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SOLVOLYSIS OF 3-SUBSTITUTED 4-HOMOADAMANTYL METHANESULPHONATES. CAN THE β-SUBSTITUENT EFFECT DISTINGUISH BETWEEN CLASSICAL AND NON-CLASSICAL ION INTERMEDIATES?

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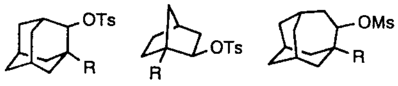
The rates of the solvolysis of 3-R-4-homoadamantyl methanesulphonates (mesylates) (3) were determined in 80% aqueous ethanol. The relative first-order rate constants at 25 °C were 1·0 (R = H), 2·29 (R = Ph), 3·26 (R = *p*-anisyl), 73·6 (R = Me) and 209 (R = Et). The methanolysis of 3 gave rearranged methyl ethers and rearranged olefins as major products together with small amounts (0·9–3·4%) of unrearranged products. The order of the accelerating effect suggests that the transition states involve significant σ-participation, despite the fact that 3 (R = H) solvolyses via a classical ion intermediate. The logarithms of the solvolysis rate constants of 3 showed linear correlations with those of 1-R-2-adamantyl tosylates (1) and 1-R-*exo*-2-norbornyl tosylates (2), indicating that the linear free-energy relationship between the β-substituent effects on the solvolysis rate is not a definite measure to distinguish between classical and non-classical intermediates.

INTRODUCTION

For many years from Winstein's suggestion[1] on the intermediacy of the bridged 2-norbornyl cation in solvolysis, various approaches have been taken to examine the validity of a number of bridged, so-called 'non-classical' ions. Among them the 2-norbornyl cation has been most extensively studied.[2] At the present stage the non-classical structure is strongly supported for this cation in non-nucleophilic media and in the solid state. However, it is still controversial whether the 2-norbornyl cation as a solvolysis intermediate is bridged or not: a pair of rapidly equilibrating classical ions has been suggested as an alternative to the non-classical ion.

Similarly to the case of the 2-norbornyl cation, the structure of the 2-adamantyl cation in solvolysis has been controversial.[3] Lenoir[4] studied the solvolysis of 1-substituted 2-adamantyl tosylates (**1**) (Scheme 1) and found a linear free energy relationship between the rates of the solvolysis of **1** and those of 1-substituted *exo*-2-norbornyl tosylates (**2**). He concluded that the classical and non-classical ions can be distinguished from each other by the β-substituent effect on the assumption that both the 1-substituted 2-norbornyl cation and the 1-substituted 2-adamantyl cation intermediates were non-classical.[4] However, it seemed to us that the method of characterizing the intermediate by the β-substituent effect should be used with caution, since no rate data are available with respect to the β-substituent effect in the solvolysis of a system which was unambiguously proved to solvolyse via a pair of rapidly equilibrating classical ions. In this context, Fărcaşiu[5] analysed the solvolysis rates of 1-alkyl-2-adamantyl sulphonates from a viewpoint of steric strain and pointed out that the experimental data can be explained without assuming the intervention of σ-bridged ions as intermediates.

The 4-homoadamantyl cation can be degenerate with respect to the Wagner–Meerwein rearrangement and 5,4-hydride shift.[6] Therefore, if bridged, it would be symmetrical like the bridged 2-norbornyl cation. Previously, Nordlander and co-workers[7] concluded from



1 **2** **3**

a : R = H
b : R = Ph
c : R = *p*-An
d : R = Me
e : R = Et

Scheme 1

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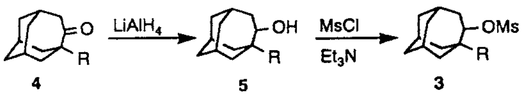


Scheme 2

the solvolysis study on ^{2}H-labelled 4-homoadamantyl tosylate that the ionization of this compound takes place without neighbouring carbon or hydrogen participation to form a localized tight ion pair. Recently, we confirmed their results by using the ^{13}C-labelled substrate.[8] Therefore, the 4-homoadamantyl system would be an appropriate model for the study of the β-substituent effect in solvolysis involving a *classical* ion intermediate. In order to examine whether the β-substituent effect on solvolysis rates provides evidence for the intermediacy of a non-classical ion, we carried out the solvolysis of a series of 3-substituted 4-homoadamantyl mesylates (**3**) and compared the rate data with those for **1** and **2**.

RESULTS

Synthesis

Lithium aluminium hydride reduction of 3-substituted 4-homoadamantanones (**4**) (Scheme 2), which were synthesized by the previously reported method,[9] gave a series of 3-substituted 4-homoadamantanols (**5**). Since

Table 1. Rate constants for the solvolysis of **3**

Mesylate	Solvent[a]	Temperature (°C)	k (s^{-1})[b]	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal K^{-1} mol^{-1})
3a	80% EtOH	25·0	$5{\cdot}37 \times 10^{-5}$	22·9	−1·1
		40·0	$3{\cdot}60 \times 10^{-4}$		
	MeOH	25·0	$6{\cdot}52 \times 10^{-6}$[c]		
3b	80% EtOH	25·0	$1{\cdot}23 \times 10^{-4}$	21·8	−3·0
		40·0	$7{\cdot}54 \times 10^{-4}$		
	MeOH	25·0	$2{\cdot}54 \times 10^{-5}$[c]		
3c	80% EtOH	25·0	$1{\cdot}75 \times 10^{-4}$	22·1	−1·6
		40·0	$1{\cdot}10 \times 10^{-3}$		
	MeOH	25·0	$4{\cdot}45 \times 10^{-5}$		
3d	80% EtOH	25·0	$3{\cdot}95 \times 10^{-3}$	19·6	−3·8
		40·0	$2{\cdot}02 \times 10^{-2}$		
	MeOH	25·0	$6{\cdot}93 \times 10^{-4}$		
3e	80% EtOH	25·0	$1{\cdot}12 \times 10^{-2}$	18·8	−4·5
		40·0	$5{\cdot}36 \times 10^{-2}$		
	MeOH	25·0	$2{\cdot}47 \times 10^{-3}$		

[a] Buffered with 0·025 M 2,6-lutidine.
[b] Determined conductimetrically within an experimental error ±2%. Average of two runs.
[c] Determined titrimetrically within an experimental error ± 2% by a single run.

