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About the Participation of σ, π and *n* Orbitals in the Solvolysis of 2- and 3-Oxo-1-Norbornyl Triflates

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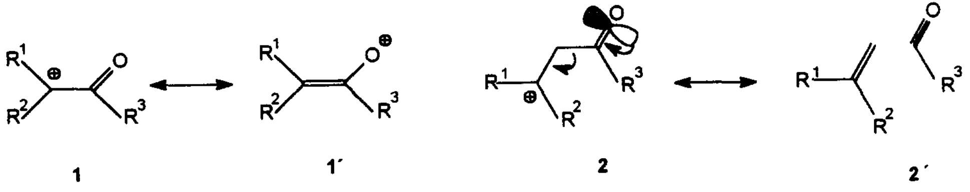
Abstract. The solvolysis of 3,3-dimethyl-2-oxo- and 2,2-dimethyl-3-oxo-1-norbornyl triflates (**6** and **8**) takes place with formation of ring contracted and fragmented products respectively. The effect of the substituents on the solvolysis rates is explained taking into account *n*- and σ-participation. This *n*,σ-participation causes changes in the structure and stability of the intermediate carbocations, which can be detected by the AM1 method. Copyright © 1996 Elsevier Science Ltd

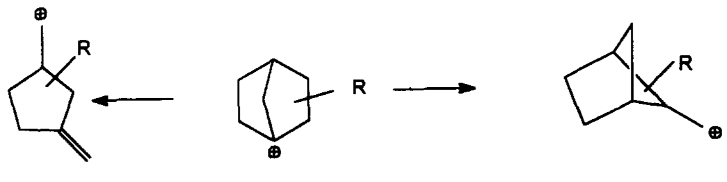
INTRODUCTION

The carbonyl group is strongly electron withdrawing. However, in recent years considerable theoretical and experimental work has been done in order to evaluate the π conjugative[1] as well as the through-bond interaction of the carbonyl lone pair (*n* participation) with the cationic p orbital[2] (Scheme 1).



Scheme 1

We have shown that the methyl substituted $\sigma(C_2\text{-}C_3)$ bond can participate in the stabilization of 1-norbornyl cations with formation of products resulting from fragmentation (**3**) or ring contraction (**5**) (Scheme 2).[3]



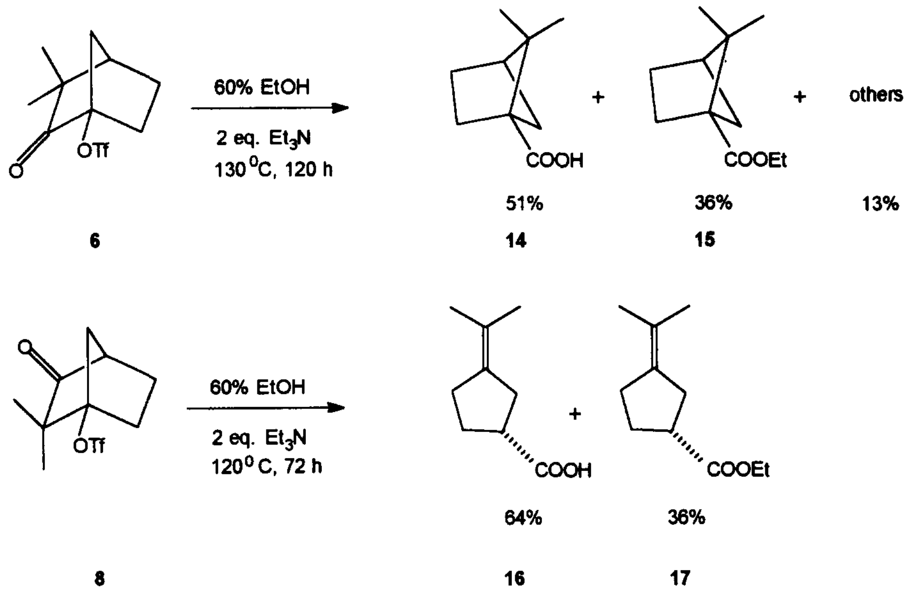
3 **4** **5**

Scheme 2

In this paper we use the substrates 3,3-dimethyl-2-oxo- and 2,2-dimethyl-3-oxo-1-norbornyl triflates (**6** and **8**)[4] to evaluate the relative importance of the above mentioned types of orbital participation in the stabilization of 1-norbornyl cations.

