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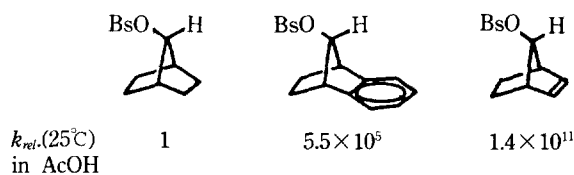
A ^{19}F NMR Study on 9-*p*-Fluorophenyl-6-Chloro- and 6-Nitrobenzonorbornen-9-yl Cations

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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 of neighboring π - bond in these derivatives, which were originally suggested by Bartlett¹ and Winstein², respectively. Their acetolytic reactivities are summarized as follows.



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 a saturated norbornyl system exerted enormous rate enhancement. On the other hand, fused ring is vastly inferior to the double bond in assisting ionization at C₉ in benzonorbornenyl derivatives. Explanations proposed for the great acceleration by double bond are: anchimeric assistance due to symmetrical nonclassical electron delocalization, or widening of the C₁-C₇-C₄ bond angle. Introduction of the 2,3-double bond pushes C₁ and C₄ further apart, causing an increasing in the C₁-C₇-C₄ angle which is favored for the formation of trigonal carbonium ion.

Tanida³ reported previously the strikingly large substituent effects observed on solvolysis rate in these benzonorbornenyl systems. The methoxy substituent increases the rate

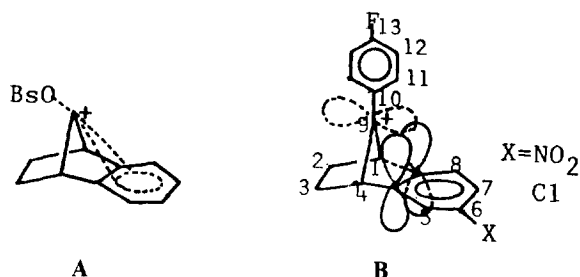


Figure 1.

by a factor of 53.7. The rate increase due to methyl is 5.7. The chloro, and nitro substituents decelerate acetolysis by factors of 0.045, and 1.4×10^{-4} , respectively. The extreme effect of substituents, $k_{\text{OCH}_3}:k_{\text{NO}_2}$ amounts to a factor of 386,000. These effects are much larger than can be accounted for by any simple electrostatic influence of the substituents and indicate that if the C₁-C₉-C₄ bond angle effect does exist, it must be relatively unimportant. On the basis of many solvolytic experiments, therefore, he suggested that the transition state must involve participation of a homobenzylic carbonium ion intermediate, which may be pictured as A in Figure 1. Therefore, it is of interest to explore the mechanism of charge stabilization of homobenzylic conjugation by fused benzene ring using ^{19}F nmr parameter. For this purpose, we have synthesized substituted 9-*p*-fluorophenylbenzonorbornenyl-9-ols, which are required in the nmr study as precursor to generate a carbonium ion.

The ^{19}F NMR spectroscopy has the advantage of the great sensitivity to electron demand of the adjacent cation center, and comparative in sensitivity to magnetic anisotropy of the solvent⁴. The ^1H chemical shifts are usually confined to a range of 13 ppm, the resonance of fluorine encompasses a much broad range of approximately 500 ppm⁵. The Gassman-Fentiman approach⁶ provides an alternative means of evaluating the electron deficiency of the developing cationic center in a system undergoing ionization, The greater the electron deficiency at the developing cationic center, the greater should be the demand on the substituted phenyl ring for electronic stabilization.

When a positive charge is dispersed into an adjacent *p*-fluorophenyl ring, the chemical shift moves downfield com-

Table 1. ^{19}F NMR Data

Ion	Substituent	δ ^{19}F
1	6-Nitro	A - 114.19
		C - 44.93
2	6-Chloro	A - 114.85
		C - 56.53
3	H	A - 115.57
		C - 62.26

Chemical shifts in δ (ppm) are referenced to external CCl_3F . A denotes alcohols and C denotes cation species.

pared to that of uncharged species. Less efficient charge delocalization in *p*-fluorophenyl ring should result in large charge dispersion by neighboring substituent. Thus, the chemical shift of the fluorine atom can provide an important information on the degree of charge delocalization through neighboring group participation. In order to obtain the ^{19}F chemical shifts for 6-substituted 9-*p*-fluorophenyl benzonorbornenyl cations, which indicated **B** in Figure 1, the corresponding carbinols were added to the mixture of $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ at -120°C . The ^{19}F nmr spectra of the cations were recorded at -100°C and the nmr data are summarized in Table 1, together with those of the corresponding carbinols.

