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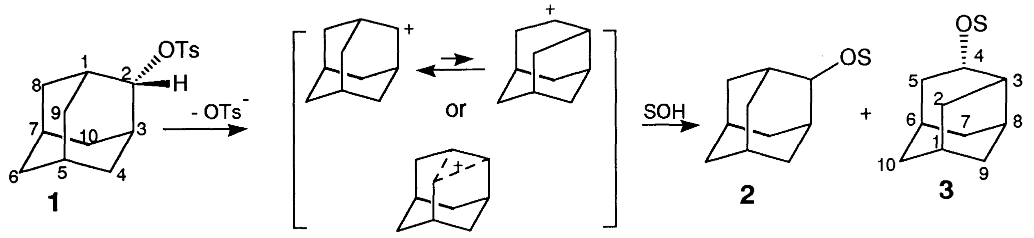
# Intermediacy of Rapidly Equilibrating Classical Cations in the Solvolyses of 4-Methylene-$2_{ax}$-adamantyl *p*-Toluenesulfonate

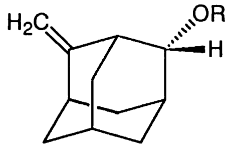
Ken'ichi TAKEUCHI,* Yumiko KURIHARA, Toshikazu KITAGAWA, and Tomomi KINOSHITA
Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606-01

Although the solvolysis of title compound affords products having an adamantyl and a protoadamantyl structure in a ratio of 39:61 in methanol and 71:29 in 2,2,2-trifluoroethanol, indicating possible formation of a nearly symmetric cation, the retention:inversion ratios in the adamantyl product in the respective solvents are 83:17 and 82:18. The product distributions along with kinetic data support the intermediacy of rapidly equilibrating classical cations.

2-Adamantyl *p*-toluenesulfonate (tosylate) (**1**) has been proposed as a typical secondary compound which undergoes limiting $S_N1$ ($k_c$) solvolyses.[1] However, it is still controversial whether the carbocation intermediate is bridged (nonclassical) or unbridged (classical).[2,3] Major retention of configuration of the 2-adamantyl product (**2**) with 64-84% (stereoselectivity estimated from solvolyses of 5-methyl-2-adamantyl substrates),[4] formation of a small amount (0.5%) of 4-protoadamantyl (tricyclo[4.3.1.$0^{3,8}$]dec-4-yl) product (**3**),[5,6] and high *exo*/*endo* reactivity ratio of an order of $10^4$ in 4-protoadamantyl solvolyses[6] have been taken as evidence for the formation of a highly unsymmetrical, weakly bridged intermediate cation.



Should the intermediate cation be bridged, the extent of bridging may be increased by introducing an appropriate substituent such as methyl into the 1-position of 2-adamantyl substrates. The increased formation of 4-methyl-4-protoadamantanol with a 2-adamantyl:4-protoadamantyl product ratio of 7:3,[7] the increased rate by a factor of 24-38 on introduction of a methyl group to the 1-position,[7] the methyl-$d_3$ kinetic isotope effect (1.05) in the solvolysis of 1-(methyl-$d_3$)-2-adamantyl tosylate,[8] and the absence (<3%) of 4-methyl-*endo*-4-protoadamantanol in hydrolysis[9] have been interpreted to show increased σ-bridging in both the transition state and the intermediate. However, the increased rate on introducing the 1-methyl substituent was also explicable on the basis of steric and inductive effects in ionization to give the classical 2-adamantyl cation.[10]



**R=H; 4a-OH**
**R=Ts; 4a-OTs**

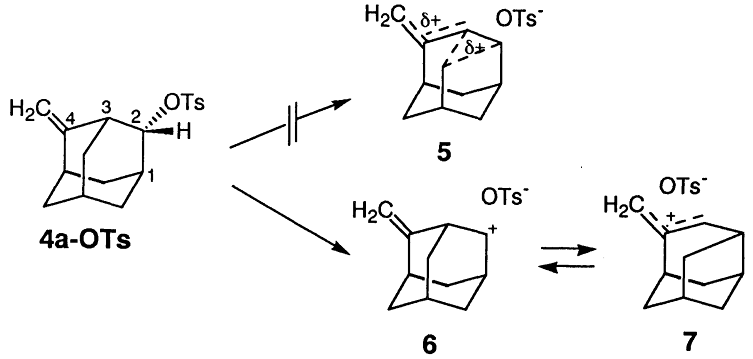
With such background, we wished to design a new system which would afford a nearly symmetrically bridged cation (if it were nonclassical) *without any substituent on the bridgehead carbon adjacent to the cationic center.* As a candidate we examined the solvolyses of 4-methylene-2$_{ax}$-adamantyl tosylate (**4a-OTs**). 4-Methylene-2$_{ax}$-adamantanol (**4a-OH**) was prepared conveniently in a different manner than a reported method:[11] the Wittig methylenation of the *t*-butyldimethylsilyl ethers of 4-oxo-2$_{ax}$-adamantanol[12] followed by desilylation with $Bu_4N^+F^-$ of the produced 4-methylene product afforded **4a-OH**.[13] The alcohol was converted into tosylate **4a-OTs** in a usual manner.[14] The rates of solvolysis were titrimetrically determined in methanol and 2,2,2-trifluoroethanol (TFE) in the presence of 2,6-lutidine: the results are given in Table 1 along with reported data of **1**. All the rate runs followed satisfactory first-order kinetics.

