

Solvolysis of chiral cyclohexylidenemethyl triflate. Evidence against a primary vinyl cation intermediate[†]

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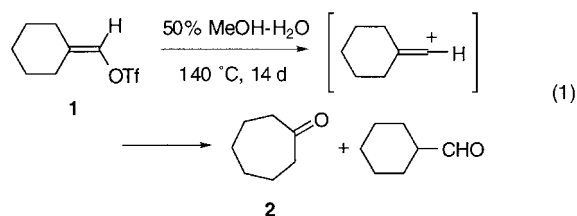
ABSTRACT: Solvolysis of (*R*)-4-methylcyclohexylidenemethyl triflate (**6**) was examined at 140 °C in various aqueous methanol and some other alcoholic solvents. The main product was (*R*)-4-methylcycloheptanone that maintains the stereochemical purity of **6**, with accompanying 4-methylcyclohexanecarbaldehyde. In the presence of bromide ion, the bromide substitution product was also obtained, mostly with inversion of configuration. It is concluded that the solvolysis does not involve the formation of the primary vinyl cation but proceeds via σ -bond participation to form the rearranged cycloheptenyl cation as an intermediate. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: vinyl triflate; vinyl cation; solvolysis; vinylic S_N2 reaction; σ -bond participation; rearrangement; chirality probe approach

INTRODUCTION

Solvolysis of vinyl triflates has been extensively studied, but most of the substrates are those activated by the α -aryl or α -alkyl group.¹ Vinyl cations were established as definite intermediates in these reactions. However, the initial suggestion of the formation of some unstable vinyl cations during the solvolysis was later discounted, e.g. 1-cyclopentenyl triflate does not react thermally via a cyclopentenyl cation but undergoes reaction via a sulfur–oxygen bond cleavage.² Similar ambiguities still remain with primary vinyl cations, which are not readily accessible owing to their instability.³ Theoretical calculations (at the correlation level) show that no classical structures of primary vinyl cations can be located as an energy-minimum species.⁴ A primary vinyl triflate such as cyclohexylidenemethyl triflate (**1**) was found to react very slowly in aqueous alcohols to give mainly the rearranged product, cycloheptanone (**2**) [Eqn. (1)].^{5,6} This rearrangement can occur through the primary vinyl cation, but Stang and Deuber⁵ suggested that it occurred directly via σ -bond participation to avoid the unstable primary cation. Nonetheless, Hanack *et al.*⁶ claimed that the primary cation must be involved because the unrear-

ranged products were also formed by nucleophilic trapping and the reaction was much more sluggish in pure methanol, showing that the transition state is polar.

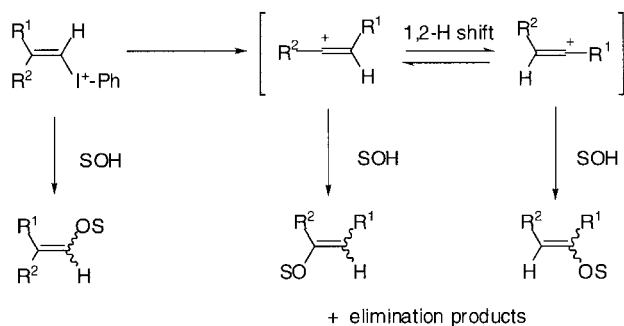


We have also encountered such ambiguities when the solvolysis of 2,2-dialkylvinylidonium salts has been examined (Scheme 1).⁷ Extensive non-stereoselective rearrangements were observed, and at the same time stereoconvergent unrearranged substitution products were formed. Similar situations were also found in the thermolysis of vinylidonium triflates.⁸ These results seemed to suggest intermediate formation of the primary vinyl cation. However barrierless interconversion is possible between the isomeric open-chain secondary vinyl cations via a 1,2-hydride shift, as the theoretical calculations show.⁷ This explains observed non-selective rearrangements. Furthermore, various theoretical considerations⁹ now show that both in-plane and out-of-plane vinylic S_N2 reactions are feasible. Hence, direct nucleophilic substitution of vinyl compounds may give not only the products of inversion but also the those of

