# The Acid Catalysed Hydration of Sabinene and α-Thujene

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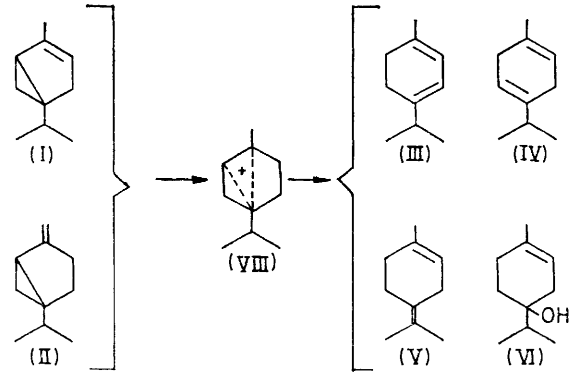
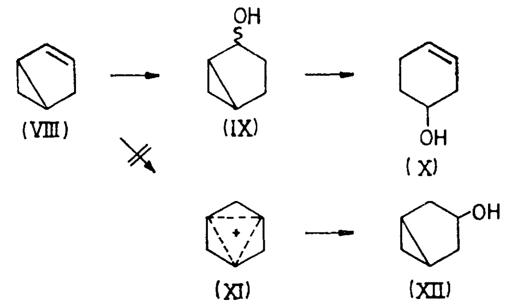
The kinetics and products of the acid catalysed hydration of sabinene (1-isopropyl-4-methylenebicyclo[3.1.0]hexane) and α-thujene (1-isopropyl-4-methylbicyclo[3.1.0]hex-3-ene) have been studied. The reactions proceed through a common carbonium ion, the rates of formation of which can be correlated with the ground state energies of the olefins.

In an extension of earlier work on the effect of ion pairing on the stereochemistry of olefin hydration,[1] we have investigated the hydration of the isomeric olefins, α-thujene (1-isopropyl-4-methylbicyclo[3.1.0]-hex-3-ene) (I) and sabinene (1-isopropyl-4-methylenebicyclo[3.1.0]hexane) (II) under conditions which minimise the effects of ion pairing. With acids,[2] both olefins are known to yield a mixture of α-terpinene (III), γ-terpinene (IV), terpinolene (V), and terpinen-4-ol (VI). These products are believed to arise *via* the ion (VII).



An investigation[3,4] of the reaction of bicyclo[3.1.0]-hex-2-ene (VIII) with acids in acetic acid or methanol



showed that the initially-formed addition product was a derivative of bicyclo[3.1.0]hexan-2-ol (IX) which subsequently rearranged to a derivative of cyclohexen-4-ol (X). No trace of reaction *via* a trishomocyclopropenyl cation (XI) to give (XII) was detected even though (XII) is stable under the reaction conditions.

Recent work[5] has indicated that α-thujene and sabinene react through the same ion, which is not a trishomocyclopropenyl cation, while a later paper[6] has indicated quantitative product differences from the two olefins. The terpinen-4-ol (VI) produced from optically active α-thujene has been shown to retain 80% of the optical activity of the starting material.[6]

## EXPERIMENTAL

*Materials.*—α-Thujene was distilled from *Eucalyptus dives* oil at 86 °C and 86 mmHg using a spinning band column; we are grateful to Dr. D. V. Banthorpe, University College London, for a gift of sabinene which had been distilled from oil of Savin. Samples of *p*-menthadienes were obtained by methods described earlier,[7] and terpinen-4-ol was a commercial sample. Sabinyl acetate was obtained from a sample of oil of Savin (supplied by Dr. D. V. Banthorpe), by preparative g.l.c., and was converted into sabinol by lithium aluminium hydride reduction.

*Analysis.*—Analysis of product mixtures was by g.l.c. Analytical work was carried out on a Perkin-Elmer F.11 chromatograph, with a 14 ft packed glass capillary column, 15% Carbowax 20 M on Chromosorb W at 170°. For confirmation of identities samples were separated on a Pye 105 chromatograph, with a 30 ft × $\frac{3}{8}$ in column, 25% Carbowax 20M on Chromosorb W at 210°, and identified by comparison of i.r. spectra with those of known samples.