RESULTS AND DISCUSSION

The solvolysis of a $2.5\text{x}10^{-2}$M solution of the triflate **6** in 60% aqueous ethanol with triethylamine as buffer ($5.0\text{x}10^{-2}$M) affords the ring-contracted acid **14**[4a] and the corresponding ester **15**[4a] (Scheme 3). The solvolysis of the triflate **8** in the same solvent yields a mixture of the fragmentation products **16**[4b] and **17**[4b] only (Scheme 3). The rate constants of the solvolysis of the triflates **6** and **8** were determined by GLC (Table 1). In contrast with the solvolysis of **6**, the solvolysis rate of **8** is very buffer concentration dependent (Table 1). This fact, as well as the very negative $\Delta S^{\neq}$ value, points to a solvolysis mechanism involving base catalyzed solvent addition to the carbonyl group[1c] in competition with the unimolecular reaction of **8**. This addition mechanism is not operative in the case of the 2-oxo-1-norbornyl triflate **6** probably due to steric hindrance. The unimolecular reaction rate of **8** was calculated by extrapolation at $[NEt_3]=0$.



Scheme 3

The solvolysis of 3,3-dimethyl-1-norbornyl triflate (7) in 60% aqueous ethanol yields only the corresponding bridgehead alcohols (~60%) and ethers (~40%).[3] However, the solvolysis of 2,2-dimethyl-1-norbornyl triflate (**9**) affords a mixture of unrearranged (14%) and ring-contracted (86%) products.[3] The rate constants *k* are given in Table 1.

The deceleration of the solvolysis rate of 3,3-dimethyl-2-oxobicyclo[2.2.2]oct-1-yl triflate (**10**) relative to the parent compound **11** (Table 2) has been ascribed to the inductive effect of the 2-oxo substituent.[5d,f] The deceleration caused by the 2-oxo substituent was found to be independent of the flexibility of the ring system, suggesting the unimportance of π-conjugative stabilization in tertiary α-keto cations.[5,7,8] In this context, it is surprising that the 2-oxo substituent in the 1-norbornyl system causes a relatively small deceleration as measured by the **6**/**7** ratio (Table 2). This fact can be satisfactorily explained accepting an enhanced hyperconjugative σ-participation of the carbonyl group provoked by the electron-need of the unstable α-keto-1-norbornyl cations. This assumption is supported by the exclusive formation of rearranged products in the solvolysis of **6** (Scheme 3) in contrast to the solvolysis of **10**, in which rearranged products were isolated only as by-products.[5]

Table 1. Rate Constants of Bridgehead Derivatives in Buffered[a] 60% Aqueous Ethanol.

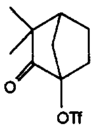
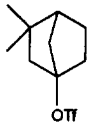
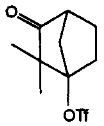
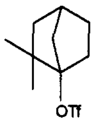
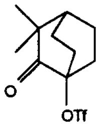
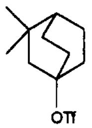
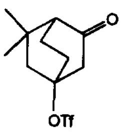
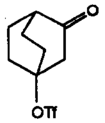
Triflate	Temp.(°C)	*k*(s^{-1})	$\Delta H^{\neq}$(kcal/mol)	$\Delta S^{\neq}$(eu)	$\Delta\Delta H^0$(kcal/mol)	Ref.[b]
6 	80.3 120.0 129.5 129.5 139.5	$7.86x10^{-8c,d}$ $4.74x10^{-6c}$ $1.40x10^{-5c}$ $1.63x10^{-5c,e}$ $2.71x10^{-5c}$	28.2	-11.8	250.4	tw
7 	80.3	$3.10x10^{-4c}$	28.7	5.5	235.5	3
8 	70.0 80.3 80.3 80.3	$2.95x10^{-5c}$ $7.35x10^{-5c}$ $2.50x10^{-4c,e}$ $2.96x10^{-5c,f}$	17.2	-35	245.6	tw
9 	80.3	$1.65x10^{-3c,d}$	26.1	2.2	235.8	3
10 	80.3 25.0	$1.76x10^{-5g}$ $4.54x10^{-10h}$	30.6	1.3	250.4	5d,e
11 	25.0	$6.0x10^{-1h}$	19.4	5.4	216.3	5d
12 	80.3 25.0	$1.77x10^{-1g}$ $2.92x10^{-h}$	20.9	0.0	228.1	5b,e
13 	80.3 25.0	2.61^{g} $2.43x10^{-3h}$	19.9	-0.7	228.8	5b,e

