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STERIC DEUTERIUM ISOTOPE EFFECT IN THE SOLVOLYSIS OF (*Z*)-[*METHYL-D*$_3$]-2-ETHYLIDENE-1-ADAMANTYL IODIDE ACCELERATED BY F-STRAIN

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The deuterium isotope effect in the solvolysis of (*Z*)- and (*E*)-[*methyl-d*$_3$]-2-ethylidene-1-adamantyl mesylates [(*Z*)- and (*E*)-1d-OMs] and iodides [(*Z*)- and (*E*)-1d-I] was studied in 2,2,2-trifluoroethanol at 25·0 °C for mesylates and at 50·0 °C for iodides. For the mesylates, which show a relatively small F-strain effect, the $(Z/E)_H$ rate ratio (117 ± 1) is essentially identical with the $(Z/E)_D$ rate ratio (116 ± 1) at 25·0 °C. On the other hand, for the iodides, which show a larger F-strain effect, the $(Z/E)_H$ rate ratio (5413 ± 57) is greater than the $(Z/E)_D$ rate ratio (5040 ± 58) at 50·0 °C. This indicates that (*Z*)-1h-I has greater F-strain than (*Z*)-1d-I in the ground state. These results again confirm that the F-strain effect in the (*Z*)-2-ethylidene-1-adamantyl derivatives exists between the (*Z*)-methyl group and the leaving group atom directly attached to the reaction centre.

INTRODUCTION

Deuterium substitution in organic compounds at the β or more distant positions with respect to the reaction centre exerts isotope effects on their reactivity in three different ways, viz., hyperconjugative, inductive and steric effects. The steric effect was proposed by Bartell[1] more than three decades ago,[1] and many pieces of supporting evidence have been reported.[2] According to this proposal, protium atoms behave as if they were larger than deuterium atoms as a consequence of the greater amplitude of vibration of their bonds.[1] Therefore, if a reaction proceeds with relief of ground-state strain, the protium derivatives should react at a faster rate than the corresponding deuterium derivatives.

This theory has been applied to solvolysis to support the importance of steric acceleration of ionization.[3–5] However, the difference in hyperconjugative and inductive effects between protium and deuterium always had to be taken into account.[2] To the authors' knowledge, only three examples relate to kinetic *steric* isotope effects in solvolysis. Karabatsos and co-workers[3] studied the solvolysis of [8-(*methyl-d*$_3$)]-1-naphthoyl chloride where the hyperconjugative effect is not transmitted to the cationic centre. The isotope effect, $k_H/k_D = 1·029$, was interpreted to show non-bonded interaction in the ground state.[3] Fry and Badger[4] examined the solvolysis of [2-(*tert-butyl-d*$_9$)]-2-adamantyl *p*-nitrobenzoate, and the isotope effect, $k_H/k_D = 1·1072$, was explained similarly. Creary *et al.*[5] studied the solvolysis of 3-methyl-*exo*-tricyclo-[3.2.1.0^{2,4}]oct-*exo*-3-yl tosylate and the *methyl-d*$_3$ analogue. The isotope effect, $k_H/k_D = 1·33$ at 50·0 °C, was interpreted in terms of non-bonded interaction between the 3-methyl group and the C-8 hydrogen.[5] In these three studies, however, the intramolecular non-bonded interaction examined was mainly the back-side strain (B-strain) or, most probably, a combination of both the back-side and front-side (F-strain) effects.

Recently, we reported that (*Z*)-2-ethylidenebicyclo-[2.2.2]oct-1-yl and (*Z*)-2-ethylidene-1-adamantyl derivatives are typical examples showing the F-strain effect caused by the leaving group atom which is directly attached to the reaction centre.[6] We succeeded also in a quantitative treatment of solvolysis rate enhancement by using MM2 steric energies.[6d] This paper reports further supporting evidence for the F-strain effect in the solvolyses of (*Z*)-2-ethylidene-1-adamantyl derivatives. The rates of solvolysis in 2,2,2-trifluoroethanol (TFE) were studied for the mesylates and iodides of the (*Z*)- and (*E*)-[*methyl-d*$_3$]-2-ethylidene-1-adamantyl and the corresponding *methyl-d*$_0$ systems. The results for the iodizes provide the first example in which the kinetic steric isotope effect has been observed in the F-strain effect in solvolysis.

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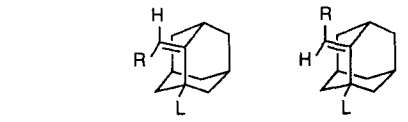


R = CH_3 (*Z*)-**1h-L** (*E*)-**1h-L**

R = CD_3 (*Z*)-**1d-L** (*E*)-**1d-L**

(L = OMs, I)

RESULTS

Isotopic purity

For introducing the *methyl-d_3* group, [*methyl-d_3*]ethylidenetriphenylphosphorane containing 99 atom% deuterium was used. No evidence for isotope scrambling was found in the final products by NMR and mass spectral analyses.

Synthesis of mesylates

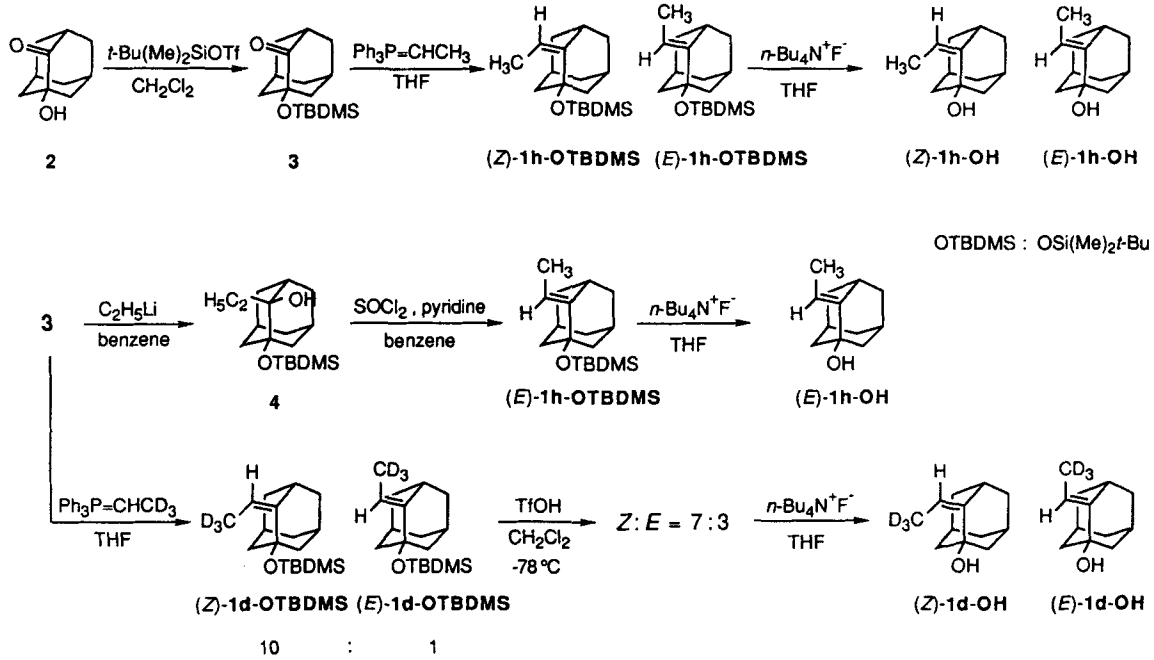
The mesylates were derived from 1-hydroxy-2-adamantanone (**2**), which was prepared from noradamantane-3-carbaldehyde via acylative ring expansion (Scheme 1).[7] The *tert*-butyldimethylsilyl (TBDMS) ether (**3**) of **2** was subjected to the Wittig ethylidenation by using ethylidenetriphenylphosphorane in THF to give a mixture of (*Z*)- and (*E*)-**1h-OTBDMS** in a ratio of 10:1 as estimated by ^{13}C NMR. After desilylation of the mixture with *n*-Bu_4NF,[8] the *Z* alcohol was isolated chromatographically and then converted into (*Z*)-**1h-OMs**. The labelled mesylate [(*Z*)-**1d-OMs**] was prepared by using [*methyl-d_3*]ethylidenetriphenylphosphorane at the Wittig ethylidenation step.