*Kinetics.*—The solvent used for all kinetic studies was dioxan–water (80 : 20 v/v), made by weight. Extraction and g.l.c. analytical procedures were similar to those described earlier.[7]

## RESULTS AND DISCUSSION

$^1$H *N.m.r. Spectroscopic Results.*—The n.m.r. spectra of α-thujene and sabinene were recorded at 220 MHz. We were unable to analyse fully the spectrum of sabinene, but we suggest it has a conformation similar to that of sabinol (XIII) which we have analysed.† Details of the n.m.r. spectra of (I) and (XIII) are given in Table 1.

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† In support of this suggestion, we note that in the pinocarveol series, where steric requirements are quite similar to the present case, the substitution of OH for H causes insignificant changes in the conformation.[8]

[1] C. M. Williams and D. Whittaker, *J. Chem. Soc.* (*B*), 1971, 672.

[2] G. A. Tolstikov, L. N. Lishtranova, and M. I. Goryaev, *Zhur. obshchei Khim.*, 1963, **33**, 683.

[3] P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, 1965, **30**, 771.

[4] P. K. Freeman, F. A. Raymond, and M. F. Grostic, *J. Org. Chem.*, 1967, **32**, 24.

[5] D. V. Banthorpe and H. ff. S. Davies, *J. Chem. Soc.* (*B*), 1968, 1339.

[6] T. Norin and L-Å. Smedman, *Acta Chem. Scand.*, 1971, **25**, 2010.

[7] C. M. Williams and D. Whittaker, *J. Chem. Soc.* (*B*), 1971, 668.

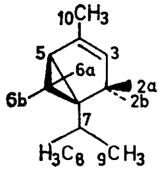
[8] R. J. Abraham, M. A. Cooper, H. Indyk, and D. Whittaker, to be published.

The analysis of the spectrum of α-thujene is straightforward except that the assignments of H(5) and H(6b) are ambiguous. We assign H(5) as the low field resonance on the grounds that it is next to the double bond and also because in bicyclo[*n*.1.0]alkanes the bridgehead protons are to low field of the cyclopropane $CH_2$ resonances.[9]

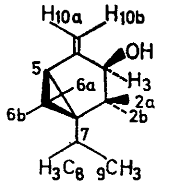
We should expect α-thujene to adopt a conformation such that C(1)–C(5) lie in a plane, since the rigid cyclopropane ring will hold the C(1)–C(2) and C(4)–C(5) bonds coplanar, while the double bond will similarly impose planarity on the fragment C(2)–C(5). The n.m.r. data support this on the following grounds. First, the vicinal couplings $J_{2a,3}$ and $J_{2b,3}$ are equal, being $2{\cdot}0 \pm 0{\cdot}3$ Hz. Secondly, the homoallylic couplings $J_{2a,10Me}$ and $J_{2b,10Me}$ are equal at $2{\cdot}2 \pm 0{\cdot}3$ Hz. Thirdly, the large value of $J_{2a,2b} = |17{\cdot}0|$ Hz suggests enhancement[10] from hyperconjugation with the *p* orbital of C(3). While the n.m.r. evidence does not prove that the conformation of the C(1)—C(5) fragment is perfectly planar, it does rule out any large deviation from planarity.

TABLE 1

$^1$H N.m.r. parameters of α-thujene[a] and sabinol[b]



(I)



(XIII)

Chemical shifts [δ (p.p.m.)]

| H | 2a | 2b | 3 | 5 | 6a | 6b | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| (I) | 2·34 | 2·11 | 4·89 | 1·30 | −0·02 | 0·68 | 1·41 | 0·87, | 0·92 | 1·70 |
| (XIII) | 1·80 | 2·03 | 4·36 | 1·61 | 1·05 | 0·76 | 1·42 | 0·93, | 0·86 | 4·87, 4·93 |

Coupling constants (Hz)

| | $J_{2a,2b}$ | $J_{2a,3}$ | $J_{2b,3}$ | $J_{5,6a}$ | $J_{5,6b}$ | $J_{6a,6b}$ | $J_{7,8Me}$ | $J_{7,9Me}$ |
|---|---|---|---|---|---|---|---|---|
| (I) | 17·0 | 2·0 | 2·0 | 3·0 | 7·5 | 3·0 | 7·0 | 7·0 * |
| (XIII) | 14·0 | 1·0 | 7·2 | 3·2 | 6·5 | 4·4 | 7·0 | 7·0 † |

* $J_{2a,10Me}$ 2·2; $J_{2b,10Me}$ 2·2; $J_{3,10Me}$ 1·6 Hz. † $J_{2b,6b}$ 2·2; $J_{3,10a} = J_{3,10b} \leqslant$ *ca.* 1; $J_{10a,10b} \leqslant$ *ca.* 1 Hz.

