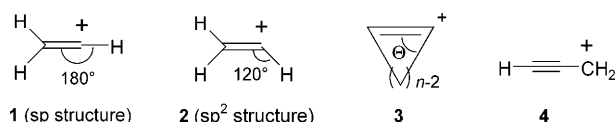


Facile Generation of a Strained Cyclic Vinyl Cation by Thermal Solvolysis of Cyclopent-1-enyl- λ^3 -bromanes**

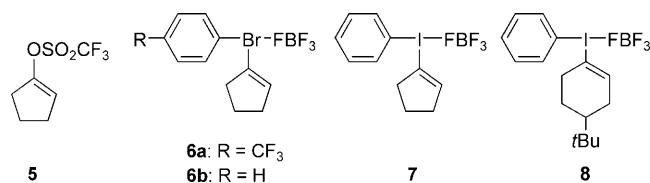
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Ever since the first direct generation of vinyl cations by solvolysis of arylvinyl bromides ($\text{ArC}(\text{Br})=\text{CH}_2$) reported in 1964 by Grob (father of vinyl cations) and Cseh,^[1] their chemistry has quickly evolved.^[2] The ease of formation of cyclic vinyl cations is dependent upon ring size, because vinyl cations prefer sp -hybridized linear arrangements at the positive carbon atom, which can be more easily accommodated by increasingly larger rings.^[3] The bent sp^2 -hybridized structure **2** of the parent vinyl cation with a $\text{C}=\text{C}-\text{H}$ bond angle of 120° is 40 kcal mol^{-1} higher in energy than the linear sp -hybridized form **1**.^[4] Ab initio calculations did not locate a



stationary-state structure for the smallest cyclic vinyl cation, cycloprop-1-enyl cation **3** ($n=3$), which opens to the propargyl structure **4**,^[4] whereas cyclobut-1-enyl cation **3** ($n=4$) is readily generated by solvolysis owing to its highly stabilized nature associated with the bridged nonclassical structure.^[5] In contrast to vinyl cations **3** ($n \geq 6$) that have larger rings, strongly bent cyclopent-1-enyl cation **3** ($n=5$, $\theta=141^\circ$)^[6] is thought to be too strained to be generated during $\text{S}_{\text{N}}1$ solvolysis.^[2] Hence, generation of a cyclopent-1-enyl cation by simple solvolysis is among one of the challenges facing modern organic chemistry and still remains to be established experimentally.^[7,8]

Over a period of 35 years, much effort has been directed toward generating the last cyclic vinyl cation **3** ($n=5$) by solvolysis. Attempted solvolysis of cyclopent-1-enyl sulfonate **5** with a superleaving group, triflate,^[2] does not exhibit unimolecular dissociation^[3] and the vinyl triflate **5** was recovered unchanged even after heating in trifluoroethanol at 100°C for 10 days.^[9] Cyclopent-1-enyl(phenyl)- λ^3 -iodane **7**



having a hyperleaving group (phenyl- λ^3 -iodanyl),^[10] which shows a leaving group ability about 10^6 times greater than that of the triflate superleaving group, is stable upon heating at 50°C in methanol for two weeks, whereas the cyclohexenyl analogue **8** readily undergoes heterolysis to give a cyclic vinyl cation under mild reaction conditions.^[11] These results indicate that even these super- and hyperleaving groups will not be good enough leaving groups to produce strained cyclopent-1-enyl cation by thermal solvolysis. The attempt to generate the cyclopent-1-enyl cation by diazotization of *N*-silylated cyclopent-1-enylamines was also found to be fruitless.^[12] Herein, we report the first solvolytic generation of the five-membered cyclic vinyl cation with a singlet ground state from cyclopent-1-enyl- λ^3 -bromanes **6**, where the reaction proceeds at a reasonable rate even at room temperature. The vastly enhanced nucleofugality of the aryl- λ^3 -bromanyl groups is a driving force for this solvolytic reaction.^[13]