The unlabelled *E* mesylate [(*E*)-**1h-OMs**] was synthesized via a different route. The silyl ether **3** was treated with ethyllithium, and the resulting alcohol **4** was dehydrated by treatment with thionyl chloride in benzene at reflux in the presence of excess of pyridine to give essentially pure (*E*)-**1h-OTBDMS**, which was then converted into (*E*)-**1h-OMs**.

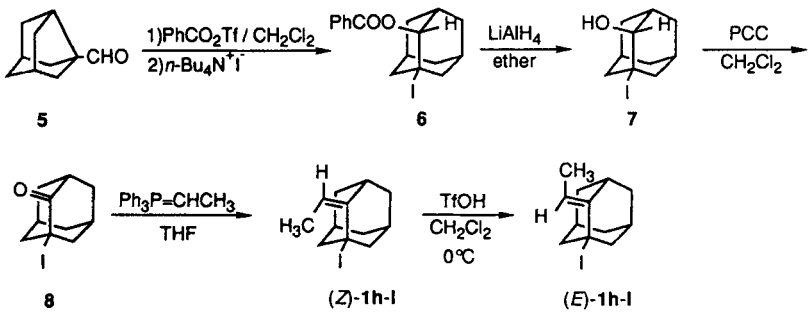
For the preparation of (*E*)-**1d-OMs**, the olefin inversion of (*Z*)-**1d-OTBDMS** was employed. Treatment of a 10:1 mixture of (*Z*)- and (*E*)-**1d-OTBDMS** with 0·01 M triflic acid (TfOH) in CH_2Cl_2 at −78 °C gave a 7:3 mixture of (*Z*)- and (*E*)-**1d-OTBDMS**, which was then desilylated and the *E* alcohol [(*E*)-**1d-OH**] was separated chromatographically. The corresponding mesylate (*E*)-**1d-OMs** was prepared in the usual manner.

Synthesis of iodides

Attempts to iodinate the bridgehead hydroxyl group with P_2I_4[9] or Me_3SiI[10] to form (*Z*)- and (*E*)-**1h-I**



Scheme 1



Scheme 2

failed; therefore, a new route was developed (Scheme 2). Acylative ring expansion of noradamantane-3-carbaldehyde (**5**) with benzoyl triflate followed by treatment with *n*-Bu_4NI gave 1-iodo-2-adamantyl benzoate (**6**). Reduction of **6** with $LiAlH_4$ followed by oxidation with pyridinium chlorochromate afforded 1-iodo-2-adamantanone (**8**). The Wittig ethylidenation of **8** by using ethylidenetriphenylphosphorane (or [*methyl-d*$_3$]ethylidenetriphenylphosphorane) gave a mixture of (*Z*)- and (*E*)-**1h-I** [or (*Z*)- and (*E*)-**1d-I**] in a ratio of 95:5 as estimated by ^{13}C NMR. Treatment of this mixture with 0·01 M TfOH in CH_2Cl_2 at 0 °C gave essentially pure (*E*)-**1h-I** [or (*E*)-**1d-I**].

Solvolysis studies

In all the solvolysis experiments, substrates which had been purified by medium-pressure liquid chromatography (MPLC) at −40 °C or recrystallization were used. Accurate determination of rates at 25·0 °C was feasible for the mesylates owing to the relatively small *Z*/*E* rate ratio (117 ± 1 for unlabelled mesylates), but it was difficult for the iodides because of the very slow rates for the *E* isomers. Therefore, the isotope effect for the mesylates was evaluated at 25·0 °C and that for the iodides at 50·0 °C. The solvolysis was conducted in anhydrous TFE in the presence of an excess of 2,6-lutidine and the rates were determined conductimetrically or titrimetrically. In the former method, the concentration of hydrogen iodide showed a linear correlation with conductivity over an [HI] range of $0–3·24 \times 10^{-3}$ M in the presence of $9·52 \times 10^{-3}$ M 2,6-lutidine in TFE at 50·0 °C. In contrast, methanesulphonic acid (MsOH) showed a slightly curved plot

Table 1. Solvolysis rates, CD_3/CH_3 rate ratios and *Z*/*E* rate ratios for 2-ethylidene-1-adamantyl derivatives in 2,2,2-trifluoroethanol

Derivative	*T* (°C)	*k* (s^{-1})	CD_3/CH_3 rate ratio[a]	*Z*/*E* rate ratio[a]	
				For CH_3	For CD_3
(*E*)-**1h-OMs**	25·0	$(3·961 \pm 0·023) \times 10^{-4}$[b,c]	1	1	
(*E*)-**1d-OMs**	25·0	$(3·998 \pm 0·018) \times 10^{-4}$[b]	1·009 ± 0·010		1
(*Z*)-**1h-OMs**	25·0	$(4·646 \pm 0·022) \times 10^{-2}$[b,d]	1	117 ± 1	
(*Z*)-**1d-OMs**	25·0	$(4·624 \pm 0·023) \times 10^{-2}$[b]	0·995 ± 0·013		116 ± 1
(*E*)-**1h-I**	50·0	$(2·507 \pm 0·019) \times 10^{-6}$[e,f]	1	1	
(*E*)-**1d-I**	50·0	$(2·597 \pm 0·021) \times 10^{-6}$[e]	1·036 ± 0·016		1
(*Z*)-**1h-I**	50·0	$(1·357 \pm 0·004) \times 10^{-2}$[g]	1	5413 ± 57	
(*Z*)-**1d-I**	50·0	$(1·322 \pm 0·004) \times 10^{-2}$[g]	0·974 ± 0·008		5090 ± 58