Table 2. Rate constants for the solvolysis of **1–3** (k_R/k_H in parentheses)

	R	σ_I[a]	k (s^{-1}) **1**[b]	k (s^{-1}) **2**[c]	k (s^{-1}) **3**[b]
a	H	0·00	$2{\cdot}41 \times 10^{-8}$ (1)[d,e]	$2{\cdot}33 \times 10^{-5}$ (1)	$5{\cdot}37 \times 10^{-5}$ (1)
b	Ph	0·12	$2{\cdot}22 \times 10^{-7}$ (9·21)	$9{\cdot}55 \times 10^{-5}$ (4·10)	$1{\cdot}23 \times 10^{-4}$ (2·29)
c	*p*-An	0·11	$4{\cdot}44 \times 10^{-7}$ (18·4)	$1{\cdot}88 \times 10^{-4}$ (8·07)	$1{\cdot}75 \times 10^{-4}$ (3·26)
d	Me	−0·01	$8{\cdot}35 \times 10^{-7}$ (34·6)[d,e]	$1{\cdot}25 \times 10^{-3}$ (53·6)	$3{\cdot}95 \times 10^{-3}$ (73·6)
e	Et	−0·01	$2{\cdot}73 \times 10^{-6}$ (113)[d,f]	$1{\cdot}90 \times 10^{-3}$ (81·5)	$1{\cdot}12 \times 10^{-2}$ (209)

[a] From Ref. 15.
[b] In 80% EtOH at 25·0 °C.
[c] In AcOH at 25·0 °C, Ref. 12.
[d] Calculated from data at higher temperatures.
[e] Ref. 11.
[f] Ref. 4.

Table 3. Rate constants for the solvolysis of **1b** and **1c** in 80% EtOH buffered with 2,6-lutidine

Substrate	Temperature (°C)	k (s^{-1})[a]	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal K^{-1} mol^{-1})
1b	25·0	$2{\cdot}22\times10^{-7}$	25·1	−4·7
	50·0	$6{\cdot}37\times10^{-6}$		
1c	25·0	$4{\cdot}44\times10^{-7}$	25·2	−3·3
	50·0	$1{\cdot}28\times10^{-5}$		

[a] Determined titrimetrically within an experimental error ±2%.

Table 4. Products of the methanolysis of **3** at 25 °C[a]

	Unrearranged products (%)[b]		Rearranged products (%)[b]			
Substrate	**6**	**7**	**8**	**9**	**10**	**11**
3a: R = H[c,d]	61	7·8				
3b: R = Ph[e]	0·9	2·5	77	19		
3c: R = *p*-An[d]	0·3	1·7	13	65		
3d: R = Me[d]	0·7	0·5	48	16	4·4	
3e: R = Et[f]	0·1	0·8	29	19		27

[a] Buffered with 0·050 M 2,6-lutidine.
[b] Absolute yields determined by ^{1}H NMR peak intensity. Reaction time: 10–16 half-lives.
[c] *exo*-2-Methoxyhomoadamantane (1·5%) and 2,4-dehydrohomoadamantane (1·7%) were also formed.
[d] Internal standard: 9-phenylfluorene (H-9).
[e] Relative yields.
[f] Internal standard: fluorene (H-9).

some tosylates were too unstable to be isolated, the alcohols **5a–e** were converted into the corresponding mesylates (**3**) by the procedure of Crossland and Servis.[10] Compounds **3b–e** were unstable above room temperature and rapidly underwent elimination. However, they were obtained in excellently pure forms by recrystallization from hexane in the presence of 2,6-lutidine.

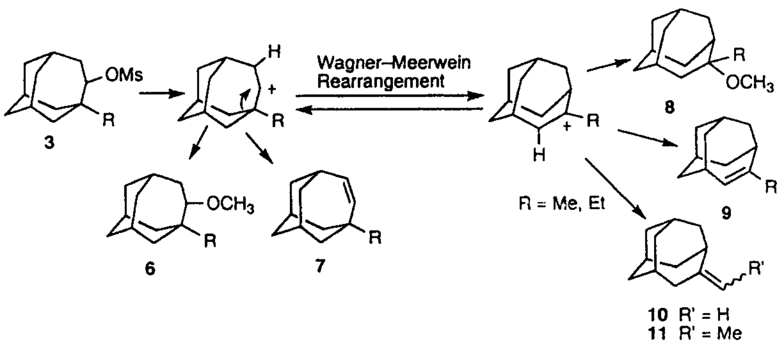
Kinetics

The rates of the solvolysis of **3** were determined conductimetrically or titrimetrically in 80% EtOH and MeOH buffered with 2,6-lutidine at 25 °C. Good first-order behaviour (r > 0·9993) was observed over 68–90% reactions. The rate constants and activation parameters are collected in Table 1.

The rate constants of the solvolysis of **1**[4,11] and **3** in 80% EtOH and those of **2**[12] in AcOH at 25 °C are summarized in Table 2. The rates of the solvolysis of **1b** and **1c** were also measured at 25 °C, since the reported rates had been obtained at high temperatures (61–91 °C).[13] The rate constants and activation parameters are summarized in Table 3.

Methanolysis products

For product studies, mesylates **3a–e** were solvolysed in methanol containing 0·050 M 2,6-lutidine at 25 °C for 10 half-lives or longer. Gas chromatographic (GC) analysis of the products was not successful owing to decomposition of the methyl ethers under the GC conditions. After evaporation of the methanol at 0 °C under vacuum, the residue was dissolved in $CDCl_3$ containing a known amount of fluorene or 9-phenylfluorene as an internal standard and analysed by ^{1}H NMR (270 MHz) at −20 °C to room temperature to determine the absolute yields of products. The results are summarized in Table 4. From **3b–e** were obtained rearranged methyl ethers **8** and olefins **9** and small amounts of unrearranged products **6** and **7** (Scheme 3).



Scheme 3

In addition, **3d** and **3e** yielded *exo*-olefins **10** and **11**, respectively, as rearranged products.

Identification of the products rests on the chemical shifts and coupling patterns of their methoxy or olefinic proton signals. The signals of **6a**,[8] **7a**[8] and **7d**[14] agreed with those reported in the literature. The signals of **6b–e**, **8d**, **9b**, **9c**, **10**, 2,4-dehydrohomoadamantane[8] and *exo*-2-methoxyhomoadamantane[8] were compared with those of unambiguously synthesized authentic samples (see Experimental). Part of **9c** might have been formed by the elimination of MeOH from **8c** during the NMR sample preparation. Actually, although 13% of **8c** was detected by ^{1}H NMR at $-20\,^{\circ}$C, it rapidly changed to **9c** at $0\,^{\circ}$C. The total yields of **6–11** were considerably lower than 100% (65–80%), presumably because of partial loss of products due to sublimation during the solvent evaporation.

DISCUSSION

Substituent effect on solvolysis rates

The 3-ethyl and 3-methyl groups accelerated the solvolysis of 4-homoadamantyl mesylate by factors of 209 and 74, respectively, whereas the 3-phenyl and 3-*p*-anisyl groups accelerated this reaction only moderately ($k_R/k_H = 2{\cdot}3$ and $3{\cdot}3$, respectively). A plot of logarithms of the rate constants against the polar substituent constants σ_I[15] (Table 2) showed a poor correlation (Figure 1). As in the solvolysis of 3-substituted 1-adamantyl tosylates,[16] a good linear correlation would be expected if only the inductive effect were important.