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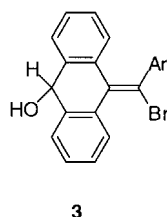
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retention. Such results were in fact observed for the solvolysis of 1-alkenylidonium salts¹⁰ and halide reactions of 2,2-dialkylvinylidonium salts.¹¹

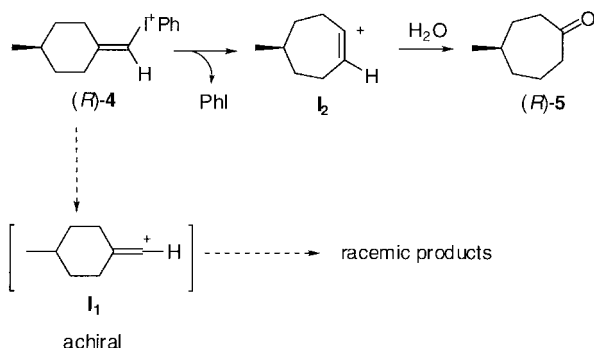


Scheme 1

It is obviously necessary to have a more definitive criterion as to whether or not an unstable intermediate such as a primary vinyl cation is involved. The chirality probe approach to this problem is most promising. For reactions of vinylic centers, an axial chirality has to be used, since the reaction center cannot be a stereocenter as in the case of reactions at the tetrahedral carbon. A chiral anthrylidene derivative **3**^{12a} and haloallene^{12b} have been used to investigate the ion-pair processes of vinylic solvolysis.



4-Substituted cyclohexylidenemethyl systems have been applied to the Grignard reaction¹³ and carbenoid chemistry.¹⁴ We have successfully employed optically active 4-methylcyclohexylidenemethyl(phenyl)iodonium tetrafluoroborate (**4**) as a chirality probe for a primary vinyl cation intermediate (Scheme 2).¹⁵

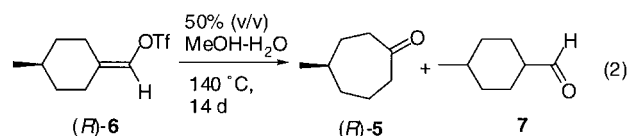


Scheme 2

The enantiomeric purity of **4** was found to be

transferred completely to the main product, 4-methylcycloheptanone (**5**), showing that no achiral intermediate such as primary vinyl cation **I1** is involved during the reaction. The rearrangement should occur stereospecifically via σ -bond participation directly leading to secondary cation **I2**.

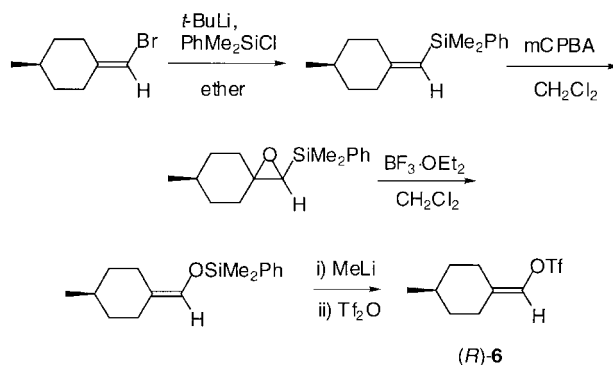
In this work, we applied a similar approach to vinyl triflate solvolysis¹⁶ under the same conditions as employed previously for the cyclohexylidenemethyl derivative **1**.⁶ Solvolysis of optically active 4-methylcyclohexylidenemethyl triflate (**6**) gave mainly the rearranged ketone **5** with retention of the optical purity [Eqn. (2)]. That is, formation of the primary vinyl cation is excluded as an intermediate, contrary to the previous conclusion.⁶



RESULTS AND DISCUSSION

Preparation of optically active vinyl triflate

(*R*)-4-Methylcyclohexylidenemethyl triflate (**6**) was prepared from the (*R*)-vinyl bromide (Scheme 3) derived from the carboxylic acid which was obtained by resolution.¹⁷ The bromide was converted in to the silyl enol ether by using the stereospecifically retained processes developed by Fleming and Newton.¹⁸ Finally, the enolate generated by desilylation was trapped by triflic anhydride to give optically active **6** of *R* configuration at an enantiomeric excess (*ee*) of about 70%, as determined by means of chiral gas chromatography.