[a] The ratios are at 25·0 °C for mesylates and at 50·0 °C for iodides.
[b] Determined conductimetrically for 0·00074 M substrate in the presence of 0·00119 M 2,6-lutudine. Error is expressed as average deviation for three runs ($r > 0·9998$).
[c] The reported value which was determined for 0·00020 M substrate in the presence of 0·00119 M 2,6-lutidine is $3·51 \times 10^{-2}$ s^{-1}; see Ref. 6b.
[d] The reported value which was determined for 0·00020 M substrate in the presence of 0·00119 M 2,6-lutidine is $4·41 \times 10^{-2}$ s^{-1}; see Ref. 6b.
[e] Determined titrimetrically by a single run for 0·020 M substrate in the presence of 0·025 M 2,6-lutidine ($r > 0·9998$). Error is expressed as a standard deviation at the 95% confidence limit ($n = 24$).
[f] A reported value is $2·48 \times 10^{-6}$ s^{-1} under the same conditions; see Ref. 6d.
[g] Determined conductimetrically for 0·00491 M substrate in the presence of 0·00952 M 2,6-lutidine. Error is expressed as average deviation for three runs ($r > 0·9999$).

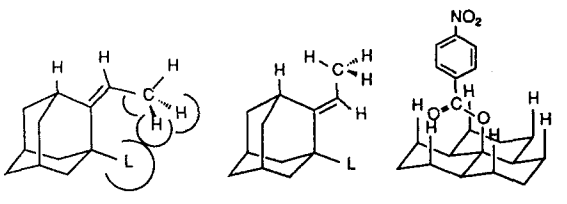
over an [MsOH] range of $0-7{\cdot}11\times10^{-4}$ M in the presence of $1{\cdot}19\times10^{-3}$ M 2,6-lutidine in TFE at 25·0 °C, although the first-order plot obtained by conductivity measurements was satisfactorily linear. Consequently, for the solvolysis of mesylates the conductivity was converted into concentration and used for rate calculations. Because of this modification, the rate data for the unlabelled mesylates are 5–10% smaller than previously reported. The rate constants obtained from three runs for the mesylates at 25·0 °C were accurate to within ±0·6%.

The rates for (*E*)-**1h-I** and (*E*)-**1d-I** were too slow, with a half-life of *ca* 3 days at 50·0 °C. Therefore, their solvolysis was followed titrimetrically, and the rates were calculated for a single run by using 24 points with an estimated error of ±0·6% at a 95% confidence limit. The rates for (*Z*)-**1h-I** and (*Z*)-**1d-I** were determined conductimetrically at 50·0 °C. The rates obtained from three runs were accurate to within ±0·3%. All the rate data are summarized in Table 1. All the substrates used in this study gave the corresponding bridgehead trifluoroethyl ether as the sole product (>99% by GLC) in trifluoroethanolysis.

DISCUSSION

F-strain effect in the *Z* substrates

Previously, we reported that the *Z*/*E* rate ratio in the solvolysis of (*Z*)- and (*E*)-**1h-L** increases with increase in the size of the leaving group L, i.e., 117 ± 1 (L = OMs) (the ratio determined in this work; a previously reported value is 126 ± 3), 1020 ± 60 (L = Cl), 2230 ± 90 (L = Br) and 9680 ± 400 (L = I) in TFE at 25·0 °C.[6d] A plot of $1{\cdot}36\times\log(k_Z/k_E)$ values against MM2 steric energy differences between the *Z* and *E* isomers gives a good linear correlation with a slope of 0·83.[6d] Consequently, it was concluded that the origin of the large *Z*/*E* rate ratios arises principally from the relief of the strain between the (*Z*)-methyl group and the leaving group atom directly attached to the reaction centre on ionization.[6d] The F-strain effect in the (*Z*)-2-ethylidene-1-adamantyl system (*Z*)-**1h-L** is in contrast to that in *trans,trans,trans*-perhydro-9b-phenalyl *p*-nitrobenzoate (**9**),[11] where the F-strain has been found to exist between the axial hydrogen and the carbonyl oxygen atom (and/or the aryl group).



(*Z*)-1h-L (*E*)-1h-L 9

Kinetic isotope effects in the *E* substrates

Obviously, there is no steric interaction between the (*E*)-methyl and the leaving group. Therefore, should a kinetic isotope effect be observed, it would to a first approximation be ascribed to electronic effects. Partial relief of steric repulsion between the (*E*)-methyl and the hydrogen at the 3-position is expected on ionization owing to flattening of the reaction centre. However, it would be slight. If such a back-strain (B-strain) effect were operative, it would work to decelerate the rate of solvolysis of (*E*)-*methyl-d*$_3$ derivatives because of the smaller steric requirement of deuterium than protium. In fact, we observed k_D/k_H ratios greater than unity: 1·009 ± 0·010 for (*E*)-**1-OMs** at 25·0 °C and 1·036 ± 0·016 for (*E*)-**1-I** at 50·0 °C.

It has been well recognized that protium is hyperconjugatively more electron donating but inductively less so than deuterium.[12] Therefore, the k_D/k_H ratios greater than unity for the *E* substrates would most probably be attributed to the inductive effect. The greater k_D/k_H ratio of the *E* iodides than that of the *E* mesylates would be rationalized by assuming a later transition state (more progressed ionization) for the iodides because of their lower reactivity. The more progressed ionization in the transition state would be more susceptible to inductive effects to give a greater k_D/k_H ratio.

Kinetic isotope effects in the *Z* substrates

In contrast to the *E* substrates, both the *Z* mesylates and *Z* iodides gave k_D/k_H ratios smaller than unity: 0·995 ± 0·013 for (*Z*)-**1-OMs** at 25·0 °C and 0·974 ± 0·008 for (*Z*)-**1-I** at 50·0 °C. In the present adamantyl system, hyperconjugative effects are precluded, since allylic conjugation in the transition state is prohibited for geometric reasons.[13] As stated above, an inductive effect would have resulted in k_D/k_H being greater than unity. Only steric reasons based on the smaller steric requirement of deuterium than protium can account for the results. The slower rates of the deuterium than those of protium compounds provide strong evidence for the presence of F-strain in the ground state of the *Z* substrates and its relief on ionization.