In general, an aryl group at the β-position of a centre of developing positive charge has a destabilizing inductive effect, whereas it strongly stabilizes the transition state by the benzylic resonance when attached at an α-position.[4,17] The observed small rate enhancements by the β-aryl substituents can be rationalized by the involvement of σ-participation in the transition state of ionization. The order of the accelerating effect, Et > Me > *p*-anisyl > phenyl > H, was the same as that found in the solvolysis of 1-R-*exo*-2-norbornyl tosylates (**2**). A logarithmic plot for solvolysis rates showed a fairly good linear relationship between **2** and **3** (Figure 2).

These results, however, do not necessarily mean that the intermediate 3-R-4-homoadamantyl cation has a σ-bridged structure. The relief of skeletal strain by ionization and the orbital overlap in the bridged structure, both of which are considered major driving forces for the σ-bridging of the 2-norbornyl cation, do not seem to be sufficiently large to induce the bridging of the 4-homoadamantyl cation. In fact, we[8] and Nordlander[7] have shown by the isotope labelling technique that the solvolysis of unsubstituted 4-homoadamantyl tosylate proceeds via a classical ion intermediate which undergoes rapid Wagner–Meerwein rearrangement.

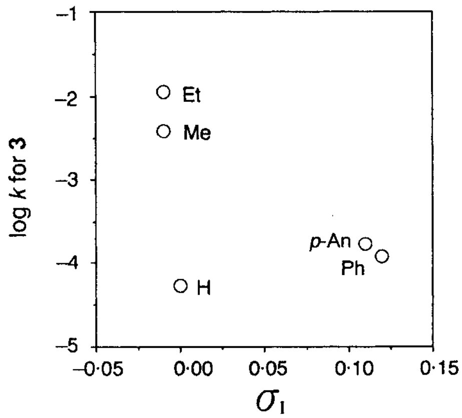


Figure 1. Plot of log k for **3** in 80% EtOH at 25 °C against σ_I

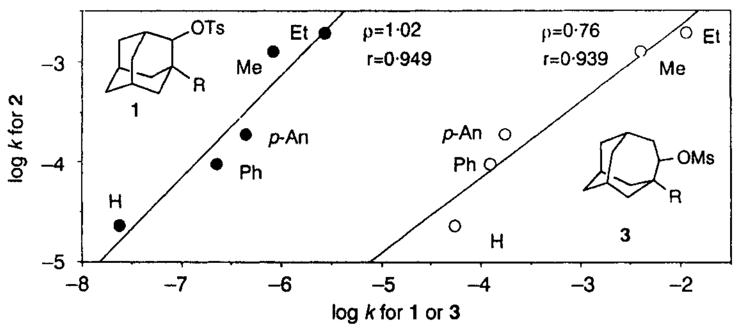


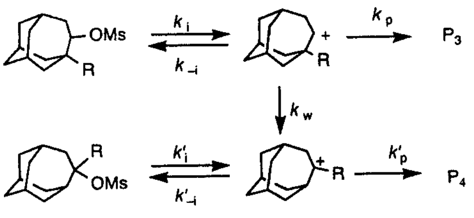
Figure 2. Plot of log k for **2** in AcOH against log k for **1** and **3** in 80% EtOH at 25 °C. (•)**1** vs **2**; (○) **3** vs **2**

Despite such an apparent discrepancy between the degrees of σ-bridging in the 2-norbornyl and the 4-homoadamantyl cation intermediates, the solvolysis rates showed very similar β-substituent effects in both the systems. Lenoir[4] studied the β-substituent effect in the solvolysis of 1-R-2-adamantyl tosylate (**1**) and found a linear free-energy relationship between logarithms of the rate constants for **1** and **2** (Figure 2). He suggested that this linearity would be general for σ-bridged ions on the assumption that both the 1-substituted *exo*-2-norbornyl cations and the 1-substituted 2-adamantyl cations are bridged. However, the observation of a similar substituent effect in the solvolysis of **3** indicates that this correlation is not characteristic of σ-bridged ions.

The two lines in Figure 2 have slopes close to 1, suggesting that the degrees of σ-participation in the transition states are not very different among the three systems. The somewhat smaller slope of the plot of **3** vs **2** than that of **1** vs **2** may be partly due to the steric effect. Thick substituents such as methyl and ethyl groups may cause steric repulsion (front strain) toward the adjacent mesylate group, resulting in acceleration of solvolysis. This effcct is expected to be most significant in **3**, in which the substituent R and the leaving group are arranged on a seven-membered ring (attempts to estimate the front strain in **3** by molecular mechanics calculations [MM2(87)] were not successful because of high flexibility of the ethylene bridge of the homoadamantane skeleton[18]).

Product distribution

Based on the fact that the 3-substituted 4-homoadamantyl cations have a classical nature, a mechanistic model for kinetic treatment can be illustrated as in Scheme 4, where P_3 and P_4 represent the unrearranged and rearranged products, respectively. Rate constants k_i, k_{-i}, k_p and k_w correspond to ionization, ion-pair return, product formation processes and Wagner–Meerwein rearrangement, respectively. Arnett *et al.*[19] reported that the heat of ionization of 2-propyl chloride is greater than those of *tert*-butyl chloride and 2-phenyl-2-propyl chloride by 10·1 and 15·0 kcal mol^{-1} (1 kcal = 4·184 kJ) in $SO_2ClF-SbF_5$, respectively. Similarly, reverse Wagner–Meerwein rearrangement from the tertiary 4-R-4-homoadamantyl cations (R = Ph, *p*-An, Me, Et) to the corresponding secondary 3-R-4-homoadamantyl cations must be energetically unfavourable and was therefore neglected in Scheme 4.



Scheme 4

Although **3b–e** gave mostly the rearranged products, small amounts (0·9–3·4%) of the unrearranged products (**6** and **7**) were detected. In this context, unsubstituted 4-homoadamantyl tosylate has been shown to solvolyse without nucleophilic solvent assistance.[7,8] Hence the formation of unrearranged products implies that the initially formed carbenium ion is subject to solvent attack before the Wagner–Meerwein rearrangement.

Steady-state treatment with respect to the 3- and 4-substituted 4-homoadamantyl cations gives the following rate expressions for the consumption of mesylate **3** and the product formation:

$$[3] = C_0 \exp\left[-\frac{k_i(k_p + k_w)}{k_p + k_w + k_{-i}} t \right] \quad (1)$$

$$[P_3]_{t=\infty} = \frac{k_p C_0}{k_w + k_p} \quad (2)$$

$$[P_4]_{t=\infty} = \frac{k_w C_0}{k_w + k_p} \quad (3)$$

where C_0 is the initial concentration of **3**.