Scheme 3

Solvolysis products

Samples of (*R*)-**6** used for solvolysis were of 68 and 73% *ee* and also a racemic mixture. The reaction was carried out in various alcoholic solvents in a sealed Pyrex tube at

Table 1. Products of solvolysis of triflate (*R*)-**6** in various solvents at 140 °C

Run	Substrate % <i>ee</i>	Solvent ^a	<i>Y</i> _{OTf} ^b	<i>N</i> _{OTf} ^c	Time (days)	Yield (%) (% <i>ee</i>)			
						(<i>R</i>)- 5	7	(<i>S</i>)- 8	(<i>R</i>)- 6
1	0	MeOH	−0.92	−0.44	28	3 (0)	3	—	68 (0)
2	73	MeOH (Br [−]) ^d			14	3 (70)	trace	12 (71)	65 (73)
3	68	80MeOH	0.47	−0.05	7	13 (67)	15	—	47 (68)
4	73	50MeOH	2.00	−0.19	14	59 (71)	17	—	0
5	73	50MeOH	2.00	−0.19	4	43 (71)	4	—	22 (73)
6	73	50MeOH (Br [−]) ^d			14	32 (71)	8	2 (64)	0
7	68	20MeOH	3.39	−0.35	7	67 (67)	7	—	3 (68)
8	68	50TFE	2.14	−0.93	14	78 (66)	8	—	5 (66)
9	68	97TFE	1.83	−2.79	14	10 (65)	trace	—	83 (68)
10	68	97HFIP	3.61	−4.27	14	13 (61)	4	—	63 (68)

^a 80MeOH = 80% (v/v) methanol–H₂O; 50MeOH = 50% (v/v) methanol–H₂O; 20MeOH = 20% (v/v) methanol–H₂O; 50TFE = 50% (v/v) trifluoroethanol–H₂O; 97TFE = 97% (v/v) 2,2,2-trifluoroethanol–H₂O; 97HFIP = 97% (v/v) 1,1,1,3,3,3-hexafluoro-2-propanol–H₂O.

^b Solvent ionizing power.²⁰

^c Solvent nucleophilicity.²⁰

^d Tetrabutylammonium bromide (0.10 mol l^{−1}) was added.

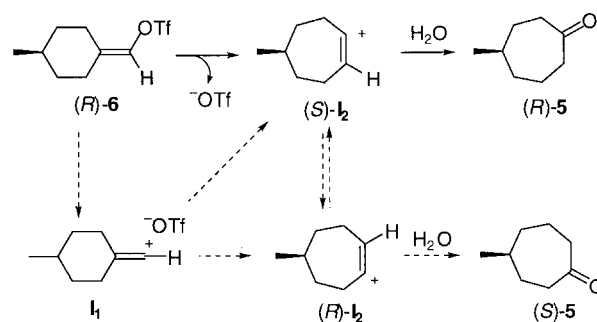
140 °C for 4–28 days. The products were analyzed by both normal and chiral gas chromatography with FID and MS detectors in comparison with authentic samples. The products include rearranged ketone **5** and 4-methylcyclohexanecarbaldehyde (**7**). The results are summarized in Table 1.

In 50% (v/v) aqueous methanol, reaction of **6** was complete in 14 days at 140 °C and gave aldehyde **7** and ketone **5** in 17 and 59% yields, respectively (run 4). The result is similar to that obtained previously with the unsubstituted triflate **1**.⁶ It is noteworthy, however, that the rearranged product **5** (71% *ee*) maintains the original stereochemical purity of the substrate (73% *ee*) within experimental errors and has the *R* configuration. The minor product **7** is achiral but was a mixture of about equal amounts of the *cis* and *trans* isomers. In a shorter reaction time of 4 days, a consistent result was obtained with 22% of the unreacted (*R*)-**6** (run 5).