Kinetic isotope effects on the *Z*/*E* rate ratios

The *Z*/*E* rate ratio presumably includes various factors, such as steric, electronic and solvation effects. However, it would be reasonable to assume that the change of the stability of carbocations on replacement of CH_3 with CD_3 would be of similar magnitude for the *Z* and

E carbocations. Solvation of carbocations would be assumed to be essentially constant even on replacing CH_3 with CD_3. These premises may be supported by the fact that the mesylates, which show a relatively small F-strain effect, exhibit essentially identical *Z*/*E* rate ratios for protium and deuterium derivatives (117 ± 1 and 116 ± 1, respectively). Hence the difference between the $(Z/E)_H$ and $(Z/E)_D$ rate ratios would be a good measure of the difference in the F-strain effect between CH_3 and CD_3. In contrast to the mesylates, for the iodides where the F-strain effect is enormous, the $(Z/E)_H$ rate ratio is greater than the $(Z/E)_D$ rate ratio by a factor of 1·063 ± 0·024 (5413 ± 57 vs 5090 ± 58). This indicates that (*Z*)-**1h-I** has greater F-strain than (*Z*)-**1d-I** by as much as 0·04 ± 0·02 kcal mol^{-1} (1 kcal = 4·184 kJ).

Previously, we have shown from solvolysis rates and MM2 calculations that the net F-strain in (*Z*)-**1h-I** of *ca* 4·5 kcal mol^{-1} decreases to *ca* 1·5 kcal mol^{-1} in (*Z*)-**1h-OMs**.[6d] Since the steric isotope effect would decrease similarly, (*Z*)-**1h-OMs** is expected to have greater F-strain than (*Z*)-**1d-OMs** by *ca* 0·013 kcal mol^{-1}. This predicts that the $(Z/E)_H$ rate ratio is greater than the $(Z/E)_D$ ratio by 1%, in good agreement with the rate ratios of 117 ± 1 and 116 ± 1 for $(Z/E)_H$ and $(Z/E)_D$, respectively.

On the basis of Bartell's procedure,[1] we estimated the non-bonded isotope effect in (*Z*)-2-ethylidene-1-adamantyl derivatives. From lack of the parameters for H···I interaction, the calculations were performed for H···O, H···Cl and H···Br interactions for the two methyl-hydrogen atoms in the close positions (the interaction between the furthest methyl-hydrogen and the bridgehead heteroatom was negligibly small) by using the potential function of Scott and Scheraga[14] and the geometries which were obtained by MM2(87) calculations [the MM2(87) program was obtained from QCPE]. The calculated non-bonded isotope effects, 0·007, 0·008 and 0·011 kcal mol^{-1} for (*Z*)-**1-OH** [in place of (*Z*)-**1-OMs**], (*Z*)-**1-Cl** and (*Z*)-**1-Br**, respectively, are in line with the observed value for (*Z*)-**1-I** of 0·04 ± 0·02 kcal mol^{-1}. MM2(87) calculations also showed reasonable values of 0·012, 0·017, 0·020 and 0·023 kcal mol^{-1} for (*Z*)-**1-OH**, (*Z*)-**1-Cl**, (*Z*)-**1-Br** and (*Z*)-**1-I**, respectively. Hence both Bartell's theory and MM2 appear to give reasonable estimates of steric deuterium isotope effects in solvolysis.

CONCLUSION

The notion that the relief of F-strain between the leaving group atom directly attached to the reaction centre and the (*Z*)-methyl group in (*Z*)-2-ethylidene-1-adamantyl derivatives has again been supported by applying steric kinetic isotope effects. The results also represent the first example of the demonstration of the deuterium kinetic isotope effect on F-strain in solvolysis.

EXPERIMENTAL

Melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 1640 spectrophotometer. ^1H NMR spectra were recorded on a Hitachi R24 (60 MHz) or JEOL FX90A (89·55 MHz) spectrometer with TMS as internal standard. ^{13}C NMR spectra were obtained on a JEOL FX90A (22·5 MHz) spectrometer with the δ values being calculated on the basis of the central line of the chloroform-*d* triplet (77·00 ppm). Mass spectra were recorded on a Hitachi M-80 gas chromatograph–mass spectrometer equipped with a Hitachi M-003 data processor. TFE was stored over 5Å molecular sieves and distilled. The other solvents used for syntheses were dried by standard methods. Elemental analyses were performed by the Microanalytical Centre, Kyoto University.

2-Oxo-1-adamantyl tert-butyldimethylsilyl ether (**3**). To a solution of 1-hydroxy-2-adamantanone (**2**) (3·25 g, 19·0 mmol) and 2,6-lutidine (5·5 ml) in CH_2Cl_2 (21 ml) was added *tert*-butyldimethylsilyl triflate (5·1 ml, 23·1 mmol) at 0 °C over 9 min. After being stirred for 1 h, the reaction mixture was diluted with CH_2Cl_2 (40 ml), washed with water (2 × 40 ml), 10% aqueous HCl (2 × 40 ml), saturated aqueous $NaHCO_3$ (2 × 40 ml) and saturated aqueous NaCl (2 × 40 ml), and dried ($MgSO_4$). Evaporation of solvent, followed by MPLC [SiO_2, hexane–diethyl ether (95:5)] afforded **3** (3·94 g, 74%), m.p. 57·0–58·0 °C, IR(CCl_4): 2929, 2857, 1730, 1472, 1348, 1248, 1173, 1127, 1056, 990, 920 cm^{-1}. ^1H NMR (89·55 MHz, $CDCl_3$): δ 0·13 (s, 6 H), 0·87 (s, 9 H), 1·66–2·34 (m, 12 H), 2·69 (br s, 1 H). ^{13}C NMR (22·5 MHz, $CDCl_3$): δ 18·3, 79·0 (C), 30·0, 47·6 (CH), 35·0, 38·5, 48·0 (CH_2), −2·4, 25·9 (CH_3), 213·5 (C=O).

(Z)- and (E)-2-ethylidene-1-adamantyl tert-butyldimethylsilyl ether [(*Z*)- *and* (*E*)-***1h-OTBDMS***]. To a suspension of ethyltriphenylphosphonium bromide (13·46 g, 36·3 mmol) in THF (90 ml) was added dropwise 1·6 M *n*-BuLi in hexane (22·7 ml) at room temperature under nitrogen. After stirring for 30 min, a solution of **3** (3·39 g, 12·1 mmol) in THF (25 ml) was added. The mixture was stirred at room temperature for 19 h and then at reflux for 2 h. The reaction mixture was poured into ice–water (90 ml) and extracted with diethyl ether (3 × 70 ml). The combined extracts were washed with water (2 × 85 ml) and 10% aqueous NaCl (2 × 85 ml) and dried ($MgSO_4$). Evaporation of solvent followed by MPLC (SiO_2, hexane) afforded a mixture of (*Z*)-**1h-OTBDMS** and (*E*)-**1h-OTBDMS** (2·28 g,

65%) in an approximate ratio of 10:1. (*Z*)-**1h-OTBDMS:** ^{1}H NMR (89·55 MHz, $CDCl_3$): δ 0·15 (s, 6 H), 0·91 (s, 9 H), 1·26–1·94 (m, 13 H), 2·12 (br s, 2 H), 2·41 (br s, 1 H), 5·13 (q, 1 H, J = 7·1 Hz). ^{13}C NMR (22·5 MHz, $CDCl_3$): δ −1·1, 14·3, 18·4, 26·4, 31·0, 36·0, 38·8, 44·6, 47·7, 77·9, 113·1 147·1.