Equations (2) and (3) afford the expression for the rate of Wagner–Meerwein rearrangement relative to product formation: $k_w/k_p = [P_4]_{t=\infty}/[P_3]_{t=\infty}$. From the fractions of the unrearranged and rearranged products (Table 4), the ratios k_w/k_p for **3b–e** were calculated to be 28 (**3b**), 39 (**3c**), 61 (**3d**) and 80 (**3e**). Despite the much higher stabilizing ability of α-aryl substituents than those of α-alkyl substituents, no marked change in the ratio k_w/k_p was observed for **3b–e**, indicating that the rearrangement of 3-R-4-homoadamantyl cations to the corresponding tertiary ions is not sensitive to the nature of the β-substituents. This result further supports the absence of σ-bridging in the initially formed 3-R-4-homoadamantyl cations.

CONCLUSION

The β-substituent effect on the rates of solvolysis of 3-R-4-homoadamantyl mesylates (**3**) was found to be very similar to that on the rates of solvolyses of 1-R-*exo*-2-norbornyl tosylates (**2**) and 1-R-2-adamantyl tosylates (**1**). The order of the accelerating effect of five substituents suggests that the transition states involve significant σ-participation in the three systems. Lenoir[4] interpreted the linear free-energy relationship between the rates of the solvolysis of **1** and those of **2** as evidence for the non-classical nature of 2-adamantyl cation on the assumption that the 2-norbornyl cation was non-classical. Since the solvolysis of **3** (R = H) is known to solvolyse via a classical ion,[7,8] the present results indicate that the linear free-energy relationship between the β-substituent effects on the solvolysis rate is not a definite measure to distinguish between classical and non-classical intermediates.

EXPERIMENTAL

Melting points were obtained by using capillary tubes (sealed just above the sample in the case of sublimable compounds) and are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 1600 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL GSX270 (270 MHz) spectrometer. ^{13}C NMR spectra were obtained with a JEOL GSX270 (67·8 MHz) or a JEOL FX90A (22·5 MHz) spectrometer. All chemical shifts are reported in ppm (δ) from TMS. Quantitative elemental analyses were performed by the Microanalytical Centre, Kyoto University. Absolute ethanol as a solvolysis solvent was refluxed with magnesium ethoxide and distilled. Absolute methanol as a solvolysis solvent was refluxed with sodium methoxide and distilled. DMSO was dried over molecular sieves 4A. Other anhydrous solvents used for synthesis were purified by standard procedures. 1-Phenyl- and 1-*p*-anisyl-2-adamantyl tosylates (**1b** and **1c**, respectively) were synthesized by treating the corresponding alcohols[13,20] with *p*-toluenesulphonyl chloride in pyridine: **1b**, m.p. 181–182·5 °C (lit.[13] 198·5–200 °C); **1c**, m.p. 150–151 °C (lit.[13] 161–162 °C).

3-Substituted 4-homoadamantanols (**5b–e**). 3-Substituted 4-homoadamantanones (**4b–e**)[9] were reduced with 0·5 moles of $LiAlH_4$ in dry diethyl ether.

5b: Colourless crystals, 99%, m.p. 61·5–62 °C (from hexane). IR (KBr): 3544, 3448, 2919, 1595, 1494, 1020 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7·42–7·17 (m, 5H), 3·87 (dd, 1H, J = 9·3, 4·4 Hz), 2·56 (m, 1H), 2·45 (m, 1H), 2·24–2·01 (m, 4H), 1·99–1·87 (m, 4H), 1·80–1·67 (m, 2H), 1·66–1·47 (m, 3H), 1·04 (s, 1H, OH). ^{13}C NMR (22·5 MHz, $CDCl_3$): δ 150·5 (C), 127·8 (2CH), 125·7 (2CH), 125·6 (CH), 79·2 (CH), 45·0 (C), 42·9 (CH_2), 41·8 (CH_2), 38·5 (CH_2), 36·6 (CH_2), 35·6 (CH_2), 34·3 (CH_2), 29·7 (CH), 27·9 (CH), 27·5 (CH). Analysis: calculated for $C_{17}H_{22}O$, C 84·25, H 9·15; found, C 84·23, H 9·28%.

5c: Colourless crystals, 99·8%, m.p. 61–62 °C (from hexane). IR (KBr): 3425, 1610, 1513, 1040 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7·29 (d, 2H, J = 7·1 Hz), 6·86 (d, 2H, J = 7·1 Hz), 3·81 (m, 1H, H-4), 3·79 (s, 3H, OCH_3), 2·51 (m, 1H), 2·43 (m, 1H), 2·18–1·98 (m, 4H), 1·97–1·81 (m, 4H), 1·77–1·65 (m, 2H), 1·64–1·45 (m, 3H), 1·22 (s, 1H, OH). ^{13}C NMR (67·8 MHz, $CDCl_3$): δ 157·6 (C), 142·7 (C), 127·0 (2CH), 113·6 (2CH), 79·6 (CH), 55·2 (CH_3), 44·9 (C), 42·9 (CH_2), 42·5 (CH_2), 39·0 (CH_2), 36·6 (CH_2), 35·9 (CH_2), 34·7 (CH_2), 29·9 (CH), 28·0 (CH), 27·7 (CH). Analysis: calculated for $C_{18}H_{24}O_2$, C 79·37, H 8·88; found, C 79·26, H 9·05%.

5d: Colourless crystals, 92%, m.p. 171–171·5 °C (from hexane). IR (KBr): 3448, 2900, 1448, 1022 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3·58 (m, 1H, H-4), 2·39 (m, 1H), 2·07–1·75 (m, 6H), 1·67–1·39 (m, 7H), 1·50 (s, 1H, OH), 1·28 (m, 1H), 0·96 (s, 3H, CH_3). ^{13}C NMR (22·5 MHz, $CDCl_3$): δ 79·1 (CH), 44·8 (CH_2), 43·7 (CH_2), 38·4 (CH_2), 38·2 (C), 36·8 (CH_2), 36·6 (CH_2), 36·2 (CH_2), 31·7 (CH_3), 29·8 (CH), 27·8 (CH), 27·5 (CH). Analytical data were unsatisfactory, presumably because of the hygroscopic nature. Analysis: calculated for $C_{12}H_{20}O$, C 79·94, H 11·18; found, C 79·43, H 11·26%. However, the *p*-nitrobenzoate gave satisfactory analytical data (see below).