In pure methanol (run 1), the reaction was very sluggish but not totally inhibited.⁶ The reaction becomes faster with an increasing fraction of water in mixed aqueous methanol solvents (runs 1, 3, 5 and 7). In 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), both containing 3% water, the reaction was fairly slow (runs 9 and 10). In 50% aqueous TFE (run 8), the reaction was reasonably fast, and gave results similar to those in aqueous methanol. In all solvents, the recovered substrate was not racemized, and the product (*R*)-**5** maintained essentially the stereochemical purity (*ee*) of the substrate (*R*)-**6**.

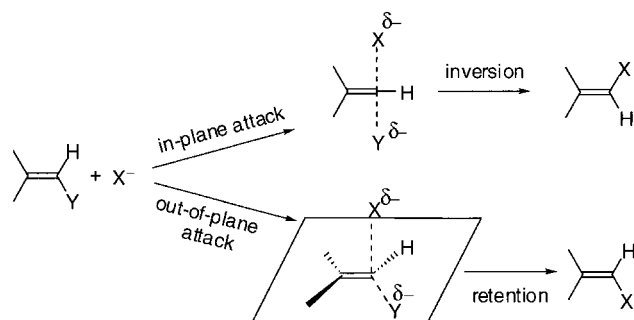
These results show that the chirality of the substrate (*R*)-**6** is essentially transferred to the main product (*R*)-**5**, indicating that no achiral intermediate such as primary vinyl cation **I**₁ is involved during the formation of (*R*)-**5** (Scheme 4). However, the unrearranged product **7** could be derived from trapping of the primary cation **I**₁, as

suggested previously for a similar reaction system.⁶ Bromide ion can be used for trapping of **I**₁ to give a chiral product. The reaction of (*R*)-**6** with tetrabutylammonium bromide in 50% aqueous methanol provided a small amount of 4-methylcyclohexylidenemethyl bromide (**8**), which was in excess of the *S* form by 64% (run 6). That is, the bromide product (*S*)-**8** is formed mainly with inversion of configuration. This is incompatible with formation via trapping of the primary cation **I**₁, which should have led to racemization. The bromide reaction more effectively occurs in methanol (run 2) to give mostly the inverted product (*S*)-**8**.

**Scheme 4**

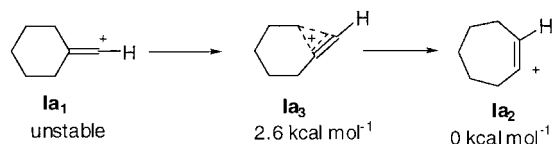
The reaction of bromide must proceed via direct vinylic attack (S_N2) mainly at the in-plane σ* orbital of the C—I bond leading to inversion of configuration,^{9,19} but accompanied by some contamination of the out-of-plane attack at the π* orbital leading to retention of configuration (Scheme 5).^{9,11} Stereodivergent substitution products of solvolysis of 1-alkenylidonium salts have been argued by these competitive mechanisms.¹⁰ The possibilities of the two pathways of vinylic S_N2 reactions have also been substantiated by theoretical calculations.⁹ However, an alternative route to the

formation of **7** is also possible for the vinyl triflate:⁶ the enol of **7** may be formed by nucleophilic reaction at the sulfonate sulfur of **6**. The transition state for this route would be polar, and the lower reactivity in pure methanol would not be unreasonable for this route.