[a] For $CS_2$ solution. [b] For $CDCl_3$ solution.

The spectroscopic data on sabinol given in Table 1 are fully consistent with C(5) being bent upwards towards H(6a), such that the dihedral angle between the planes C(1), C(2), C(4), C(5) and C(2)—C(4) is *ca.* 160°. This gives a dihedral angle between the bonds C(3)–H(3) and C(2)–H(2a) of *ca.* 90° and between C(3)–H(3) and C(2)–H(2b) of *ca.* 30°, in accord with the relative magnitude of $J_{2a,3}$ ($\leqslant 1$ Hz) and $J_{2b,3}$ (7·2 Hz). The boat conformation (possibly a flexible boat) so deduced is in agreement with earlier work[3] on the *cis*- and *trans*-bicyclo[3.1.0]hexan-3-ols. Thus, the replacement of an $sp^3$ by an $sp^2$ hybridised carbon atom at C(2) in the bicyclo[3.1.0]hexane system does not greatly affect the conformation.

The kinetic and product data on the hydration of sabinene and α-thujene are given in Tables 2 and 3. Our data differ from those reported by Norin[6] in that we have found sabinene to react more slowly than reported, and also we have obtained a greater yield of terpinen-4-ol from α-thujene. Our data are self consistent, and we can offer no explanation of these differences.

From the data in Table 2, we calculate the solvent deuterium isotope effect for α-thujene hydration $k_H/k_D = 1{\cdot}84$, consistent with rate determining protonation of the olefin. The rate of reaction of α-thujene exceeds that of the corresponding double bond of limonene[7] by a

TABLE 2

Kinetics of hydration of α-thujene and sabinene in dioxan–water (80 : 20 v/v), catalysed by sulphuric acid

| | | $10^5k_1/s^{-1}$ at | | | |
|---|---|---|---|---|---|
| Olefin | [Acid]/M | 25° | 35° | 45° | 50° |
| α-Thujene | 0·0102 | | | 1·34 | |
| | 0·048 | | | | 8·47, 4·60 † |
| | 0·103 | 1·17 | 4·58 | 16·5 | |
| Sabinene | 0·0102 | 2·61 | 9·37 | 30·7 | |

† Rate in $D_2O$–dioxan.

For α-thujene hydration $\Delta H^* = 24{\cdot}7$ kcal mol$^{-1}$; for sabinene hydration $\Delta H^* = 22{\cdot}5$ kcal mol$^{-1}$.

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[9] W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, 1967, **32**, 2977.

[10] M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, 1963, **85**, 1899.

factor of $10^3$ and the rate of reaction of sabinene exceeds that of the vinyl group of limonene by *ca.* $2 \times 10^3$.

Sabinene is hydrated more rapidly than α-thujene by a factor of 22·9 at 45°. At least part of this rate difference can be attributed to the difference in the ground state energies of the two olefins, which we calculate to be 1·3 kcal mol$^{-1}$ from the observation that the equilibrium mixture is 9% sabinene and 91% α-thujene. The energy difference is smaller than that found between α-pinene and β-pinene, and on the basis of this, together with hydrogenation and hydroboration data, Brown[11] has suggested that sabinene is stabilised by greater conjugation between the double bond and the cyclopropane ring. Our data on the conformations of the olefins support this view. Since sabinene is boat-shaped, with C(3) approaching H(6a), while α-thujene has an essentially planar cyclopentane ring, we should expect differences in the extents of cyclopropane–double bond conjugation in the two cases. The most favourable circumstances for this conjugation in a strain free system is believed to be when the cyclopropyl methinic C–H bond is perpendicular to the plane of the *p* lobes of the double bond.[12] In a strained system such as α-thujene or sabinene, the position is less clear because of distortion of bond angles at C(5). Nevertheless, it is probable that the same criteria for maximum conjugation still apply as in the strain free case. Examination of Dreiding molecular models suggests that the cyclopropane–double bond overlap is more favourable in the case of sabinene than in the case of α-thujene.