Cyclic vinyl- λ^3 -bromane **6a** was prepared by ligand exchange of $p\text{-CF}_3\text{C}_6\text{H}_4\text{BrF}_2$ ^[14] on the bromine(III) atom with potassium cyclopentenyltrifluoroborate (5 equiv) in MeCN at low temperature (-45 – 0°C) in 61 % yield.^[15] The bromane **6a** can be kept at -20°C for months without any change, but gradually decomposes under ambient conditions. Complexation of **6a** with [18]crown-6 increases the thermal stability of some labile alkynyl- λ^3 -iodanes and bromanes through hypervalent $\text{I}^{\text{III}}\cdots\text{O}$ and $\text{Br}^{\text{III}}\cdots\text{O}$ interactions.^[16,17] Thus, slow evaporation of a *n*-hexane/ethyl acetate/dichloromethane solution of a 1:2 mixture of **6a** and [18]crown-6 at 4°C afforded colorless crystals of a 1:1 complex of **6a**·[18]crown-6. This complex is thermally stable and no decomposition was detected when it was left standing under ambient conditions for two weeks. In solution (CDCl_3 , 21°C , air), the half-life ($t_{1/2}=2.5$ days) of **6a** was extended to six days when complexed to [18]crown-6.

The structure of **6a** was firmly established by single-crystal X-ray analysis of the crown ether complex, which showed the presence of two independent but closely related molecules: one of which is depicted in Figure 1. The hypervalent bromine(III) atom has contacts with three adjacent oxygen atoms (O2, O3, and O4) of [18]crown-6, which probably increases the stability of **6a**.

Solvolysis of **6a** in aqueous solvents and alcohols at 50°C predominantly produced cyclopentanone (**9**) and *p*-

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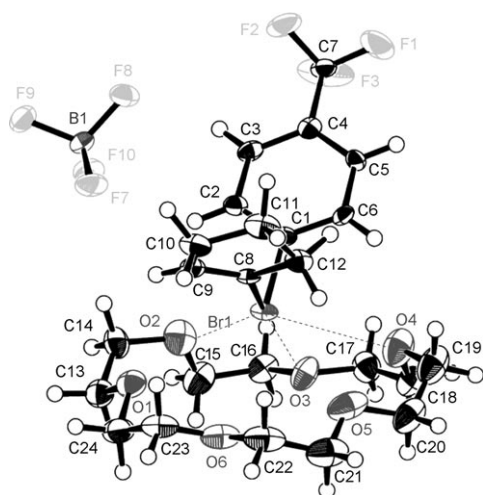


Figure 1. ORTEP drawing of the 1:1 complex **6a**–[18]crown-6 with thermal ellipsoids at 50% probability. Selected bond lengths [Å] and angles [°]: Br1–C1 1.938(5), Br1–C8 1.911(5), Br1...O2 3.055(5), Br1...O3 3.063(4), Br1...O4 3.135(5), C1–Br1–C8 97.5(2).

CF₃C₆H₄Br (**11**), along with a small amount of *o*-(cyclopent-1-enyl)bromobenzene **10** (Table 1). No formation of a radical product (i.e. cyclopentene) was detected by careful GC analysis. The initial solvolysis product in EtOH seemed to be

Table 1: Solvolysis of bromane **6a** at 50 °C for four hours.^[a]

Entry	Solvent	Yield [%] ^[b]		
		9	10	11
1	H ₂ O	71	5 ^[c]	63
2	MeOH ^[d]	73	4 ^[c]	60
3	EtOH ^[d]	65	2 ^[e]	62 ^[e]
4	EtOH/H ₂ O (60:40 (v/v))	60	7 ^[c]	61

[a] [**6a**] = 0.01 M, under argon. [b] Yield based on GC analysis. [c] Yield of isolated product. [d] After the reaction, the mixture was treated with a 35 % aqueous HCl solution. [e] Yield based on ¹H NMR analysis. R = CH₃ or CH₃CH₂.

cyclopentenyl ethyl ether (R = CH₃CH₂), which was transformed into ketone **9** under the solvolysis conditions by acid-catalyzed hydrolysis with HBF₄ generated in situ. In fact, the time course of solvolysis in [D₆]EtOH in the presence of excess pyridine clearly demonstrated the initial formation of [D₅]cyclopentenyl ethyl ether, followed by its hydrolysis to [D₁]-**9** (Figure 2).