Scheme 5. Vinylic S_N2 mechanisms

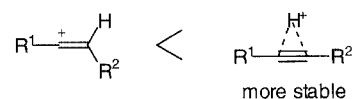
If the primary cation **I**₁ was formed, could it be trapped by any nucleophiles before rearrangement? Theoretical calculations (at the MP2/6–31G* level)²⁰ of cationic species related to the present reaction system show that the primary cation **Ia**₁ is too unstable to be located in a local energy minimum in the gas phase, as is the case for other primary cations.⁴ The bridged form **Ia**₃, similar to the transition state for the rearrangement of **Ia**₁ to cycloheptenyl cation **Ia**₂, is in an energy minimum, and it is only 2.6 kcal mol^{−1} (1 kcal = 4.184 kJ) higher in energy than **Ia**₂ (Scheme 6). If the primary cation **I**₁ were formed during the solvolysis, the rearrangement to **I**₂ should have been barrierless, and considerable racemization of the rearranged product **5** should have been observed.



Scheme 6

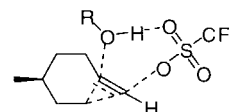
In conclusion, the primary vinyl cation **I**₁ should not be involved in the reactions of triflate **6**, and the solvolysis must occur mainly via σ -bond participation to give directly a chiral secondary cation **I**₂ with accompanying S_N2 -type reactions to lead to unrearranged products such as **7** and **8**. Stereospecific formation of (*R*)-**5** from (*R*)-**6** indicates that the initially formed cation (*S*)-**I**₂ is trapped by the nucleophilic solvent without racemization. This is also remarkable considering that the open-chain analogs of the secondary vinyl cation undergo a barrierless 1,2-hydride shift (Scheme 1).⁷ The hydrogen-bridged form is more stable than the classical form of the vinyl cation and has a linear structure of the skeleton $R^1-C-C-R^2$ as

shown below.⁷



The corresponding seven-membered cation should have a considerable angle strain, and the barrier for the 1,2-hydride shift of cation **Ia**₂, which corresponds to the interconversion of (*S*)-**I**₂ and (*R*)-**I**₂, would be fairly high; the barrier was in fact found to be 23.2 kcal mol^{−1} by *ab initio* MO calculations at the MP2/6–31G* level (M. Fujita, Y. Sakanishi, M. Nishii, H. Yamataka and T. Okuyama, to be published).

In any case, the main reaction of the solvolysis involves heterolysis of the leaving group with participation of the β -bond, and the transition state is expected to be still considerably polar. The solvolysis rates deduced from conversions of the substrate are compatible with this view only within aqueous methanol of varying compositions. However, in TFE and HFIP, which are good solvents for ionization (i.e. large Y_{OTs} values²⁰), the reaction was unexpectedly slow. Nucleophilicity of the solvent (e.g. evaluated from N_{OTs} values²⁰) seems also to facilitate the solvolysis of **6**. Although the intramolecular σ -bond participation is necessary to assist the heterolysis, the nucleophilic solvent participation in the polar transition state must also promote the solvolysis reaction of the triflate. A possible structure of the transition state is depicted below.



EXPERIMENTAL

Proton and ¹³C NMR spectra were recorded on a JEOL Excalibur 400 spectrometer as solutions in CDCl₃. Optical rotations were measured on a Perkin-Elmer 243B polarimeter. Gas chromatographs used for the product and/or *ee* determinations were Shimadzu 14B with DB-1 (30 m × 0.25 mm i.d.) and 17A with chiral columns (Chrompack-Chirasil-DEX CB, 25 m × 0.25 mm i.d., and Supelco BETA DEX 325 and 120, 30 m × 0.25 mm i.d.). GC–MS was conducted on a JEOL Automass System II.

Alcohols were distilled before use and glass-distilled water was used. Tetrabutylammonium bromide (Wako) was used without purification. Authentic samples of (*R*)-**5** and (*R*)-**8** were obtained as described previously.¹⁵ 4-Methylcyclohexanecarbaldehyde (**7**) was prepared according to the literature procedure.²¹

Preparation of (*R*)-4-methylcyclohexylidene-methyl triflate (**6**)

To a solution of (*R*)-**8**¹⁷ of 85% *ee* (1.1 g) in diethyl ether (14 ml) was added 1.56 M *t*-BuLi in pentane (9.0 ml) dropwise at -78°C in 5 min. After stirring for an additional 90 min at -78°C , Me_2PhSiCl (1.05 ml) was added to the mixture. The mixture was then allowed to warm to room temperature, quenched by addition of water and extracted with ether diethyl ($\times 3$). The extracts were purified by chromatography (SiO_2 , eluent hexane) to give (*R*)-1-dimethylphenylsilylmethylene-4-methylcyclohexane (0.90 g, 63% yield) as a colorless oil.