5e: Colourless crystals, 98%, m.p. 42·5–45 °C (from hexane). IR (KBr): 3419, 2902, 1447, 1013 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3·77 (m, 1H, H-4), 2·42 (m, 1H), 2·02 (m, 1H), 1·95–1·75 (m, 5H), 1·68–1·35 (m, 8H), 1·37 (s, 1H, OH), 1·24 (m, 1H), 1·10 (m, 1H), 0·84 (t, 3H, J = 7·4 Hz). ^{13}C NMR (22·5 MHz, $CDCl_3$): δ 74·9 (CH), 44·8 (CH_2), 39·8 (C), 39·6 (CH_2), 38·3 (CH_2), 37·0 (CH_2), 36·7 (CH_2), 36·2 (CH_2), 36·1 (CH_2), 29·9 (CH), 27·5 (2CH), 7·7 (CH_3). Analysis: calculated for $C_{13}H_{22}O$, C 80·35, H 11·41; found, C 80·17, H 11·66%.

3-Methyl-4-homoadamantyl p-*nitrobenzoate*. To a solution of **5d** (89 mg, 0·49 mmol) in dry THF (0·75 ml) was added a solution of 1·66 M *n*-BuLi (0·30 ml, 0·49 mmol) in hexane at −30 °C, and the mixture was stirred at −30 °C for 30 min. A solution of *p*-nitrobenzoyl chloride (freshly recrystallized from hexane, 92 mg, 0·50 mmol) was added at −30 °C, and stirring was continued at −30 °C for 1·2 h and at room temperature for 3 h. After removal of the solvent, the residue was dissolved in diethyl ether (15 ml) and the insoluble material was removed by filtration. Evaporation of the ether from the filtrate gave a pale yellow solid. Recrystallization from hexane gave **5d** as pale yellow crystals (17 mg, 11%), m.p. 96·5–97 °C (from hexane). IR (KBr): 2900, 1710, 1528, 1349, 1286 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8·30 (d, 2H, J = 9·1 Hz), 8·22 (d, 2H, J = 9·1 Hz), 5·06 (m, 1H, H-4), 2·55 (m, 1H), 2·19 (m, 1H), 2·08 (m, 1H), 2·03–1·83 (m, 4H), 1·79–1·43 (m, 8H), 0·95 (s, 3H, CH_3). ^{13}C NMR (67·8 MHz, $CDCl_3$): δ 164·1 (C), 150·5 (C), 136·5 (C), 130·6 (2CH), 123·5 (2CH), 83·3 (CH), 43·2 (CH_2), 42·4 (CH_2), 38·9 (CH_2), 38·1 (C), 37·9 (CH_2), 37·3 (CH_2), 36·1 (CH_2), 31·9 (CH_3), 30·1 (CH), 27·8 (CH), 27·7 (CH). Analysis: calculated for $C_{19}H_{23}NO_4$: C 69·28, H 7·04; found, C 69·26, H 7·18%.

4-Homoadamantyl mesylate (**3a**). To a solution of

5a[8] (99 mg, 0·59 mmol) and triethylamine (90 mg, 0·89 mmol) in CH_2Cl_2 (3·0 ml) was added methanesulphonyl chloride (76 mg, 0·66 mmol) dropwise at −10 °C. The mixture was stirred for 25 min and the solution was poured into cold water (20 ml) and extracted with CH_2Cl_2 (20 ml). The extract was washed with cold 10% HCl (20 ml) and cold 10% NaCl (20 ml) and dried ($MgSO_4$). Removal of the solvent followed by recrystallization from hexane gave **3a** (90 mg, 62%) as colourless plates, m.p. 55–56 °C (from hexane). IR (KBr): 2906, 2849, 1447, 1344, 1167, 905 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4·97 (m, 1H, H-4), 2·98 (s, 3H, MsO), 2·55 (m, 1H), 2·37 (m, 1H), 2·06 (m, 1H), 1·99–1·69 (m, 8H), 1·62–1·39 (m, 5H). ^{13}C NMR (67·8 MHz, $CDCl_3$): δ 87·9 (CH), 41·8 (CH_2), 39·6 (CH_2), 38·5 (CH_3), 38·1 (CH), 35·8 (CH_2), 35·4 (CH_2), 34·9 (CH_2), 29·8 (CH_2), 29·1 (CH), 26·7 (CH), 26·6 (CH). Analysis: calculated for $C_{12}H_{20}O_3S$, C 58·98, H 8·25; found, C 58·71, H 8·31%.

3-Substituted 4-homoadamantyl mesylates (**3b–e**). A typical procedure is as follows. To a solution of **5e** (116 mg, 0·60 mmol) and triethylamine (121 mg, 1·2 mmol) in CH_2Cl_2 (3·0 ml) was added methanesulphonyl chloride (76 mg, 0·66 mmol) dropwise at −10 °C. After 10 min, the solution was transferred to a separating funnel with CH_2Cl_2 (25 ml) and washed with cold water (25 ml), cold 5% $NaHCO_3$ (25 ml) and cold 10% NaCl (25 ml). The extracts were mixed with 2,6-lutidine (128 mg, 1·2 mmol) and dried ($MgSO_4$). The solvent was evaporated at 0 °C under vacuum and the residual oil was dissolved in dry benzene (4 ml). The insoluble material was removed by filtration through a 0·5 μm membrane filter. Most of the benzene was evaporated to give a semi-solid, which was recrystallized from dry hexane at −20 °C to afford 75 mg of **3e**. The samples of **3b–e** were stored at −78 °C.

3b: Recrystallized at room temperature, yield 17%, colourless needles, m.p. 73 °C (decomposed to **9b**). IR (KBr): 2916, 1496, 1445, 1336, 1172, 887 cm^{-1}. ^{1}H NMR ($CDCl_3$): 7·41 (m, 2H), 7·31 (m, 2H), 7·18 (m, 1H), 4·79 (m, 1H, H-4), 2·69–2·55 (m, 2H), 2·32–1·47 (m, 13H), 1·82 (s, 3H, MsO). ^{13}C NMR (67·8 MHz, $CDCl_3$): δ 150·9 (C), 128·1 (2CH), 126·3 (CH), 126·2 (2CH), 92·5 (CH), 44·4 (C), 44·0 (CH_2), 41·3 (CH_2), 37·7 (CH_2), 37·1 (CH_2), 36·2 (CH_3), 35·9 (CH_2), 35·4 (CH_2), 30·1 (CH), 27·9 (CH), 27·5 (CH). Analysis: calculated for $C_{18}H_{24}O_3S$, C 67·47, H 7·55; found, C 67·45, H 7·74%.

