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THE SOLVOLYSIS OF 5-KETO-2-NORBORNYL BROSYLATES

Joe C. Greever* and Donald E. Gwynn

Department of Chemistry

University of Arkansas

Fayetteville, Arkansas 72701

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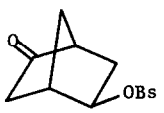
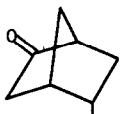
Numerous studies have shown the 2-norbornyl cation to exhibit a remarkable degree of exo-stereospecificity upon nucleophilic substitution.[1] Some recent work,[2-4] however, has shown this stereospecificity to be lost upon incorporation of an electron withdrawing substituent located either α or β to the developing cationic center. We wish to report a similar observation in the solvolysis study of 5-keto-exo- and endo-2-norbornyl brosylates[‡] (I and II, respectively), a system in which a deactivating carbonyl group is situated three carbons distant from the site of ionization.



I



II

The acetolysis of I and II was carried out in refluxing anhydrous acetic acid buffered with a molar equivalent of sodium acetate for 48 hours. The reaction product in each case was observed to contain unreacted brosylate and at least six components by gas chromatographic analysis. Among these products nortricyclanone (III), dehydronorcamphor (IV) and the 5-keto-exo- and endo-2-norbornyl acetates (V and VI, respectively) were identified by comparison of spectra of collected products to those of authentic samples. The relative ratios of these products are shown in Table I. Each identified product was shown to be stable under the conditions of the solvolysis reaction precluding the possibility that any observed product might be secondary to the reaction.

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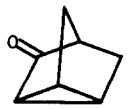
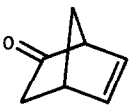
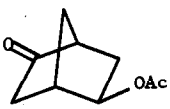
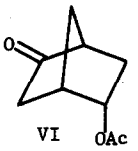
‡I-OBs, m.p. 115-116°, was obtained from the corresponding acetate[5] upon hydrolysis and derivatization. The keto-alcohol corresponding to I was converted to the ethylene ketal, oxidized by a Sarett oxidation and reduced with lithium aluminum hydride to the ethylene ketal-alcohol corresponding to II. Ketal hydrolysis and derivatization gave II, m.p. 94-94.5°. Both compounds gave satisfactory spectral and analytical data.

Table I.

Acetolysis Products from 5-Keto-2-norbornyl Brosylates

Brosylate	Product Percentages[a]				
	 III	 IV	 V	 VI	Major unidentified components
I	65.4	11.6	13.1	4.5	5.4
II	8.9	0.6	66.9	10.9	4.8 and 8.9

[a]Determined from peak area measurements on a 15 ft. 5% Carbowax 20 M column at 200°.

Table II.

Acetolysis Rates of 2-Norbornyl Brosylates

Compound	Ref.	Temp. °C	Rate, sec^{-1}	k,rel.
5-Keto-exo-2-norbornyl brosylate (I)		100	$(1.36 \pm 0.09) \times 10^{-5}$	
		84.5	$(3.96 \pm 0.03) \times 10^{-6}$	
		75	$(1.65 \pm 0.03) \times 10^{-6}$	
		25[a]	8.5×10^{-9}	0.050
5-Keto-endo-2-norbornyl brosylate (II)		110	$(6.65 \pm 0.00) \times 10^{-6}$	
		100	$(1.95 \pm 0.06) \times 10^{-6}$	
		75	$(1.88 \pm 0.03) \times 10^{-7}$	
		25[a]	2.0×10^{-10}	0.0012
7-Keto-exo-2-norbornyl tosylate	2	25[a]	1.44×10^{-8}	
			4.32×10^{-8}[b]	0.25
7-Keto-endo-2-norbornyl tosylate	2	25[a]	8.66×10^{-8}	
			2.60×10^{-7}[b]	1.52
exo-2-Norbornyl brosylate	6	25	8.79×10^{-5}	516
endo-2-Norbornyl brosylate	6	25[a]	2.52×10^{-7}	1.5
Cyclohexyl brosylate		25[a]	1.71×10^{-7}	1.0