The solvolysis of **6a** does take place even at room temperature (Scheme 1). In dichloromethane at 20 °C, 1-chloro- (**12**) and 1-fluorocyclopentene (**13**) were the major products produced in 48 % and 43 % yield, respectively. Use of a more nucleophilic solvent like dichloroethane increased the yield of **12** to 54 % at the expense of the competing

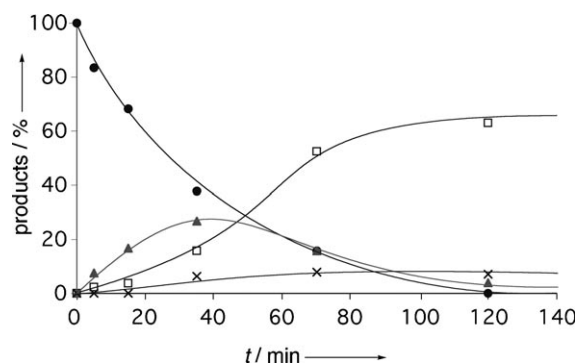
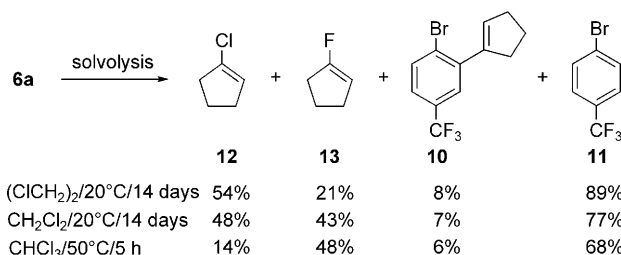


Figure 2. Time-course for solvolysis of **6a** (0.01 M) in [D₆]EtOH in the presence of pyridine (22 equiv) at 50 °C under argon, as determined by ¹H NMR spectroscopy. (●) **6a**, (▲) [D₅]cyclopentenyl ethyl ether, (□) [D₁]-**9**, (×) **10**.



Scheme 1. Solvolysis of bromane **6a** in chloroalkanes.

formation of **13**, whereas a lower yield of **12** (14 %) was observed in a less nucleophilic solvent like chloroform. All of these solvents transfer the chlorine atom to electron-deficient carbocations via the intermediacy of chloronium ions.^[15] The formation of ketone **9** and 1-substituted cyclopentenones **10**, **12**, and **13** provides firm evidences for the intermediacy of the cyclopent-1-enyl cation during the thermal solvolysis of **6a**.

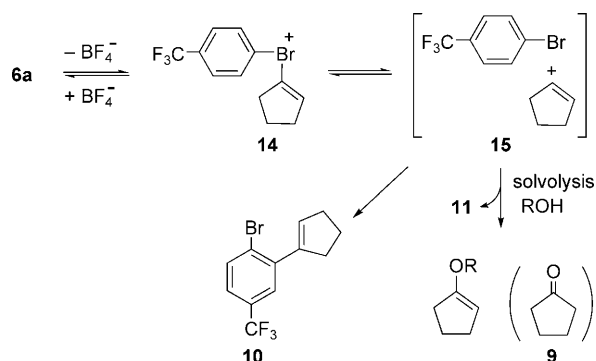
Rates for solvolysis of **6** were measured spectrophotometrically in aqueous ethanol (60 % vol) at different temperatures in the 40–65 °C range by monitoring the decrease in absorbance at 240 nm (see Figure S1 in the Supporting Information). The pseudo first-order rate constants k_{obsd} were obtained throughout each run and the values for triplicate runs were averaged (Table 2). The electron-withdrawing *p*-CF₃ group of **6a** increased the rate of solvolysis at 50 °C by a factor of 17 compared to the unsubstituted **6b**, probably because of the enhanced nucleofugality of the *p*-(trifluoromethyl)phenyl-λ³-bromanyl group.^[18] The positive