3c: Recrystallized at room temperature, yield 27%, colourless crystals, purity 97% (by ^{1}H NMR), m.p. 73 °C (decomposed to **9c**). IR (KBr): 2931, 1515, 1342, 1171 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7·34 (d, 2H, $J = 9·1$ Hz), 6·87 (d, 2H, $J = 9·1$ Hz), 4·72 (dd, 1H, $J = 9·3$, 1·6 Hz, H-4), 3·80 (s, 3H, OCH_3), 2·68–2·53 (m, 2H), 2·29–1·70 (m, 10H), 1·87 (s, 3H, MsO), 1·66–1·45 (m, 3H). ^{13}C NMR (67·8 MHz, $CDCl_3$): δ 157·5 (C), 143·0 (C), 127·2 (2CH), 113·0 (2CH), 92·8 (CH), 55·3 (CH_3), 43·8 (CH_2), 43·6 (C), 41·0 (CH_2), 37·6 (CH_2), 36·7 (CH_2), 35·93 (CH_2), 35·89 (CH_3), 35·1 (CH_2), 29·8 (CH), 27·5 (CH), 27·1 (CH).

3d: Recrystallized at −20 °C, yield 80%, colourless crystals, decomposed to olefins at room temperature. ^{1}H NMR ($CDCl_3$, −20 °C): δ 4·62 (m, 1H, H-4), 3·03 (s, 3H, MsO), 2·51 (m, 1H), 2·12–1·32 (m, 14H), 1·04 (s, 3H). ^{13}C NMR (67·8 MHz, $CDCl_3$, −20 °C): δ 91·3 (CH), 42·8 (CH_2), 42·5 (CH_2), 38·6 (CH_3), 38·2 (C), 37·68 (CH_2), 37·66 (CH_2), 36·5 (CH_2), 35·5 (CH_2) 32·2 (CH_3), 29·5 (CH), 27·2 (CH), 27·0 (CH).

3e: Recrystallized at −20 °C, yield 46%, colourless crystals, purity ⩾99% (by ^{1}H NMR), decomposed to olefins at room temperature. ^{1}H NMR ($CDCl_3$, −20 °C): δ 4·87 (m, 1H), 3·04 (s, 3H, MsO), 2·48 (m, 1H), 2·17–2·03 (m, 2H), 1·99–1·77 (m, 5H), 1·74–1·29 (m, 8H), 1·17 (m, 1H), 0·87 (t, 3H, $J = 7·6$ Hz, CH_3). ^{13}C NMR (67·8 MHz, $CDCl_3$, −20 °C): δ 87·5 (CH), 42·4 (CH_2) 40·1 (C), 39·1 (CH_3), 37·9 (CH_2), 37·50 (CH_2), 37·46 (CH_2), 36·9 (CH_2), 35·8 (CH_2), 35·6 (CH_2), 29·7 (CH), 27·1 (CH), 26·9 (CH), 7·4 (CH_3).

3-Substituted 4-methoxyhomoadamantanes (**6b–e**). A typical procedure is as follows. To a solution of **5b** (107 mg, 0·44 mmol) in DSMO (1·32 ml) were added CH_3I (250 mg, 1·8 mmol) and finely divided KOH (114 mg, 2·0 mmol), and the mixture was stirred for 2·5 h. The solution was poured into water (11 ml) and extracted with diethyl ether (3 × 6 ml). The combined extracts were washed with water (3 × 25 ml) and dried ($MgSO_4$). Preparative TLC [SiO_2, hexane–diethyl ether (19 : 1)] gave 69 mg of **6b**.

6b: Yield 61%, colourless crystals, m.p. 26–27 °C. IR (KBr): 2902, 1496, 1444, 1098, 751, 698 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7·38 (m, 2H), 7·26 (m, 2H), 7·13 (m, 1H), 3·28 (m, 1H, H-4), 2·77 (s, 3H, OCH_3), 2·67 (m, 1H), 2·32–1·70 (m, 11H), 1·62–1·45 (m, 3H). ^{13}C NMR (67·8 MHz, $CDCl_3$): δ 152·7 (C), 127·3 (2CH), 125·9 (2CH), 125·0 (CH), 89·5 (CH), 57·7 (CH_3), 44·6 (C), 41·3 (CH_2), 41·2 (CH_2), 39·1 (CH_2), 36·5 (CH_2), 36·01 (CH_2), 36·00 (CH_2), 30·5 (CH), 28·4 (CH), 28·0 (CH). Analysis: calculated for $C_{18}H_{24}O$, C 84·32, H 9·44; found, C 84·10, H 9·70%.

6c: Yield 28%, colourless crystals, m.p. 66·5–67 °C (from hexane). IR (KBr): 2899, 1609, 1513, 1252, 1094, 827 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7·29 (d, 2H, $J = 8·9$ Hz), 6·80 (d, 2H, $J = 8·9$ Hz), 3·78 (s, 3H, OCH_3), 3·23 (m, 1H, H-4), 2·79 (s, 3H, OCH_3), 2·63 (m, 1H), 2·23 (m, 1H), 2·17–1·98 (m, 4H), 1·97–1·83 (m, 4H), 1·82–1·69 (m, 2H), 1·68–1·44 (m, 3H). ^{13}C NMR (67·8 MHz, $CDCl_3$): δ 156·9 (C), 145·1 (C), 126·8 (2CH), 112·5 (2CH), 89·6 (CH), 57·8 (CH_3), 55·1 (CH_3), 44·1 (C), 41·5 (CH_2), 41·2 (CH_2), 39·1 (CH_2), 36·5 (CH_2), 36·3 (CH_2), 36·1 (CH_2), 30·5

(CH), 28·4 (CH), 28·0 (CH). Analysis: calculated for $C_{19}H_{26}O_2$, C 79·68, H 9·15; found, C 79·41, H 9·42%.

6d: Yield 26%, colourless oil. IR (liquid film): 2899, 1447, 1099, 1083 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3·30 (s, 3H, OCH_3), 2·94 (m, 1H, H-4), 2·17 (m, 1H), 2·08–1·94 (m, 2H), 1·92–1·75 (m, 5H), 1·65–1·36 (m, 6H), 1·23 (m, 1H), 0·96 (s, 3H, CH_3). ^{13}C NMR (67·8 MHz, $CDCl_3$): δ 88·9 (CH), 57·5 (CH_3), 43·5 (CH_2), 41·0 (CH_2), 38·7 (C), 38·2 ($2CH_2$), 37·3 (CH_2), 36·5 (CH_2), 32·3 (CH_3), 30·4 (CH), 28·2 (CH), 27·9 (CH). Analysis: calculated for $C_{13}H_{22}O$, C 80·5, H 11·41; found, C 80·51, H 11·60%.

