# A ¹H-NMR Study on Substituent Effects in 9-p-Fluoro-phenylbenzonorbornenyl Cations

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The solvolytic behavior of anti-7-norbornenyl- and anti-9-benzonorbornenyl systems provides one of the most important evidence for the homoallylic- and homobenzylic participation in these derivatives, which were originally suggested by Bartlett[1] and Winstein[2], respectively. Their acetolytic reactivities are summarized as follows

k_{rel} (25°C)   1 5.5×10^5 1.4×10^{11}
in AcOH
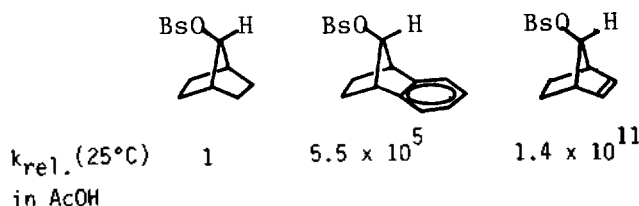
In case of anti-7-benzonorbornenyl brosylate, the acetolysis rate was faster than that of saturated 7-norbornyl brosylate by factor of 5.5×10^5, in contrast to much large factor of 1.4×10^{11} provided by the double bond of anti-7-norbornenyl derivative. The mere introduction of double bond into saturated norbonyl system exerted the enormous rate enhancement. On the other hand, fused benzen ring is vastly inferior to the double bond in assisting ionizating at C_9 in benzonorbornenyl derivatives. However, it is also clearly indicated that the acetolysis reaction involves participation of the benzene ring.

Tanida[3] reported previously the strikingly large substituent effects observed on carbonium ion reaction in this benzonorbornenyl system. When two methoxy substituents are introduced in the symmetrical 6 and 7 position, the rate was increased by a factor of 3000 relative to the rate of nonsubstituted derivative, while on methoxy substituent in the 6 position increases the rate by a factor of 54. Moreover, solvolysis of 9-aryl benzonorbornenyl-9-notrobenzoates provided an excellent linear Hammett plot and a value of the reaction constant $\rho^+ = -5.10$, consistent with subtantial homobenzylic participation during solvolysis. On basis of many solvolysis experiments, therefore, it was suggested that a nonclassical transition state, indicated in A, is formed in the ionization stage.

It is well known the rate data can give information only with regard to the transition state, and not with respect to the ionic intermediate formed subsequently to the transition state. Therefore, it is of interest to examine the precise structure of ionic intermediate formed after ionization, and it may be possible to obtain a information for the precise structure by nmr studies under stable ion condition.

Accordingly, we have synthesized substituted 9-p-fluoro-phenylbenzonorbornenyl-9-ols, which are required in the nmr study as the starting material to generate a carbonium ion, by our modified method of Wittig's procedure[4]. In order to obtain the chemical shifts for substituted 9-p-fluorophenyl-benzonorbornenyl cations which indicated B in Figure 1,
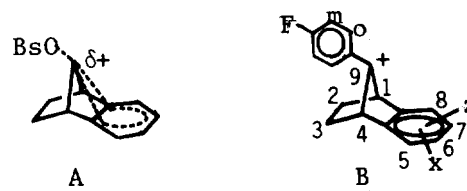

Figure 1

Table 1. 250 MHz ¹H NMR Data

No	Substituent		δHm^a	δHo	$\Delta\delta Ho^d$
1	5-OCH₃	A[b]	6.82	7.28	1.44
		C[c]	7.57	8.72	
2	6-OCH₃	A	6.84	7.31	1.37
		C	7.53	8.68	
3	6,7-(OCH₃)₂	A	6.82	7.29	0.87
		C	7.30	8.16	
4	5,8-(OCH₃)₂	A	6.82	7.28	1.55
		C	7.54	8.83	
5	5-CH₃	A	6.86	7.24	1.42
		C	7.52	8.66	
6	6-CH₃	A	6.87	7.28	1.26
		C	7.46	8.54	
7	6,7-(CH₃)₂	A	6.86	7.29	1.07
		C	7.42	8.36	
8	5,8-(CH₃)₂	A	6.81	7.22	1.32
		C	7.48	8.54	
9	H	A	6.67	7.26	1.60
		C	7.65	8.86	

[a] Chemical Shifts in δ(ppm) are referenced to internal CH₂Cl₂. [b] A denotes carbinol and [c] C denotes cation species. [d] $\Delta\delta H_o$ value are calculated from the chemical shift of cation and carbinol, respectively.

the cations was prepared from a mixture of corresponding carbinols in FSO_3H/SO_2ClF at -120°C. The ¹H nmr spectra of the cations were recorded at -90°C and the nmr data are summarized in Table 1, together with the those of the corresponding carbinols.