(Z)- and (E)-2-ethylidene-1-adamantanol [*(Z)- and (E)-1h-OH*]. To a 10:1 mixture of (*Z*)- and (*E*)-**1h-OTBDMS** (2·28 g, 7·8 mmol) in THF (35 ml) was added a 1·0 M solution of *n*-Bu_4NF in THF (15·6 ml) and the resulting solution was refluxed for 17 h under nitrogen. The reaction mixture was stirred with 4% aqueous NH_4Cl (40 ml) and extracted with diethyl ether (3 × 60 ml). The combined extracts were washed with water (2 × 60 ml) and 10% aqueous NaCl (2 × 60 ml) and dried ($MgSO_4$). Evaporation of solvent followed by MPLC [SiO_2, hexane–diethyl ether (9:1)] afforded (*Z*)-**1h-OH** (1·24 g, 89%) and (*E*)-**1h-OH** (0·13 g, 9%) in that sequence. (*Z*)-**1h-OH:** m.p. 104·5–105·0 °C (from hexane). IR (CCl_4): 3612, 2919, 2852, 1446, 1343, 1212, 1177, 1118, 1092, 966, 937 cm^{-1}. ^{1}H NMR (89·55 MHz, $CDCl_3$): δ 1·57–2·29 (m, 13 H), 1·89 (d, 3 H, J = 7·3 Hz), 2·43 (br s, 1 H), 5·15 (q, 1 H, J = 7·2 Hz). ^{13}C NMR (22·5 MHz, $CDCl_3$): δ 74·8, 146·8 (C), 30·6, 43·8, 112·4 (CH), 35·6, 38·6, 47·4 (CH_2), 13·4 (CH_3). Analytical data were unsatisfactory, probably owing to its hygroscopic nature. Analysis: calculated for $C_{12}H_{18}O$, C 80·85, H 10·18; found, C 80·43, H 9·92%. (*E*)-**1h-OH:** m.p. 77·0–77·5 °C (from pentane). IR (CCl_4): 3601, 2923, 2852, 1550, 1451, 1341, 1220, 1178, 1121, 1091, 1007, 936 cm^{-1}. ^{1}H NMR (89·55 MHz, $CDCl_3$): δ 1·66–2·29 (m, 13 H), 1·60 (d, 3 H, J = 6·7 Hz), 3·03 (br s, 1 H), 5·34 (q, 1 H, J = 6·8 Hz). ^{13}C NMR (22·5 MHz, $CDCl_3$): δ 71·8, 148·4 (C), 30·5, 32·9, 108·0 (CH), 35·7, 37·7, 47·2 (CH_2), 11·9 (CH_3). Analytical data were unsatisfactory, probably owing to its hygroscopic nature. Analysis: calculated for $C_{12}H_{18}O$, C 80·85, H 10·18; found, C 80·26, H 10·09%.

(Z)-2-Ethylidene-1-adamantyl mesylate [*(Z)-1h-OMs*]. To a solution of (*Z*)-**1h-OH** (0·300 g, 1·68 mmol) in THF (3 ml) was added dropwise 1·6 M *n*-BuLi in hexane (1·05 ml) at −40 °C over 2 min. After stirring at −40 °C for 50 min, methanesulphonyl chloride (0·193 g, 1·68 mmol) in THF (3 ml) was added and stirring continued for 4 h, then the solution allowed to warm slowly to 10 °C over 1·5 h. After most of the solvent had been removed with a rotary evaporator, hexane was added. An insoluble white precipitate was removed by filtration. Evaporation of solvent followed by MPLC at −40 °C [SiO_2, hexane–diethyl ether (9:1)] afforded pure (*Z*)-**1h-OMs** (0·206 g, 48%) and a mixture of (*Z*)-**1h-OMs** and (*Z*)-**1h-OH** (0·117 g) in sequence. (*Z*)-**1h-OMs**: m.p. 61·0-61·5 °C (from pentane). IR (CCl_4): 2925, 2855, 1550, 1452, 1362, 1345, 1177, 1051, 1040, 970, 938, 899, 879 cm^{-1}. ^{1}H NMR (89·55 MHz, $CDCl_3$): δ 1·11-2·91 (m, 13 H), 1·80 (d, 3 H, J = 7·1 Hz), 3·04 (s, 3 H), 5·25 (q, 1 H, J = 7·0 Hz). ^{13}C NMR (22·5 MHz, $CDCl_3$): δ 94·1, 142·5 (C), 31·1, 44·7, 113·6, (CH), 34·8, 37·9, 43·8 (CH_2), 13·3, 41·0 (CH_3). Analysis: calculated for $C_{13}H_{20}O_3S$, C 60·91, H 7·86; found, C 60·71, H 8·07%.

(E)-2-Ethylidene-1-adamantanol [*(E)-1h-OH*] *by using ethyllithium.* To a 0·45 M solution of C_2H_5Li in pentane (15·5 ml), which was generated from Li shots and ethyl bromide in pentane, was added a solution of **3** (1·49 g, 5·32 mmol) in benzene (15 ml) at 0 °C over 23 min. After the solution had been stirred for 10 min at room temperature and then at reflux for 1 h water (25 ml) was added. The reaction mixture was extracted with diethyl ether (3 × 30 ml). The combined extracts were washed with 10% aqueous NaCl (3 × 35 ml) and dried ($MgSO_4$). Evaporation of solvent with a rotary evaporator afforded 1-*tert*-butyldimethylsilyloxy-2-ethyl-2-adamantanol (**4**) (1·88 g, 100%) as a pale yellow oil. ^{1}H NMR (60 MHz, CCl_4): δ 0·10 (s, 6 H), 0·72–0·90 (m, 12 H), 1·37–2·48 (m, 16 H) ^{13}C NMR (89·55 MHz, $CDCl_3$): δ 18·1, 76·3, 77·4 (C), 30·2 33·1, 33·7 (CH), 25·2, 30·6, 31·5, 37·2, 41·5, 41·7 (CH_2), −2·0, −1·9, 6·4, 25·8 (CH_3).

To $SOCl_2$ (0·816 g, 6·85 mmol) in benzene (21 ml) was added a solution of **4** (1·652 g, 6·04 mmol) and pyridine (1·467 g, 18·5 mmol) in benzene (10·5 ml) at 0 °C over 17 min. The resulting mixture was stirred for another 25 min at 0 °C, then for 45 min at room temperature, and heated at reflux for 30 min. The reaction mixture was poured into ice–water (70 g) and extracted with diethyl ether (3 × 40 ml). The combined extracts were washed with 10% HCl (3 × 30 ml) and saturated aqueous NaCl (3 × 30 ml) and dried ($MgSO_4$). Evaporation of solvent followed by MPLC (SiO_2, hexane) afforded essentially pure (*E*)-**1h-OTBDMS** (1·400 g, 90% based on **3**) as a colourless oil. ^{1}H NMR (60 MHz, $CDCl_3$): δ 0·10 (s, 6 H), 0·92 (s, 9 H), 1·30–1·93 (m, 10 H), 1·55 (d, 3 H, J = 6·6 Hz), 2·07 (br s, 2 H), 3·02 (br s, 1 H), 5·47 (q, 1 H, J = 7·0 Hz). ^{13}C NMR (89·55 MHz, $CDCl_3$): δ −1·5, 12·0, 18·4, 26·0, 30·8, 32·9, 36·1, 37·8, 47·9, 74·5, 108·9, 148·2.