To a solution of the silane (0.90 g) in CH_2Cl_2 (35 ml) was added a solution of *m*CPBA (0.77 g) in CH_2Cl_2 (20 ml) dropwise in the presence of a small amount of aqueous NaHCO_3 in 20 min at 0°C . The mixture was stirred for 90 min and extracted with CH_2Cl_2 ($\times 3$) after addition of aqueous NaHCO_3 . The extracts were purified by chromatography (SiO_2 , eluent 6% diethyl ether in hexane) to give a diastereomeric mixture of the epoxide (0.91 g, 95% yield) as a colorless oil.

To a solution of the epoxide (50 mg) in CH_2Cl_2 (1 ml) was added $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (24 μl) at -78°C . The mixture was stirred for 15 min, quenched with aqueous NaHCO_3 at -78°C , extracted with diethyl ether ($\times 3$) and purified by chromatography (SiO_2 , eluent 3% diethyl ether in hexane) to give (*R*)-1-dimethylphenylsilyloxymethylene-4-methylcyclohexane (31 mg, 62% yield) as a colorless oil.

To a mixture of 0.83 M MeLi in diethyl ether (1.0 ml) and 1,2-DME (1 ml) was added 1,2-DME solution containing the silyl enol ether (105 mg) at -78°C . After stirring at 0°C for 60 min, triflic anhydride (0.15 ml) was added at -78°C . The mixture was allowed to warm to room temperature and stirred overnight. After quenching with aqueous NaHSO_3 , the mixture was extracted with pentane and purified by chromatography (SiO_2 eluent hexane) to give (*R*)-4-methylcyclohexylidenemethyl triflate (**6**) (54 mg, 52% yield) as a colorless oil. Chiral GC analysis using Chirasil-DEX CB indicated that the retention time of (*R*)-**6** (17.2 min) is shorter than that of (*S*)-**6** (18.1 min) at a column temperature of 90°C . The *ee* of the *R* isomer was 73% in this run. $[\alpha]_{\text{D}}^{20} = -7.3$ ($c = 1.15$, CHCl_3) (73% *ee*); ^1H NMR (400 MHz, CDCl_3) δ 6.34 (s, 1H), 2.77–2.70 (m, 1H), 2.20–2.12 (m, 1H), 2.00–1.93 (m, 1H), 1.83–1.78 (m, 3H), 1.59–1.50 (m, 1H), 1.05–0.93 (m, 2H), 0.90 ppm (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 133.3, 127.6, 118.6 (q, $J = 318.5$ Hz), 35.6, 34.6, 32.2, 29.3, 25.5, 21.8 ppm; MS (EI), m/z (relative intensity, %) 258 (6, M^+), 107 (78), 79 (76), 69 (83), 55 (100); HRMS (EI), calculated for $\text{C}_9\text{H}_{13}\text{SO}_3\text{F}_3$ (M) 258.0538, found 258.0557.

Another experiment gave (*R*)-**6** of 68% *ee*. Racemic **6** was also prepared in the same way from the racemic starting material.

Product determinations

About 2 mg of a sample of **6** was dissolved in 4 ml of an alcoholic or aqueous solvent in a Pyrex tube in the absence of any salt or in the presence of tetrabutylammonium bromide (0.1 M). The sealed tube was left in a silicone oil bath at $140 \pm 1^{\circ}\text{C}$ for 4–28 days. Products were extracted with diethyl ether or pentane containing tetradecane as an internal standard for GC determination. After removal of most of the solvent, the residual solution was subjected to GC and GC–MS.

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