Table 1. Titrimetric Rates of Solvolyses of 2-Adamantyl Tosylate (**1**) and 4-Methylene-2$_{ax}$-adamantyl Tosylate (**4a-OTs**)a)

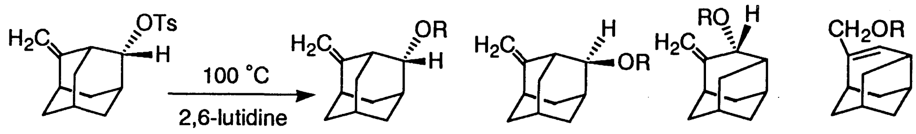
| Compound | Solvent | Temp/°C | k /s$^{-1}$ b) | Relative rate | | $\Delta H^{\ddagger}_{298}$ | $\Delta S^{\ddagger}_{298}$ |
|---|---|---|---|---|---|---|---|
| | | | | MeOH | TFE | /kJ mol$^{-1}$ | /J K$^{-1}$mol$^{-1}$ |
| **1** | MeOH | 25 | $2.90 \times 10^{-9}$ c) | 1.0 | | | |
| | TFEd) | 25 | $1.51 \times 10^{-6}$ c) | | 1.0 | | |
| **4a-OTs** | MeOH | 25 | $1.27 \times 10^{-9}$ e) | 0.44 | | 123 | -1.8 |
| | | 75 | $1.86 \times 10^{-6}$ | | | | |
| | | 100 | $3.42 \times 10^{-5}$ | | | | |
| | TFEd) | 25 | $6.13 \times 10^{-7}$ e) | | 0.41 | 88.7 | -67 |
| | | 35 | $2.28 \times 10^{-6}$ | | | | |
| | | 50 | $1.06 \times 10^{-5}$ | | | | |

a) The concentrations of substrate and 2,6-lutidine were $2.5 \times 10^{-3}$ and $5 \times 10^{-3}$ M, respectively. b) Determined by a single run. In all cases the correlation coefficient for the first-order plot was greater than 0.999 within an experimental error of ±2%. c) Ref. 1b. d) 2,2,2-Trifluoroethanol. e) Extrapolated from data at higher temperatures.

The rates of solvolyses of **4a-OTs** were slower than those of parent 2-adamantyl tosylate (**1**) by the factors of 2.3 and 2.5 in methanol and TFE, respectively, at 25 °C. However, these decelerating effects of the methylene substituent are much smaller than the effect of that substituent in 3-methylenebicyclo[2.2.2]oct-1-yl triflate which solvolyzes 159 times slower than bicyclo[2.2.2]oct-1-yl triflate in 80% ethanol at 25 °C.[15] Presumably, the developing positive charge in the transition state of ionization of **4a-OTs** is delocalized to C(3) by σ-conjugation and further to the methylene substituent by allylic conjugation. Nevertheless, the σ-conjugation in the transition state does not appear to be directly concerned with the formation of an intermediate σ-bridged cation as depicted by **5**. The following product studies supported the intermediacy of rapidly equilibrating cations **6** and **7**.



The solvolyses of **4a-OTs** (0.04 M) were carried out in MeOH and TFE for five half-lives at 100 °C in the presence of excess 2,6-lutidine (0.05 M) to give the four products, $2_{ax}$- and $2_{eq}$-alkoxy-4-methyleneadamantanes (**4a-OR** and **4e-OR**, respectively), *exo*-4-alkoxy-5-methyleneprotoadamantane (**8-OR**), and 5-(alkoxymethyl)-4-protoadamantene (**9-OR**) (Chart 1). The identification of the products rests on $^{13}C$ and $^{1}H$ NMR and GLC.16)



| 4a-OTs | 4a-OR | 4e-OR | 8-OR | 9-OR |
|---|---|---|---|---|
| In MeOH, R=Me | 32.6 | 6.6 | 49.7 | 11.1 |
| In TFE, R=$CF_3CH_2$ | 58.0 | 13.0 | 28.3 | 0.7 |

Chart 1. Product distributions (%) in the solvolyses of **4a-OTs**.