The chemical shift of fluorine atom in 6-nitrobenzonorbornenyl cation (1) appears at -44.93 ppm and that of 6-chlorobenzonorbornenyl cation (2) at -56.53 ppm. The difference of ^{19}F chemical shift between 6-nitro substituted ion 1 and unsubstituted benzonorbornenyl cation (3) was 17.33 ppm, and the corresponding value between 6-chloro substituted ion 2 and unsubstituted ion 3 was 5.73 ppm. Certainly, the signal of the fluorine atom in ion 1 and ion 2 was shifted considerably downfield compared to that of unsubstituted ion 3 which appeared not to be compatible with any simple electrostatic influence of the substituent. However, the chemical shift of fluorine atom in 6-chloro substituted ion 2 appears upfield (2.33 ppm) compared to that of 7-*p*-fluorophenyl-norbornenyl cation⁷ (-54.2 ppm), in spite of the destabilizing inductive influence of the chlorine substituent in benzene ring. The influence of substituent also appeared strongly in the case of the nitro derivatives. These results clearly indicate that the mechanism of charge stabilization of the substituted benzonorbornenyl cations must involve participation of the fused benzene ring. The aromatic π orbitals in benzonorbornenyl cations may interact with the empty *p* orbital of the carbocationic center (C_9), causing positive charge to be delocalized into fused benzene ring (homobenzylic delocalization)⁸. However, the interaction between the empty *p* orbital and fused benzene ring in the 6-chloro and 6-nitro substituted cations seems to be much weaker than that of in the unsubstituted cation when comparison is made between ^{19}F NMR data of these ions. The reason is that a deactivating substituent was introduced into the aromatic ring, which might lead to a considerable influence on degree of polarization of the HOMO, as pictured **B** in Figure 1, in the fused benzene ring.

Experimental

NMR Spectra. The ^{19}F nmr spectra were recorded at

-100°C on a Bruker AC-80 spectrometer operating at 75.39 MHz in the FT mode in 5 mm tube. Data were accumulated by using 32768 data points, spectra widths of 6000 Hz, and pulse angle of 60° . Chemical shifts are reported ppm from external CCl_3F .

Carbocation. The cations were prepared by slow addition of a solution of the alcohols in dichloromethane- d_2 to a rapidly stirred solution of $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ at -120°C using a cation generation apparatus. The colors of the ionic solutions are shown pale-yellow.

Synthesis of Alcohols. A 6-chloro- and 6-nitrobenzonorbornen-9-one, which were used as starting compounds for the syntheses of the desired alcohols, were obtained in good yields by our modification of Wittig's procedure⁹. The substituted 9-*p*-fluorophenylbenzonorbornen-9-ols were prepared by the Grignard reaction of the corresponding ketone with *p*-fluorobromobenzene, and these alcohols were purified by column chromatography.

9-*p*-Fluorophenyl-6-chlorobenzonorbornen-9-ol. ^1H NMR (CDCl_3); δ 1.27 (m, 2H), 1.95 (s, 1H), 2.42 (m, 2H), 3.46 (t, 2H), 6.80 (t, 2H), 6.91 (m, 3H), 7.24 (dd, 2H). ^{13}C NMR (CDCl_3); δ 25.5(C2), 25.6(C3), 50.5(C4), 51.1(C1), 91.7(C9), 114.8(C14), 121.6(C7), 122.4(C5), 126.1(C8), 129.3(C13), 131.3(C6), 137.5(C12), 143.7(C10), 147.1(C11), 161.6(C15). ^{19}F NMR (CDCl_3); δ -114.85 . IR (KBr) (cm^{-1}); 3398(s), 2952(s), 1603(m), 1510(s), 1448(m), 1256(m), 1226(s), 1164(m), 1112(s), 1036(m), 840(s), 820(s), 566(m).

9-*p*-Fluorophenyl-6-nitrobenzonorbornen-9-ol. ^1H NMR (CDCl_3); δ 1.30 (m, 2H), 2.07 (s, 1H), 2.54 (m, 2H), 3.63 (t, 2H), 6.82 (t, 2H), 7.20 (m, 3H), 7.90 (m, 2H). ^{13}C NMR (CDCl_3); δ 25.1(C2), 25.2(C3), 51.1(C4), 51.2(C1), 92.0(C9), 115.1(C14), 116.6(C5), 121.7(C13), 122.3(C8), 129.4(C13), 136.8(C12), 146.6(C6), 146.6(C11), 153.1(C10), 161.8(C15). ^{19}F NMR (CDCl_3); δ -114.19 . IR (KBr) (cm^{-1}); 3503(s), 2977(s), 1620(m), 1515(s), 1344(s), 1307(m), 1077(s), 843(s), 811(s), 743(m), 570(m), 521(m).

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