(*E*)-**1h-OTBDMS** (1·400 g, 4·79 mmol) was desilylated as described for the preparation of (*Z*)-**1h-OH** by refluxing with *n*-Bu_4NF (9·8 mmol) in THF for 24 h under nitrogen. The usual work-up followed by MPLC [SiO_2, hexane–diethyl ether (9:1)] afforded (*E*)-**1h-OH** (0·627 g, 75%).

(E)-2-Ethylidene-1-adamantyl mesylate [*(E)-1h-OMs*]. The procedure described for the preparation of (*Z*)-**1h-OMs** was followed. A solution of (*E*)-**1h-OH** (0·200 g, 1·12 mmol) in THF (3 ml) was treated with 1·6 M *n*-BuLi in hexane (0·7 ml) and then with MsCl

(0·129 g, 1·12 mmol) at −40 °C for 4 h. Work-up followed by MPLC at −30 °C [SiO_2, hexane–diethyl ether (9:1)] afforded (*E*)-**1h-OMs** (0·163 g, 57%) and (*E*)-**1h-OH** (0·073 g, 37%) in this sequence. (*E*)-**1h-OMs:** m.p. 61·5–62·0 °C (from pentane). IR (CCl_4): 2923, 2855, 1550, 1451, 1341, 1178, 1044, 1000, 971, 935, 897 cm^{-1}. ^1H NMR (89·55 MHz, $CDCl_3$): δ 1·31–2·73 (m, 13 H), 1·62 (d, 3 H, $J = 6·8$ Hz), 3·06 (s, 3 H), 5·45 (q, 1 H, $J = 6·8$ Hz); ^{13}C NMR (22·5 MHz, $CDCl_3$) δ 92·7, 143·0 (C) 31·2, 33·9, 110·8 (CH), 35·2, 37·1, 44·5 (CH_2), 12·0, 40·9 (CH_3). Analysis: calculated for $C_{13}H_{20}O_3S$, C 60·91, H 7·86; found, C 60·83, H 8·00%.

(Z)- and (E)-[methyl-d_3]-2-ethylidene-1-adamantyl mesylate [*(Z)- and (E)-1d-OMs*]. Ethyl-2,2,2-d_3-triphenylphosphonium bromide was prepared following a literature procedure[15]. A mixture of ethyl-2,2,2-d_3 bromide (12·3 g, 0·11 mol), which was prepared from ethyl-2,2,2-d_3 alcohol (Aldrich, 99 atom%) and PBr_3, and triphenylphosphine (28·1 g, 0·11 mol) in benzene (27 ml) was heated at 135 °C in an autoclave for 21 h. The resulting crude solid was recrystallized from water and dried to give ethyl-2,2,2-d_3-triphenylphosphonium bromide (39·8 g, 99%). ^1H NMR analysis showed no signal at δ 1·40 due to unlabelled ethyltriphenylphosphonium bromide within a detection limit (2%).

Following the procedure described for the preparation of (*Z*)-**1h-OMs**, **3** (2·90 g, 10·3 mol) was treated in THF (36 ml) with [*methyl-d_3*]ethylidenetriphenylphosphorane, which was generated in THF (46 ml) from ethyl-2,2,2-d_3-triphenylphosphonium bromide (7·45 g, 20·0 mol) and 1·6 M *n*-BuLi in hexane (15 ml). Usual work-up followed by MPLC (SiO_2, hexane) afforded a 10:1 mixture of (*Z*)- and (*E*)-**1d-OTBDMS** (1·32 g, 43%).

To the above mixture (0·600 g, 2·06 mmol) of (*Z*)- and (*E*)-**1d-OTBDMS** was added 0·01 M TfOH in CH_2Cl_2 (20 ml) at −78 °C, and the resulting solution was stirred for 1 h. The reaction mixture was diluted with diethyl ether (40 ml), washed with saturated aqueous $NaHCO_3$ (20 ml) and saturated aqueous NaCl (20 ml) and dried ($MgSO_4$). Evaporation of the solvent with a rotary evaporator afforded a mixture of (*Z*)- and (*E*)-**1d-OTBDMS** in an approximate ratio of 68:32 as estimated by ^1H NMR. The cleavage of the mixture (1·16 g, 3·91 mol) of (*Z*)- and (*E*)-**1d-OTBDMS** by treatment with *n*-Bu_4NF (1·0 M in THF, 8·0 ml) afforded (*Z*)-**1d-OH** (0·497 g, 70%) and (*E*)-**1d-OH** (0·113 g, 16%). Separation of the isomeric alcohols was conducted as described for the preparation of (*Z*)- and (*E*)-**1h-OH**. Mass spectra for the labelled alcohol gave a molecular ion peak at *m/z* 181 which is greater than the molecular ion peak for the unlabelled alcohol by 3 mu. Analysis of the peak intensities of *m/z* 181 and 178 for the labelled alcohol indicated that the isotopic purity was greater than 99%.

A solution of (*Z*)-**1d-OH** (0·150 g, 0·83 mmol) in THF (1·5 ml) was treated with 1·6 M *n*-BuLi in hexane (0·53 ml) and then with MsCl (0·096 g, 0·83 mmol) at −50 °C for 4·5 h. The usual work-up followed by MPLC [SiO_2, hexane–diethyl ether (9:1)] at −40 °C afforded (*Z*)-**1d-OMs** (0·092 g, 43%) and unreacted (*Z*)-**1d-OH** (0·057 g, 38%).

(*E*)-**1d-OMs** was also synthesized in a similar way from (*E*)-**1d-OH** (0·104 g, 0·57 mmol) and 1·6 M *n*-BuLi in hexane (0·36 ml) and MsCl (0·065 g, 0·57 mmol). Separation of the crude product by MPLC at −40 °C [SiO_2, hexane–diethyl ether (9:1)] gave (*E*)-**1d-OMs** (0·081 g, 54%) and (*E*)-**1d-OH** (0·048 g, 46%).

