refluxing over calcium hydride for 4 h followed by distillation under reduced pressure, b.p. 88 °C at 3 mmHg. A solution of the alcohol in dimethyl sulphoxide (1 : 5 v/v), contained in a flask fitted with a reflux condenser and a calcium chloride tube to minimise losses of the volatile products, was heated in an oil-bath at 170 °C for the required period. For those reactions which were sampled periodically, samples (0.5 ml) were withdrawn (after cooling the mixture) and were added to water (1.0 ml); the products were then extracted into pentane (0.5 ml). When the products were analysed only at the end of the full reaction period the products were distilled directly from the mixture (170 °C) and were collected in a trap at −80 °C. The products were analysed by g.l.c. using a column of polypropylene carbonate at 20 °C.

The products from dehydrating alcohols (V), (VI), and (VII) were identified by (a) n.m.r. spectroscopic analysis after isolation by preparative g.l.c., *viz.* (I) and (II) [6] and both alkenes from (VII), (b) comparison with dehydration mixtures formed under different dehydration conditions,[3] and (c) comparison with samples synthesised by alternative methods, *viz.* (III) [12] and (IV).[3,6]

(i) 2-*Methylpent*-4-*en*-2-*ol* (V). Three separate experiments (170 °C for 14 h) gave the following distribution of products: [% (I), (II), (III), (IV)] (a) 42.4, 32.3, 24.4, 0.9, (b) 46.6, 30.8, 22.0, 0.6, (c) 40.6, 32.5, 26.4, 0.5; average 43.2, 31.9, 24.2, 0.7 (lit.,[6] 42.9, 31.8, 23.9, 1.4). The distribution of products as a function of time is given in the Table. Dehydration of [$^2H_6$](V) gave 61.1, 16.6, 20.5, and 1.8% respectively.[6] The mass spectra of the dienes generated by dehydrating alcohols (V), [$^2H_1$](V), and [$^2H_6$](V) in dimethyl sulphoxide were recorded by m.s.–g.l.c. The dienes generated by dehydrating (V) in [$^2H_6$]-dimethyl sulphoxide gave the same mass spectra as those formed using undeuteriated dimethyl sulphoxide, *viz. m/e* 82 (*P*).

A solution of the alcohol (0.5 ml) in dimethyl sulphoxide (2.0 ml) was added to a small quantity of freshly activated molecular sieve (4A), and the mixture was heated at 170 °C for 16 h. G.l.c. analysis of a sample (0.5 ml) withdrawn after this time indicated that no dehydration had occurred, although the normal yellow colour had developed. The molecular sieve was then removed and the heating was continued for 6 h giving the dienes in 68, 18, 13, and 1% yield respectively.

Aniline (3 drops) was added to a solution of the alcohol (0.5 ml) in dimethyl sulphoxide (2.0 ml), and the solution was then heated at 170 °C for 16 h. The overall yield of dienes was extremely low and analysed as 73, 22, 2, and 2% yield, respectively.

(ii) 4-*Methylpent*-4-*en*-2-*ol* (VI). Heating at 165 °C for 14 h gave the following distribution of products: [% (I), (II), (III), (IV)] 37.5, 0, 57.5, 5.

A solution of the alcohol (0.5 ml) in dimethyl sulphoxide (2.0 ml) was added to a small quantity of freshly activated molecular sieve (4A) and the mixture was heated at 170 °C for 2 h. No dehydration had occurred after this time. The molecular sieve was removed and heating was continued. The distribution of products as a function of time is given in the Table.

(iii) 2-*Methylpentan*-2-*ol* (VII). Four separate experiments (170 °C for 14 h) gave 2-methylpent-1-ene and 2-methylpent-2-ene in the following percentages (a) 43.0, 57.0, (b) 46.9, 53.1, (c) 43.1, 56.9, (d) 42.5, 57.5%; average 43.9 and 56.1%, respectively. The overall yield of the distilled products was 60%. For comparison, 2-methylbutan-2-ol gives 2-methylbut-1-ene (41%) and 2-methylbut-2-ene (59%), and 2-methylhexan-2-ol gives 2-methylhex-1-ene (46%) and 2-methylhex-2-ene (54%).[5]

The dehydration of [$^2H_6$](VII) in four separate experiments (170 °C for 14 h) gave the following distribution of products: (a) 26.5, 73.5, (b) 30.2, 69.8, (c) 29.4, 70.6, (d) 28.4, 71.6%; average 28.6 and 71.4%, respectively.

Behaviour of Primary Dehydration Products (I) *and* (II) *under Dehydration Conditions*.—Samples of 4-methylpenta-1,3-diene (I) and 2-methylpenta-1,4-diene (II) were heated separately in dimethyl sulphoxide at 170 °C for 24 h. G.l.c. analysis after this time indicated that neither diene had rearranged.

A sample of (I) was added to a solution of alcohol (VII) (2.5 ml) in dimethyl sulphoxide (14 ml), and the solution was heated at 165 °C for 14 h. G.l.c. analysis of the isolated products indicated that besides the expected dehydration products of alcohol (VII), the diene (I) had rearranged to a mixture of (I) (72.5%), (III) (24.5%), and (IV) (3.0%); no (II) was formed.

A similar experiment performed in [$^2H_6$]dimethyl sulphoxide and analysed by g.l.c.–m.s. indicated that neither the alkenes formed from alcohol (VII), nor the dienes present after rearrangement of (I) contained deuterium.

[8/120 *Received*, 24*th January*, 1978]

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[11] A. I. Vogel, 'Practical Organic Chemistry,' Longman, London, 1956, 3rd edn., p. 258.

[12] W. Crilly, Ph.D. Thesis, Edinburgh, 1972.