The ratio between the adamantyl (**4a-OR** and **4e-OR**) and protoadamantyl (**8-OR** and **9-OR**) products is 39:61 in methanolysis and 71:29 in trifluoroethanolysis.17) These product distributions suggest that, if the intermediate cation were bridged, the $\sigma$-bridging would be nearly symmetric. In this context, it is generally accepted that exclusive formation of a retention product is a prerequisite in postulating a bridged cation. However, a considerable amount of equatorial (rear-side attack) product (**4e-OR**) was formed with essentially constant axial:equatorial (**4a-OR**:**4e-OR**) ratios in the adamantyl product, i.e., 83:17 (in MeOH) and 82:18 (in TFE).18) These similar axial:equatorial product ratios despite marked difference in the solvent nucleophilicity1b) indicate that a $k_S$ process is unimportant. The equatorial stereoselectivity of 17-18% despite advanced symmetric nature of the intermediate cation is more reasonably explained in terms of a pair of rapidly equilibrating classical cations **6** and **7** than assuming a nonclassical cation **5**.

It might be argued that the nonclassical cation as depicted by **5** should not exist since delocalization of positive charge to the methylene group permits the existence of an allylic cation **7**. However, such argument favoring the existence of **7** on the one hand leads to the support of the intermediacy of a classical ion **6** on the other. Although the present results do not permit a definitive answer to the question whether the parent 2-adamantyl cation is partially bridged4-7) or hyperconjugatively stabilized,2,3) it is suggested that a stabilizing substituent on the C(1) bridgehead position allows a 2-adamantyl cation to exist in a classical form in solvolyses.

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13) The spectral data agreed with those reported in Ref. 11.

14) **4a-OTs**: mp 74.0-74.5 °C; $^{13}C$ NMR ($CDCl_3$) δ = 21.2, 26.3, 32.5, 32.6, 35.7, 37.3, 37.9, 38.5, 42.9, 86.0, 105.3, 127.1, 129.3, 134.7, 144.0, 150.7. Anal. Found: C, 67.83; H, 7.08%. Calcd for $C_{18}H_{22}O_3S$: C, 67.89; H, 6.96%.

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16) The products were stable under the solvolysis conditions except that **4a-OMe** underwent slow addition of methanol to the double bond to give an addition product, whose yield (2.9%) was added to that of **4a-OMe**. Structural assignments were made by comparing the $^{13}C$ and/or $^{1}H$ NMR spectra of crude products with those of reported compounds[11] **4a-OH**, **4e-OH** and **4e-OMe** and of some new compounds, **4a-OMe**, **8-OH**, **8-OMe** and **9-OMe**, obtained in this work as a major component in a mixture. $^{13}C$ NMR ($CDCl_3$): **4a-OMe** δ = 27.3, 31.0, 33.2, 36.0, 38.2 (two peaks), 39.3, 42.5, 55.2, 84.4, 103.6, 154.0; **8-OH** δ = 31.4, 32.2, 35.3, 36.0, 37.2, 39.4, 40.5, 42.5, 74.5, 114.0, 155.9; **8-OMe** δ = 31.4, 31.8, 35.3, 35.4, 37.0, 37.9, 41.1, 42.3, 55.5, 83.4, 115.2, 149.9. The *exo* configuration of **8-OR**'s was determined by comparing their $^{13}C$ NMR data with those of **8-OH** (97% pure) whose configuration was established by $^{1}H$ NMR NOE difference experiments. Assignment of the structure of **9-OMe** rests on $^{1}H$ NMR ($CDCl_3$, 270 MHz) signals of two nonequivalent methylene protons of the $MeOCH_2$ group at δ 3.80 (1H, d, J = 11.5 Hz) and 3.85 (1H, d, J = 11.5 Hz), and an olefinic proton at δ 6.10 (1H, d, J = 7.0 Hz).

17) In hydrolysis in 80% acetone the ratio was 56:44 with the **4a-OH**:**4e-OH**:**8-OH**:**9-OH** ratio of 47.0:8.6:41.6:2.8.

18) It is unlikely that **4e-OMe** was formed owing to the configurational change of **4a-OTs** or its ion pair to the corresponding equatorial form in solvolysis since 2-methoxy-2,4-methanoadamantane, which is formed only in the methanolysis of **4e-OTs**, was not detected. The details will be reported in a full paper.

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