6e: Yield 39%, colourless oil. IR (liquid film): 2902, 2846, 1446, 1372, 1098, 1083 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3·28 (s, 3H, OCH_3), 3·14 (m, 1H, H-4), 2·20 (m, 1H), 2·05 (m, 1H), 1·96–1·35 (m, 13H), 1·21 (m, 1H), 1·05 (m, 1H), 0·78 (t, 3H, $J = 7·4$ Hz, CH_3). ^{13}C NMR (67·8 MHz, $CDCl_3$): δ 84·3 (CH), 56·7 (CH_3), 40·6 (CH_2), 40·4 (C), 39·7 (CH_2), 38·3 (CH_2), 37·9 (CH_2), 37·5 (CH_2), 36·7 (CH_2), 36·4 (CH_2), 30·4 (CH), 27·83 (CH), 27·78 (CH), 8·0 (CH_3). Analysis: calculated for $C_{14}H_{24}O$, C 80·71, H 11·61; found, C 80·82, H 11·66%.

4-Methoxy-4-methylhomoadamantane (**8d**). A solution of 4-homoadamantanone **4a**[8] (105 mg, 0·64 mmol) in THF (2·0 ml) was added dropwise to 1·01 M CH_3Li[21] in diethyl ether (0·90 ml, 0·91 mmol) under N_2, and the mixture was refluxed for 1 h. CH_3I (180 mg 1·3 mmol) was added dropwise at room temperature, and the solution was refluxed for 2 days. Evaporation of the solvent gave a yellow oil. Water (2 ml) was added and the mixture was extracted with diethyl ether (5 × 2 ml). The combined extracts were dried over $MgSO_4$. The solvent was evaporated to give a pale yellow oil, which was purified by MPLC [SiO_2, hexane–diethyl ether (9 : 1)] to afford **8d** as a colourless oil (57 mg, 46%). IR (liquid film): 2898, 1447, 1363, 1117, 1073 cm^{-1}. ^1H NMR ($CDCl_3$): 3·13 (s, 3H, OCH_3), 2·15–1·93 (m, 4H), 1·91–1·64 (m, 8H), 1·58–1·45 (m, 4H), 1·27 (s, 3H, CH_3). ^{13}C NMR (67·8 MHz, $CDCl_3$): δ 81·5 (C), 49·3 (CH_2), 48·7 (CH_3), 39·4 (CH), 38·2 (CH_2), 37·3 (CH_2), 36·9 (CH_2), 32·4 (CH_2), 30·8 (CH_2), 30·7 (CH), 27·9 (CH), 27·7 (CH), 26·9 (CH_3). Analysis: calculated for $C_{13}H_{22}O$, C 80·35, H 11·41; found, C 80·42, H 11·64%.

4-Phenyl-4-homoadamantene (**9b**). Mesylate **3b**, synthesized from 234 mg of **5b** (0·97 mmol) as described above, was refluxed in hexane (28 ml) for 0·1 h. The hexane was evaporated and the residue was dissolved in CH_2Cl_2 (30 ml), washed with 2% $NaHCO_3$ (30 ml) and 10% NaCl (20 ml) and dried ($MgSO_4$). Evaporation of the solvent followed by MPLC (SiO_2, hexane) gave **9b** (160 mg, 74%) as a colourless oil. IR (liquid film): 2908, 2841, 1645, 1443, 954, 766, 750, 697 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7·32–7·13 (m, 5H), 6·20 (dd, 1H, $J = 8·8$, 1·7 Hz, H-5), 2·82 (m, 1H, H-3), 2·44 (m, 1H, H-6), 2·15 (m, 2H, H-1 and H-8), 1·99–1·73 (m, 10H). ^{13}C NMR (67·8 MHz, $CDCl_3$): δ 150·2 (C), 144·8 (C), 135·2 (CH), 128·1 (2CH), 126·2 (CH), 125·5 (2CH), 37·3 (CH), 36·6 (CH_2), 34·1 ($2CH_2$), 34·0 ($2CH_2$), 32·2 (CH), 29·5 (2CH). Analysis: calculated for $C_{17}H_{20}$, C 91·01, H 8·99; found, C 91·05, H 9·14%.

4-p-Anisyl-4-homoadamantene (**9c**). Mesylate **3c** (189 mg) was refluxed in hexane–diethyl ether (20 ml, 1 : 1) for 2 h. The solution was filtered through SiO_2 (0·5 g) and evaporated to give a pale yellow solid. The crude product was recrystallized from hexane to afford **9c** (36 mg, 26%) as colourless crystals, m.p. 105–106 °C (from hexane). IR (KBr): 2902, 1643, 1511, 1289, 1244, 1182, 1035 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7·23 (d, 2H, $J = 8·9$ Hz), 6·82 (d, 2H, $J = 8·9$ Hz), 6·13 (dd, 1H, $J = 8·9$, 1·8 Hz, H-5), 3·79 (s, 3H, OCH_3), 2·78 (m, 1H), 2·42 (m, 1H), 2·15 (m, 2H), 1·96–1·74 (m, 10H). ^{13}C NMR (67·8 MHz, $CDCl_3$): δ 158·2 (C), 149·6 (C), 137·3 (C), 133·7 (CH), 126·6 (2CH), 113·5 (2CH), 55·3 (CH_3), 37·3 (CH), 36·7 (CH), 34·2 ($2CH_2$), 33·9 ($2CH_2$), 32·1 (CH), 29·5 (2CH). Analysis: calculated for $C_{18}H_{22}O$, C 84·99, H 8·72; found, C 84·86, H 8·92%.

4-Methylenehomoadamantane (**10**). To a stirred suspension of methyltriphenylphosphonium bromide (1·26 g, 3·54 mmol) in diethyl ether (8·8 ml) was added a 2·05 M solution of *n*-butyllithium in hexane (1·72 ml) dropwise under a N_2 atmosphere. The mixture was stirred for 30 min and 4-homoadamantanone **4a**[8] (194 mg, 1·18 mmol) in diethyl ether (3·5 ml) was added dropwise at room temperature. The reaction mixture was refluxed overnight and subsequently quenched with water (10 ml). The precipitated phosphonium salt was filtered and washed with diethyl ether (10 ml). The filtrate was washed with water (4 × 5 ml) and dried ($MgSO_4$). Evaporation of the solvent followed by medium-pressure liquid chromatography (SiO_2, hexane) gave **10** (129 mg, 67%) as a colourless oil. IR (liquid film): 3066, 2896, 1627, 1443, 1100, 891, 874 cm^{-1}. (lit.[22] 3050, 2930, 1615, 1430, 1110, 890, 875 cm^{-1}). ^1H NMR ($CDCl_3$): δ 4·74 (q, 1H, $J = 2·2$ Hz), 4·55 (q, 1H, $J = 2·2$ Hz), 2·68 (m, 1H), 2·57 (m, 2H), 2·04 (m, 1H), 1·98–1·85 (m, 6H), 1·60–1·46 (m, 6H). ^{13}C NMR (67·8 MHz, $CDCl_3$): δ 157·3 (C), 108·7 (CH_2), 42·4 (CH_2), 42·1 (CH), 37·9 ($2CH_2$), 37·7 ($2CH_2$), 36·0 (CH_2), 29·9 (CH), 27·4 (2CH). Analysis: calculated for $C_{12}H_{18}$, C 88·82, H 11·18; found, C 88·73, H 11·40%.