1-Iodo-2-adamantyl benzoate (*6*). To a solution of benzoyl triflate (5·74 g, 22·6 mmol) in CH_2Cl_2 (23 ml) was added a solution of 1-noradamantanecarbaldehyde (**5**) (2·83 g, 18·8 mmol) in CH_2Cl_2 (19 ml) over 15 min under nitrogen, while the temperature of the solution was kept below 6 °C in an ice–water bath. After stirring for 5 min, *n*-Bu_4NI (10·44 g, 28·3 mmol) was added. The mixture was stirred at 0 °C for 6 h and then at room temperature for 14 h. The reaction mixture was poured into ice–water (60 ml) and extracted with diethyl ether (3 × 120 ml). The combined extracts were washed with 10% aqueous $Na_2S_2O_3$ (2 × 120 ml) and saturated aqueous NaCl (2 × 120 ml) and dried ($MgSO_4$). Evaporation followed by MPLC [SiO_2, hexane–diethyl ether (95:5)] afforded **6** (5·00 g, 70%), m.p. 118·5–119·0 °C (from hexane). IR (CCl_4): 3071, 2933, 2860, 1725, 1603, 1451, 1341, 1273, 1176, 1111, 1070, 1027, 708, 689, 654 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 1·42–3·17 (m, 13 H), 5·37 (d, 1 H, $J = 3·0$ Hz), 7·18–7·62 (m, 3 H), 7·94–8·30 (m, 2 H) ^{13}C NMR (22·5 MHz, $CDCl_3$): δ 49·5, 130·4, 165·1 (C), 31·7, 32·1, 34·9, 81·6, 128·3, 129·7, 132·9(CH), 30·0, 35·4, 46·7, 51·3 (CH_2). Analysis: calculated for $C_{17}H_{19}IO_2$, C 53·42, H 5·01, I 33·20; found, C 53·62, H 4·93, I 32·94%.

1-Iodo-2-adamantanol (*7*). A solution of **6** (4·75 g, 12·4 mmol) in diethyl ether (50 ml) was added dropwise to $LiAlH_4$ (0·566 g, 14·9 mmol) in diethyl ether (40 ml) at room temperature. The reaction mixture was stirred for another 40 min and then worked up in usual manner. Separation by MPLC [SiO_2, hexane–diethyl ether (9:1)] gave pure **7** (2·76 g, 80%), m.p. 58.5–59·0 °C (from pentane). IR (CCl_4): 3563, 2917, 2858, 1451, 1350, 1287, 1225, 1107, 1070, 1057, 1020, 960, 940, 689, 650 cm^{-1}. ^1H NMR (89·55 MHz, $CDCl_3$): δ 1·23–3·06 (m, 13 H), 2·43 (s, 1 H), 4·04 (d, 1 H, $J = 2·3$ Hz); ^{13}C NMR (22·5 MHz, $CDCl_3$): δ 63·3 (C), 32·3, 32·9, 36·1, 80·1 (CH), 29·1, 35·6, 36·0, 45·6, 51·1 (CH_2). Analysis: calculated for $C_{10}H_{15}IO$, C 43·18, H 5·44, I 45·63; found, C 43·22, H 5·53, I 45·40%.

1-Iodo-2-adamantanone (**8**). To a suspension of pyridinium chlorochromate (2·93 g, 13·6 mol) in CH_2Cl_2 (24 ml) was added a solution of **7** (2·51 g, 9·0 mmol) in CH_2Cl_2 (34 ml) and the resulting mixture was stirred under nitrogen at room temperature for 20 h. Diethyl ether (30 ml) was added to the reaction mixture, then the solution was passed through a column of Florisil (40 g). Evaporation followed by MPLC [SiO_2, hexane–diethyl ether (9:1)] afforded **8** (2·18 g, 87%), m.p. 116·0–117·0 °C (from hexane–benzene). IR (CCl_4): 2933, 2859, 1729, 1452, 1285, 1050, 1024, 994, 876, 630 cm^{-1}; ^1H NMR (89·55 MHz, $CDCl_3$): δ 1·71–2·36 (m, 8 H), 2·54–3·10 (m, 5 H) ^{13}C NMR (22·5 MHz, $CDCl_3$): δ 57·1, 206·7 (C), 31·3, 46·8 (CH), 34·2, 38·3, 53·4 (CH_2). Analysis: calculated for $C_{10}H_{13}IO$, C 43·50, H 4·75, I 45·96; found, C 43·49, H 4·61, I 45·75%.

(Z)-2-Ethylidene-1-iodoadamantane [*(Z)-1h-I*]. To a suspension of ethyltriphenylphosphonium bromide (3·62 g, 10·1 mmol) in THF (23 ml) was added dropwise 1·6 M *n*-BuLi in hexane (6·3 ml) at room temperature under nitrogen. After stirring for 30 min, a solution of **8** (1·40 g, 5·1 mmol) in THF (18 ml) was added. The resulting mixture was stirred for another 15 min, poured into ice–water (80 ml) and extracted with diethyl ether (3 × 90 ml). The combined extracts were washed with water (2 × 90 ml) and 10% aqueous NaCl (2 × 90 ml) and dried ($MgSO_4$). Evaporation of solvent followed by MPLC (SiO_2, hexane) afforded *(Z)*-**1h-I** (1·17 g, 80%), m.p. 25·0–26·0 °C (from pentane). IR (CCl_4): 2926, 2854, 1654, 1448, 1294, 1203, 1034, 1014, 982, 946, 873, 708, 648 cm^{-1}. ^1H NMR (89·55 MHz, $CDCl_3$): δ 1·88 (br s, 8 H), 2·05 (d, 3 H, J = 7·5 Hz), 2·46 (br s, 1 H), 2·78 (br s, 3 H), 5·41 (q, 1 H, J = 7·5 Hz). ^{13}C NMR (22·5 MHz, $CDCl_3$): δ 48·7, 144·7 (C), 33·2, 47·7, 116·5 (CH), 35·4, 38·6, 56·7 (CH_2), 14·1 (CH_3). Analysis: calculated for $C_{12}H_{17}I$, C 50·02, H 5·95, I 44·04; found, C 49·93, H 5·92, I 44·07%.

(E)-2-ethylidene-1-iodoadamantane [*(E)-1h-I*]. A solution of *(Z)*-**1h-I** (0·682 g, 2·37 mmol) in 0·01 M TfOH in CH_2Cl_2 (24 ml) was stirred at 0 °C for 1 h. The reaction mixture was diluted with diethyl ether (20 ml), washed with saturated aqueous $NaHCO_3$ (2 × 20 ml) and saturated aqueous NaCl (2 × 20 ml) and dried ($MgSO_4$). Evaporation of solvent with a rotary evaporator afforded essentially pure *(E)*-**1h-I** (0·670 g, 98%), m.p. 24·0–25·0 °C. IR (CCl_4): 2942, 2855, 1666, 1448, 1285, 1215, 1107, 1024, 943, 879, 658, 607 cm^{-1}. ^1H NMR (89·55 MHz, $CDCl_3$): δ 1·63 (d, 3 H, J = 6·7 Hz), 1·69–2·07 (m, 8 H), 2·46–3·23 (m, 5 H), 5·76 (q, 1 H, J = 6·7 Hz). ^{13}C NMR (22·5 MHz, $CDCl_3$): δ 61·8, 146·3 (C), 33·3, 34·4, 120·4 (CH), 35·3, 37·5, 55·3 (CH_2), 12·9 (CH_3). Analysis: calculated for $C_{12}H_{17}I$, C 50·02, H 5·95, I 44·04; found, C 50·26, H 5·95, I 44·12%.