Table 2: Observed rate constants ($10^4 k_{\text{obsd}}$ [s⁻¹]) for the solvolysis of bromanes **6** in EtOH/H₂O (60:40 (v/v)).

Entry	6	T [°C]					ΔH^\ddagger [cal mol ⁻¹]	ΔS^\ddagger [cal mol ⁻¹ K ⁻¹]
		40	50	55	60	65		
1	6a	1.32	4.42	9.54	19.3	32.1	26.8	9.13
2	[D ₃]- 6a	–	4.18	–	–	–	–	–
3	6b	–	0.262	–	–	–	–	–

value ($9.13 \text{ cal mol}^{-1} \text{ K}^{-1}$) of the activation entropy is in good agreement with an S_N1 type solvolysis of **6a**.

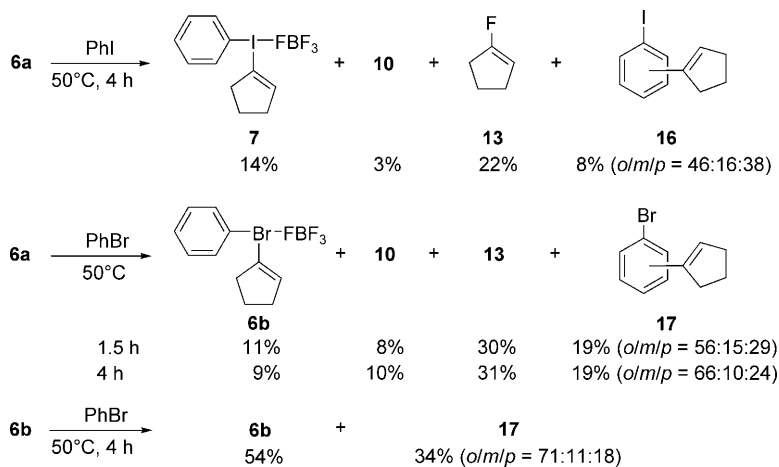
Scheme 2 depicts a reaction mechanism involving the formation of the cyclopent-1-enyl cation by solvolysis of **6a** in alcohols. Bromane **6a** will be equilibrated with the more active bromonium ion **14** in alcohols, most probably being



Scheme 2. Reaction mechanism for the solvolysis of bromane **6a**.

stabilized by the coordination of solvent molecules to the positively charged hypervalent bromine(III) atom.^[16b] Heterolysis of the vinylic C–Br^{III} bond with reductive elimination of bromobenzene **11** will initially generate the intimate ion-molecule pair **15**, which affords cyclopent-1-enyl ether (and/or **9**) and *o*-substituted bromobenzene **10**, the latter probably being produced through internal return (recombination) of the ion-molecule pair **15**.^[19]