Products of methanolysis of 4-homoadamantyl mesylate (**3a**). A solution of **3a** (51 mg, 0·21 mmol) in methanol (5·5 ml) containing 0·050 M 2,6-lutidine was heated in a constant-temperature bath (25 °C) for 305 h (10 half-lives). After the solvent had been removed on an ice–water bath under vacuum, 9-phenylfluorene [35·1 mg, 0·145 mmol, δ 5·03 (H-9)] was added as an internal standard. The mixture was dissolved in $CDCl_3$ (1 ml) and subjected to ^1H NMR analysis (room temperature, pulse interval 20 s). The yields of products were determined by integrating the following signals: **6a**, δ 3·27 (s, 3H, OCH_3, lit.[23] δ 3·20); **7a**, δ 6·03 (dd, 2H, $J = 3·5$, 5·9 Hz, H-4 and 5, lit.[6b] δ 6·10); *exo*-2-methoxyhomoadamantane, δ 3·31 (s, 3H, OCH_3, lit.[8] δ 3·31); 2,4-dehydrohomoadamantane, δ 0·73 (m, 2H, H-3 and 4).

Products of methanolysis of 3-phenyl-4-homoadamantyl mesylate (**3b**). A solution of **3b** (47 mg, 0·15 mmol) in MeOH (20 ml) containing 0·050 M 2,6-lutidine was heated in a constant-temperature bath (25 °C) for 124 h (16 half-lives). After the solvent had been evaporated, diethyl ether (50 ml) was added to the resulting oil. The mixture was washed with 10% NaCl (20 ml), cold 5% HCl (20 ml), 10% NaCl (20 ml), 5% $NaHCO_3$ (20 ml) and saturated NaCl (20 ml) and dried ($MgSO_4$). The solvent was evaporated, and the residue was dissolved in $CDCl_3$ and subjected to ^1H NMR analysis (room temperature, pulse interval 20 s). The yields of products were determined by integrating the following signals: **6b**, δ 3·24 (m, 1H, H-4), 2·78 (s, 3H, OCH_3); **7b**, δ 6·02 (dd, 1H, $J = 8·7$, 10·6 Hz, H-5), 5·85 (d, 1H, $J = 10·6$ Hz, H-4); **8b**, δ 2·89 (s, OCH_3); **9b**, δ 6·20 (dd, 1H, $J = 1·7$, 8·8 Hz, H-5).

Products of methanolysis of 3-p-anisyl-4-homoadamantyl mesylate (**3c**). A solution of **3c** (27 mg, 0·076 mmol) in MeOH (1·9 ml) containing 0·050 M 2,6-lutidine was heated in a constant-temperature bath (25 °C) for 71·2 h (16 half-lives). After the solvent had been removed on an ice–water bath under vacuum, the residue was dissolved in $CDCl_3$ (0·8 ml) containing 9-phenylfluorene [13·4 mg, 0·0554 mmol, δ 5·06 (H-9)] as an internal standard and subjected to ^1H NMR analysis (−20 °C, pulse interval 10 s). The yields of products were determined by integrating the following signals: **6c**, δ 2·79 (s, 3H, OCH_3; **7c**, 6·00 (dd, 1H, $J = 8·6$, 10·7 Hz, H-5), 5·80 (d, 1H, $J = 10·7$ Hz, H-4); **8c**, δ 2·90 (s, 3H, OCH_3); **9c**, δ 6·14 (dd, 1H, $J = 1·6$, 8·8 Hz, H-5).

Products of methanolysis of 3-methyl-4-homoadamantyl mesylate (**3d**). A solution of **3d** (97 mg, 0·38 mmol) in MeOH (12 ml) containing 0·050 M 2,6-lutidine was heated in a constant-temperature bath (25 °C) for 3·25 h (12 half-lives). After the solvent had been removed on an ice–water bath under vacuum, the residue was dissolved in $CDCl_3$ (1·0 ml) containing 9-phenylfluorene [35·5 mg, 0·46 mmol, δ 5·05 (H-9)] as an internal standard and subjected to ^1H NMR analysis (−10 °C, pulse interval 20 s). The yields of products were determined by integrating the following signals: **6d**, δ 3·30 (s, 3H, OCH_3); **7d**, δ 5·94 (dd, 1H, $J = 8·5$, 10·5 Hz, H-5), 5·57 (d, 1H, $J = 10·5$ Hz, H-4) [lit.[14] 6·6–6·0 (m, 2H)]; **8d**, δ 3·13 (s, 3H, OCH_3); **9d**, δ 5·70 (m, 1H, $J = 8·6$, 1·6 Hz, H-5); **10**, δ 4·74 (q, 1H, $J = 2·0$ Hz, =CH), 4·55 (q, 1H, $J = 2·0$ Hz, =CH).

Products of methanolysis of 3-ethyl-4-homoadamantyl mesylate (**3e**). A solution of **3e** (75 mg, 0·28 mmol) in MeOH (13·5 ml) containing 0·050 M 2,6-luidine was heated in a constant-temperature bath (25 °C) for 65 min (14 half-lives). After the solvent had been removed on an ice–water bath under vacuum, the residue was dissolved in $CDCl_3$ (1·0 ml) containing fluorene [23·8 mg, 0·143 mmol, δ 3·90 (H-9)] as an internal standard and subjected to ^1H NMR analysis (−20 °C, pulse interval 20 s). The yields of products were determined by integrating the following signals: **6e**, δ 3·29 (s, 3H, OCH_3); **7e**, δ 6·01 (dd, 1H, $J = 8·4$, 10·8 Hz, H-5); **8e**, δ 3·06 (s, 3H, OCH_3); **9e**, δ 5·66 (dd, 1H, $J = 8·7$, 1·4 Hz, H-5); **11** (*E* and *Z*-isomers), δ 5·26 (q, 1H, $J = 6·7$ Hz, =CH), δ 5·09 (q, 1H, $J = 6·8$ Hz, =CH).

Kinetic procedure. The preparation of 80% ethanol and the kinetic methods were described previously.[24] All measurements were conducted in the presence of 0·025 M 2,6-lutidine with 0·02 M or $(1–2) \times 10^{-4}$M substrate concentrations for titrimetric or conductimetric measurements, respectively. The first-order rate constants were calculated by the least-squares method.

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