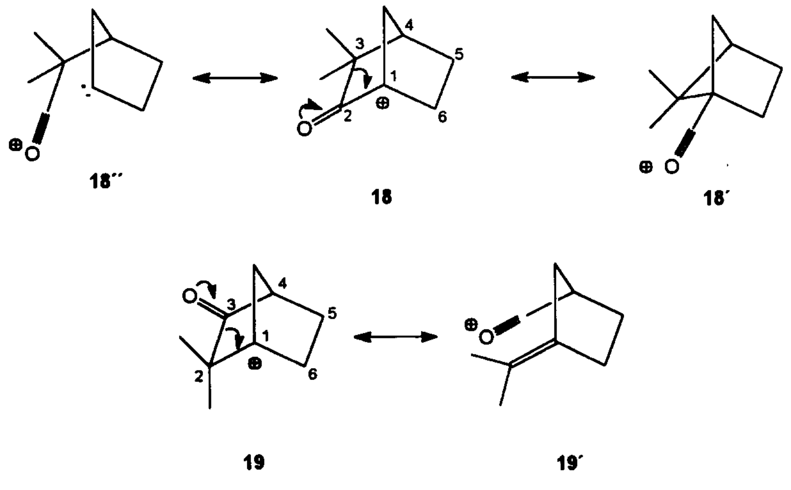
Table 1. (Continuation).

[a]$[Et_3N]/[Substrate]=2.0$. [b]tw= This work. [c]Determined by GLC (experimental error ±5%). [d]Extrapolated from other temperatures. [e]At $[Et_3N]/[\mathbf{8}]=10/1$. [f]Extrapolated at $[Et_3N]=0$. [g] Extrapolated from other temperatures and solvents.[5,6] [h]Values in 80% EtOH.

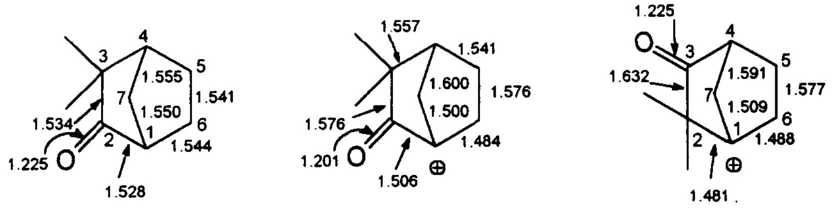
Table 2. Effect of the Introduction of Oxo Substituent on the Solvolysis Rates of Bridgehead Triflates

6/7= 2.54×10^{-4} (60% EtOH, 80.3°C)	**10/11**= 7.50×10^{-10} (80% EtOH, 25°C)
8/9= 1.79×10^{-2} (60% EtOH, 80.3°C)	**12/11**= 4.87×10^{-3} (80% EtOH, 25°C)

The charge delocalization in the bicyclic skeleton can be represented, among others, by the limiting structures **18**, **18'** and **18''**(Scheme 4), the limiting structure **18''** (favoured by *n*-participation) probably contributing less than **18'** because only ring contracted products were found. The enhanced participation of the limiting structures **18'** and **18''** is indicated by significant structural distortions, calculated by the AM1 method.[9,10] Thus, the C_1-C_2 bond of cation **6** is longer than the C_1-C_6 bond; the C_2-C_3 bond suffers a lengthening and the C=O bond a shortening in comparison with the pattern ketone **6H** (Scheme 5).