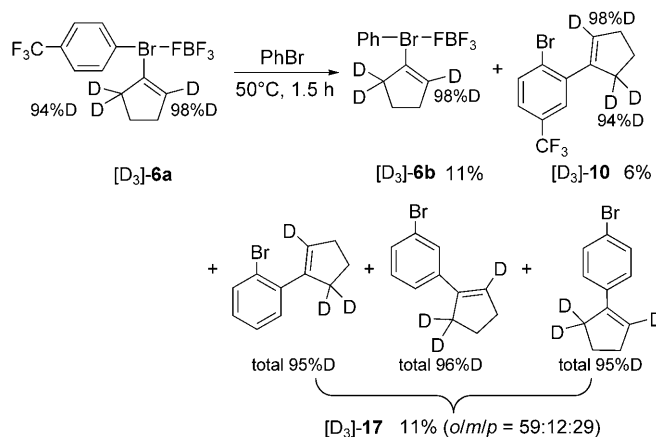
Interestingly, isolation of phenyl- λ^3 -iodane **7** (14%) and phenyl- λ^3 -bromane **6b** (9–11%) in the solvolysis of **6a** in PhI and PhBr (Scheme 3) clearly indicates that, in addition to the *o*-, *m*-, and *p*-positions of these halobenzenes, the cyclopentenyl cation formed will be captured by the halogen atoms: with the iodine atom probably being more effective than the bromine atom. The *o*/*m*/*p* isomer ratios of cyclopentenylbromobenzene **17** change slightly depending on the reaction conditions. The increased *ortho* selectivity (66%) for the formation of **17** was observed upon prolonged heating



Scheme 3. Solvolysis of bromanes **6** in PhI and PhBr. Bromane **6a** (10%) was recovered in the solvolysis run in PhBr after 1.5 h.

(4 h) of **6a**, probably suggesting the involvement of the internal return of an intimate ion-molecule pair.^[11] In fact, the solvolysis of phenyl- λ^3 -bromane **6b** in PhBr showed a higher *ortho* selectivity (71%).

An alternative β -elimination pathway that yields cyclopenta-1,2-diene and/or less likely cyclopentyne, and the subsequent addition of nucleophiles, could produce the solvolysis products even though these unsaturated five-membered carbocycles are highly strained and are calculated to be high-energy species.^[7,20] Solvolysis of trideuterated cyclopent-1-enyl- λ^3 -bromane [**D**₃]-**6a**, prepared from 2,2,5,5-tetradeuterated cyclopentanone, was carried out in PhBr (Scheme 4). All of the vinylic and the allylic deuterium labels



Scheme 4. Solvolysis of trideuterated λ^3 -bromane [**D**₃]-**6a** in PhBr.

were essentially retained in the solvolysis products. Similar results were obtained from the solvolysis of [**D**₃]-**6a** in PhI. These results are not compatible with the β -elimination-addition pathway, which expects loss of the deuterium labels to some extent.

Relatively large β -deuterium isotope effects were evaluated in the S_N1 solvolysis of vinyl triflates:^[21] the k_H/k_D value is 1.25 for (*E*)-MeCD=C(Me)OTf and 1.54 for Me₂C=C(CD₃)OTf in aqueous ethanol (60% vol) at 75 °C. In marked contrast, bromane [**D**₃]-**6a** showed a small secondary kinetic isotope effect of 1.06 at 50 °C (calculated using data from Table 2). This small deuterium isotope effect for [**D**₃]-**6a** would be attributable to a small degree of hyperconjugative delocalization of positive charge onto the C2- and C5-hydrogen atoms in the transition state, which results from the expected large ring strain for the effective hyperconjugation, even though the dihedral angle between the developing empty orbital at the reaction site and the C2–H bond is nearly 0°. Calculations indicate that in the singlet ground state of the cyclopent-1-enyl cation the positive charges are mostly distributed at C1⁺ (+0.431), C3H₂ (+0.175), and C4H₂ (+0.209), but that the charges at C2H and C5H₂ are less positive

(+0.093 in both cases).^[7] These calculations are in good agreement with the observed small deuterium isotope effect, which strongly suggests an S_N1 type solvolysis of the bromane **6a** in aqueous ethanol (60 % vol).

In conclusion, thermal solvolysis of cyclopent-1-enyl-(aryl)- λ^3 -bromanes **6** has provided firm evidences for the generation of cyclopent-1-enyl cation in solution under mild reaction conditions. It should be emphasized that the solvolytic generation of the five-membered cyclic vinyl cation must rely heavily on the very high leaving group ability of the aryl- λ^3 -bromanyl groups.

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