(Z)- and (E)-[methyl-d_3]-2-ethylidene-1-iodoadamantane [*(Z)- and (E)-1d-I*]. Following the procedure described for the preparation of *(Z)*- and *(E)*-**1h-I**, **8** (1·40 g, 5·07 mol) was treated in THF (18 ml) with [*methyl-d_3*]-ethylidenetriphenylphosphorane which was generated from ethyl-2,2,2-d_3-triphenylphosphonium bromide (3·65 g, 9·75 mmol) and 1·6 M *n*-BuLi in hexane (6·1 ml) in THF (23 ml). The usual work-up followed by MPLC (SiO_2, hexane) afforded *(Z)*-**1d-I** (0·950 g, 64%). Treatment of *(Z)*-**1d-I** (0·63 g, 2·16 mmol) with 0·01 M TfOH in CH_2Cl_2 (22 ml) at 0 °C followed by the usual work-up afforded essentially pure *(E)*-**1d-I** (0·594 g, 94%).

Product of solvolysis of (Z)-1h-OMs in TFE. A solution of *(Z)*-**1h-OMs** (0·080 g, 0·31 mmol) in 0·050 M 2,6-lutidine in TFE (7·8 ml) was stirred at 25 °C for 5 min (20 half-lives). GLC analysis (PEG 20 M column, 2 m × 3 mm i.d.) of the reaction mixture exhibited the formation of a single product. After most of solvent had been removed with a rotary evaporator, the residue was diluted with diethyl ether (20 ml) and the ether solution was washed with water (15 ml), 10% HCl (15 ml), saturated aqueous $NaHCO_3$ (2 × 15 ml) and water (15 ml) and dried ($MgSO_4$). Evaporation of the solvent afforded 1-trifluoroethoxy-(*Z*)-2-ethylideneadamantane (0·080 g, 99%) as a pale yellow oil. IR (CCl_4): 2927, 2854, 1700, 1539, 1448, 1280, 1163, 1127, 1101, 972 cm^{-1}. ^1H NMR (89·55 MHz, $CDCl_3$): δ 1·25-2·47 (m, 13 H), 1·82 (d, 3 H, J = 7·4 Hz), 3·84 (q, 2 H, J = 8·6 Hz), 5·20 (q, 1 H, J = 7·3 Hz). ^{13}C NMR (22·5 MHz, $CDCl_3$): δ 80·0, 144·1 (C), 30·6, 44·2, 114·3 (CH), 35·7, 38·7, 41·8 (CH_2), 13·5 (CH_3), 59·2 (q, J = 34 Hz, $-OCH_2CF_3$), 124·5 (q, J = 278 Hz, CF_3).

Product of solvolysis of (E)-1h-OMs in TFE. From *(E)*-**1h-OMs** (0·071 g, 0·28 mmol) in 0·050 M 2,6-lutidine in TFE (6·9 ml) at 25·0 °C for 5·5 h (11 half-lives) was obtained 1-trifluoroethoxy-(*E*)-2-ethylideneadamantane (0·075 g, 100%) as a pale yellow oil. IR (CCl_4): 2923, 2854, 1671, 1448, 1418, 1380, 1276, 1219, 1158, 1101, 1087, 1005, 974, 854 cm^{-1}. ^1H NMR (89·55 MHz, $CDCl_3$): δ 1·41–1·91 (m, 10 H), 1·60 (d, 3 H, J = 6·8 Hz), 2·22 (br s, 2H), 3·06 (br s, 1 H), 3·89 (q, 2 H, J = 8·6 Hz), 5·37 (q, 1 H, J = 6·8 Hz). ^{13}C NMR (22·5 MHz, $CDCl_3$): δ 77·3, 144·4 (C), 30·4, 33·0, 109·9 (CH), 35·8, 37·6, 43·0 (CH_2), 11·9 (CH_3), 60·0 (q, J = 34·2 Hz, $-OCH_2CF_3$), 124·4 (q, J = 277·3 Hz, CF_3).

Product of solvolysis of (Z)-1h-I in TFE. From *(Z)*-**1h-I** (0·055 g, 0·19 mmol) in 0·050 M 2,6-lutidine in TFE (4·8 ml) at 40 °C for 30 min (13·6 half-lives) was

obtained 1-trifluoroethoxy-(*Z*)-2-ethylideneadamantane (0·044 g, 88%) as a pale yellow oil.

Product of solvolysis of (*E*)-**1h-I** *in TFE.* From (*E*)-**1h-I** (0·048 g, 0·17 mmol) in 0·050 M 2,6-lutidine in TFE (4·2 ml) at 100 °C for 3·5 h (7·7 half-lives) was obtained 1-trifluoroethoxy-(*E*)-2-ethylideneadamantane (0·035 g, 82%) as a pale yellow oil.

Kinetic methods. For the titrimetric method, the solvolysis was conducted in the presence of 0·025 M 2,6-lutidine with 0·020 M substrate concentration in TFE. The developed acid was titrated with 0·01 M KOH–ethanol by using bromcresol green–methyl red as indicator after an aliquot in an ampoule (1·000 ml) had been quenched in 10 ml of cold acetone. Good first-order kinetics were obtained over three half-lives.

For the conductimetric method, a conductivity cell (cell constant 0·1005) was filled with TFE solution (20 ml) containing 0·00119 M 2,6-lutidine (for mesylate solvolysis) or 0·00952 M 2,6-lutidine (for iodide solvolysis) and the system was thermally equilibrated. A 20 μl volume of THF solution containing a substrate at a concentration of 25–60% was injected under magnetic stirring and the specific conductance ($\varkappa$) of the reaction mixture was recorded against reaction time.

Treatment of conductance data. The specific conductance ($\varkappa$) of methanesulphonic acid (MsOH) in TFE in the presence of 0·00119 M 2,6- lutidine was measured in the concentration range of MsOH from 0 to $7{\cdot}11 \times 10^{-4}$ M. The plot of $\varkappa$ vs concentration of MsOH (C) was non-linear. The conductance data were fitted by the least-squares method to the equation $\varkappa = \alpha + \beta C + \gamma C^{1/2}$, giving $\alpha = 4{\cdot}23$, $\beta = 4{\cdot}73 \times 10^5$ and $\gamma = -1{\cdot}71 \times 10^3$. The $C_{calc.}$ values calculated from measured $\varkappa$ values by using this equation gave good first-order kinetics. For hydrogen iodide, the plot of $\varkappa$ vs C was linear within the concentration ranges of this work. Therefore, first-order rate constants were determined by using measured $\varkappa$ values.

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