Scheme 4



Scheme 5. Some significative bond-lengths (in Å) showing *n* and σ-participation

The through-bond interaction of a β-carbonyl lone pair with a cationic p orbital has been proposed as hyperconjugative interaction in β-keto cations **2** (Scheme 1).[10]The solvolysis of the 3-oxobicyclo[2.2.2]oct-1-yl system showed that the cation would be 4-5 kcal/mol more stable than expected from the electron-withdrawing effect of the carbonyl group.[5a] The solvolysis rate deceleration caused by the introduction of a 3-oxo substituent in the 1-norbornyl system is similar to the observed in the bicyclo[2.2.2]octyl system (cf. the rate ratios **8/9** and **12/11**, Table 2). Thus, the *n*,σ-participation produces a marked stabilization of the bridgehead cations in both cases. However, only in the case of the 1-norbornyl cation **8** this participation can be considered as a real "frangomeric effect",[11] because only fragmented products were isolated. The contribution of the canonical structure **19'** (Scheme 4) is suggested by the AM1 calculated[9] C_1-C_2 bond shortening and C_2-C_3 lenthening in relation to the parent ketone **6H** (Scheme 5).

The solvolysis reactions of many bridgehead derivatives were found to be dominated by strain changes upon change of hybridization of the reacting C-atom fron sp^3 to sp^2 in going to the transition state. In agreement with this, good linear correlations between the rates of solvolysis (ln *k*) of bridgehead derivatives and the heats of formation, $\Delta\Delta H^0(R^+\text{-}RH)$, of the carbocations and the corresponding hydocarbons were found.[12] The values of $\Delta H^0(RH)$, $\Delta H^0(R^+)$ and $\Delta\Delta H^0(R^+\text{-}RH)$ of the bridgehead triflates **6-13**, calculated by the AM1 method,[9] are given in Table 1. The $\Delta\Delta H^0(R^+\text{-}RH)$ values were plotted against the experimental values of -ln *k* at 80.3°C in Figure 1.

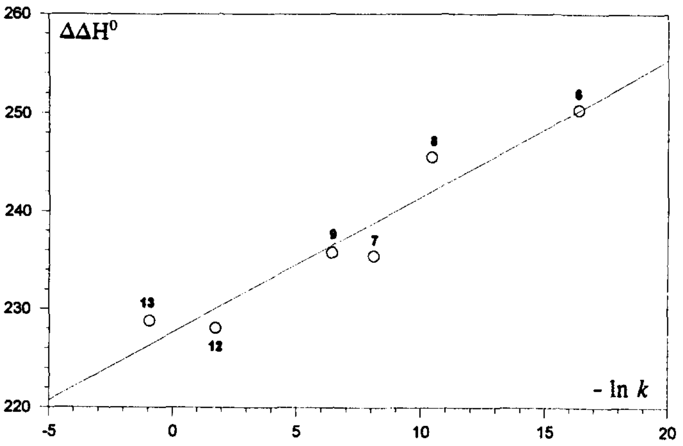


Figure 1

There is a fair correlation (r=0.957; $\sigma(\ln k)=1.87$) excluding substrate **10**, (probably due to the two extrapolations made in the value of ln k listed in Table 1), showing that the very different contributions of n and σ-participation in our substrates can be satisfactorily accounted for by the easy to use AM1 method.

In summary, the solvolysis of the 1-norbornyl triflates **6** and **8** give an insight into the effect of n and σ-participation on the stability of oxo substituted bridgehead cations. The substituent effects can be satisfactorily accounted for by the AM1 method.

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EXPERIMENTAL

The syntheses of the triflates **6** and **8** as well as the spectroscopic data of the solvolysis products **14**, **15**, **16** and **17** have been described in previous papers.[4a,b]

General procedure for the solvolysis of triflates 6 and 8. A solution of the triflate (3.5 mmol) and triethylamine (7 mmol) in 140 ml of 60% aqueous ethanol was heated in a glass ampoule (130°C/2 days in the case of **6** and 120°C/3 days in the case of **8**). The reaction mixture was poured into 200 ml of 0.1N hydrochloric acid and extracted with diethyl ether 3x50 ml). The acids **14** and **16** were separeted by extraction with saturated solution of $NaHCO_3$. The products of the solvolysis were purified by column chromatography and identified spectroscopically. The distribution of the products was determined by GLC (OV 101, 25m)

The kinetics of the solvolysis were monitored by GLC (OV 101, 25m) taking samples at appropriate times using 2-adamantanone (in the case of **6**) and *trans*-decalone (in the case of **8**) as internal standards.

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