The nmr signals of the ortho- and meta protons in p-fluorophenyl ring shows a characteristic splitting pattern due to spin-spin coupling with the fluorine atom. A resonance signal of the ortho protons appears at downfield as a quartet compared to that of the meta protons which is observed as triplet, and this resonance signal can be well distinguish from another resonance signals.

The ¹H chemical shifts of the cations were shifted to more downfield compared to those of the corresponding carbinol. Comparing the chemical shift of the ortho protons in nonsub-

482 *Bull. Korean Chem. Soc., Vol. 10, No. 5, 1989*

Communications to the Editor

stituted cation (ion 9) with that of the substituted cations, it also indicates that the substituents in fused benzene ring exerted a considerable influence on the charge delocalization.

The difference of a chemical shift of the ortho protons in ion (1) which containes one methoxy groups at C-5 give a slightly large $\Delta\delta H_o$ value (1.44 ppm) relative to that of ion (2) (1.37 ppm) which contains also one methoxy group at C-6. This result reveals large charge delocalization into *p*-fluorophenyl ring in case of ion (1). In other word, the 6 substituent is much more effective to charge deloclaization through homobenzylic participation.

Surprisingly, the $\Delta\delta H_o$ value for the ion (3) shows exceptionnally high compared to that of the ion (4), even though these cations have two methoxy groups in fused benzene ring. In series of methyl substituted cations, their nature in cationic intermediates is a very similar to that of methoxy substituted cations.

From the result of ^{1}H nmr studies, we confirm that the position of substituent in fused benzene ring is a very impor-

tant factor to the charge delocalization in substituted benzonorbonenyl cations. Unfortunately, the ^{1}H nmr data does not appear to provide the precise structure of cationic intermediate. To help resolve this problem, the ^{13}C nmr studies on these cations are currently under investigation.

References

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Chemoselective Oxidation of Sulfides to Sulfones with Selenium Dioxide–Hydrogen Peroxide

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Chemoselective conversion of sulfides to sulfones would provide synthetic chemists with a useful tool since organosulfur compounds are widely used in organic synthesis. Most commonly used oxidizing agents for sulfides to sulfones such as H_2O_2, MCPBA, and $KMnO_4$ have limitations: incomplete conversion to sulfoxides or oxidation of other functional groups.

We have found that SeO_2-H_2O_2 system is a chemoselective oxidizing agent for conversion of sulfides to sulfones. Neither this system nor its application to oxidation of organic compounds is new.[1,2] In fact, SeO_2-H_2O_2 system has been used for selective oxidation of sulfides to sulfoxides by Mikolajczyk[3] and for oxidation of secondary amines to nitrones by Murahashi.[4] However, in contrast with Mikolajczyk's report, SeO_2-H_2O_2 system in the present work efficiently oxidized sulfides to sulfones but did not affect other functional groups such as double bonds and hydroxy groups. A representative example is the oxidation of crotyl phenyl sulfide. To a mixture of crotyl phenyl sulfide (0.164g, 1.00 mmol) and selenium dioxide (0.222g, 2.00 mmol) in methanol (2 ml) was added dropwise an aqueous 30% hydrogen peroxide solution (0.227g, 2.00 mmol) at room temperature. Tlc of the reaction mixture indicated that the starting material disappeared quickly and the product was the mixture of the sulfoxide and the sulfone in almost 1:1 ratio. The sulfoxide was converted into the sulfone in 1 hr. The reaction mixture was partitioned between methylene chloride and water layers. Glc analysis of the organic layer indicated the yield of sulfone

Table 1. Oxidation of Sulfides to Sulfones with SeO_2-H_2O_2[a]

Entry	Sulfide	Product	Yield, %[b,c]
1			70(75)
2			73(76)
3			72(78)
4			80(82)
5			85(88)
6			72

[a]Oxidation completed within 1 hr at room temperature. [b]Isolated yields. [c]Yields in parentheses are isolated ones.

was 75%. The product in organic layer was purified on a silica gel column to afford pure crotyl phenyl sulfone (0.137g,