TABLE 3

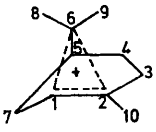
Products of hydration of α-thujene and sabinene in dioxan–water (80 : 20 v/v) containing 0·0102M-sulphuric acid at 45°

| | Unchanged olefin | Composition of products (%) | | | |
|---|---|---|---|---|---|
| *t*/h | (%) | α-Terpinene | γ-Terpinene | Terpinolene | Terpinen-4-ol |
| α-Thujene | | | | | |
| 3 | 86 | 16 | 29 | 5 | 51 |
| 6 | 77 | 19 | 29 | 4 | 47 |
| 9 | 65 | 18 | 26 | 4 | 53 |
| 13·3 | 53 | 16 | 23 | 4 | 57 |
| 24 | 31 | 16 | 22 | 5 | 57 |
| 30 | 25 | 14 | 23 | 5 | 58 |
| 37 | 17 | 17 | 24 | 4 | 55 |
| Sabinene | | | | | |
| 0·25 | 88 | | | | |
| 0·5 | 74 | | | | |
| 0·75 | 54 | 15 | 21 | 3 | 60 |
| 1·0 | 43 | 13 | 25 | 2 | 59 |
| 1·5 | 26 | 14 | 22 | 2 | 62 |
| 2·0 | 15 | 15 | 25 | 3 | 60 |

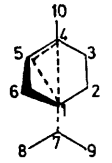
The products of reaction of the two olefins, listed for reactions under identical conditions in Table 3, indicate almost identical product compositions. These are close enough to confirm that α-thujene and sabinene do react *via* the same carbonium ion, the differences probably resulting from a small fraction of attack on the ion before it has reached its energy minimum.

If sabinene is hydrated at 25°, then the g.l.c. analysis shows an extra product occurring initially to 4% but rapidly disappearing. This product had a retention time close to that of terpinen-4-ol. From the work of Norin,[6] we suggest that it is probably either the *cis*- or *trans*-sabinene hydrate; a smaller peak nearby may well be the other isomeric alcohol.

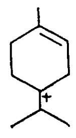
Our product data are consistent with the common intermediate in the hydration of sabinene and α-thujene being the ion (XV). This ion reacts in a manner which shows some similarity to reaction of the ion (XIV) produced from the pinenes.



(XIV)



(XV)



(XVI)

Reaction at C(2) (pinane) or C(4) (thujane) yields a tertiary alcohol with an unrearranged carbon skeleton,[4] which in either case is unstable and reverts to the ion; reaction at C(1) (pinane) is not duplicated by reaction at C(5) (thujane) since this would give the relatively unstable bicyclo[2.2.0]hexane system. Ring opening reactions are similar, attack of water at C(7) (pinane) or C(1) (thujane) giving rise to an alcohol. Since (XV) gives rise to terpinen-4-ol retaining 80% of the optical activity of the starting material, the ion must have a conformation similar to that drawn, so that attack of water is mainly from above, and optical activity is preserved. Ring opening could also take place spontaneously to give the ion (XVI), which has been shown[7] to yield α-terpinene, γ-terpinene, and terpinolene in the ratio 3 : 4 : 2; this should also yield racemic terpinen-4-ol, and so may be the source of the racemic fraction of the material referred to above. Reaction initiated by loss of a proton from C(6), C(2), or C(7) could also lead to the observed olefins, but there is no evidence to support this route.

In contrast to pinene hydration, ion (XV) does not eliminate by loss of a proton from C(3) to give thujene. Non-reversibility is, however, a common feature of olefin hydration reactions.[13]

[2/1792 *Received*, 31*st July*, 1972]

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[11] S. P. Acharya, H. C. Brown, A. Suzuki, S. Nozawa, and M. Itoh, *J. Org. Chem.*, 1969, **34**, 3015.

[12] B. R. Ree and J. C. Martin, *J. Amer. Chem. Soc.*, 1970, **92**, 1660.

[13] A. J. Kresge, Y. Chiang, P. H. Fitzgerald, R. S. McDonald, and G. H. Schmid, *J. Amer. Chem. Soc.*, 1971, **93**, 4907.