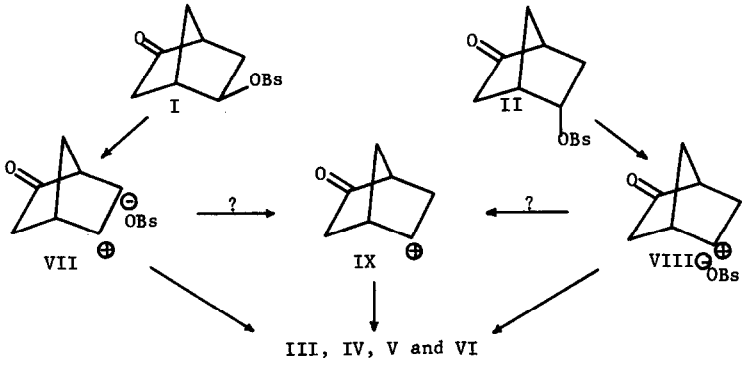
[a]Rate value extrapolated from higher temperatures.

[b]Calculated rate for the corresponding brosylate using a factor of three to relate the reactivity of the tosyl derivative to the brosylate.[7]

Both brosylates were observed to give good first order kinetics over several half lives in anhydrous acetic acid. These and other rate data of interest are presented in Table II.

Inspection of these data clearly indicates a significant influence exerted by the C-5 carbonyl in I and II upon the formation and reactivity of the corresponding cationic intermediates. Thus the formation of both endo- and exo-substitution products represents a marked departure from the exclusive exo-stereospecificity usually observed with the norbornyl system. Furthermore, introduction of the C-5 carbonyl has resulted in a very large rate retardation for I and II when compared to the unsubstituted exo- and endo-2-norbornyl brosylates (Table II), factors of ca. 10^4 and 10^3, respectively. These results suggest the formation of highly reactive classical cationic intermediates from I and II, devoid of any possible neighboring σ-electron delocalization and best represented by the ion pairs VII and VIII (Scheme I). Further dissociation to the common ion intermediate IX must be unimportant in view of the widely different product compositions from these two reactions.

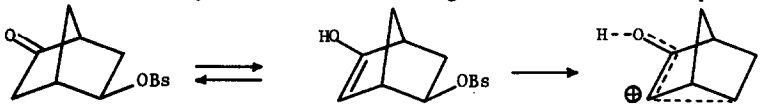
As seen in Table I the major disparity in the solvolytic product compositions from I and II is in the relative proportion of elimination to substitution which has occurred. The exo-brosylate (I) is seen to give very predominantly the elimination products III and IV while the endo-derivative (II) gives mostly substitution products V and VI. This result may reflect the greater difficulty in solvent approach to C-2 for ion pair VII thereby producing a corresponding increase in proton elimination.



Scheme I

An alternative mechanism to be considered for the exo-derivative I is one involving participation by the π-electron system of enol form X to produce the intermediate XI. Enol partici-

pation has been found responsible for the very large rate acceleration and stereospecific product formation observed in the solvolysis of 2-keto-7-norbornyl derivatives.[8,9] The absence of these two features for the present system would seem to negate this mechanistic possiblity.



I X XI

Comparison of the solvolytic rates for the 5-keto and 7-keto-2-norbornyl brosylates (Table II) shows a remarkable difference in the influence of the carbonyl upon the reactivity of these two systems. Surprisingly the 5-keto epimers are seen to be less reactive than their 7-keto counterparts even though the deactivating carbonyl substituent is one intervening carbon further removed from the site of ionization. The exo/endo ratios for the 5-keto and 7-keto systems, are factors of 40 and 0.17, respectively. The striking difference in the rate ratios for the two systems would indicate that the influence of the carbonyl is not associated with a deactivation selective for the exo-epimers as has been argued by Gassman and Marshall[2] but rather this deactivation must be dependent on the specific orientation of the carbonyl dipole with respect to the site of ionization. Apparently then the major influence of the carbonyl substituent in these systems is best envisioned as a repulsive field effect between the electron deficient carbonyl carbon and the developing cationic center at C-2.

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