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STRUCTURAL CHANGES IN 2-ARYLNORBORNEN-2-YL CATIONS WITH INCREASING ELECTRON DEMAND. CAN STABLE CARBOCATION STUDIES ILLUMINATE SOLVOLYSIS TRANSITION STATE STRUCTURES?

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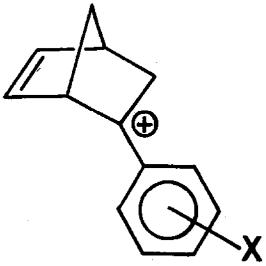
A pmr study of a series of 2-aryl-2-norbornyl cations in superacid media revealed non-linear free-energy behavior for a plot of the H(1) *versus* H(3) chemical shifts which was interpreted in terms of C(1)-C(6) bond participation for the *p*-trifluoromethylphenyl cation and those more electron demanding.[1] Our cmr study of the arylnorbornyl cations confirms this result. On the other hand, Brown finds that the solvolysis of the 2-aryl-2-norbornyl *p*-nitrobenzoates[2] does not reveal an increase in the *exo:endo* rate ratio with increasing electron demand over the same range of substituents. We now report our cmr study of a series of 2-arylnorbornen-2-yl cations 1a-e for comparison with Brown's solvolytic investigation of the same system, in which the observation of an increase in the *exo:endo* rate ratio seems to be interpreted as evidence for π-participation.[3]



1a -e

Solutions of 2-arylnorbornen-2-yl cations 1c-e, generated by dissolving "Freon-11" solutions of the corresponding alcohols in FSO_3H at -78°, are stable at low temperatures. The spectra of cations 1c, 1d, and 1e were recorded at -30°, -60°, and -80°, respectively. Cations 1a and 1b were prepared at -78° employing a limited amount of FSO_3H diluted with SO_2ClF to prevent addition of FSO_3H across the double bond. Their spectra are reported at -30°. The cmr data for cations 1a-e are summarized in Table 1. Chemical shift assignments were made by comparison with those found for the parent ketone[4] and with the aid of off-resonance FT spectra.

Table 1. ^{13}C Chemical Shifts for 2-Aryl-2-Norbornenyl Cations (1a-e)[a].

Derivative	$C^+(s)^b$	$C_1(d)$	$C_7(t)$	$C_4(d)$	$C_5(d)$	$C_6(d)$	$C_3(t)$
p-$C_6H_4OCH_3$	226.8	56.5	54.2	42.8	150.8	128.6	43.4
3,4-$C_6H_3(CH_3)_2$	242.6	59.7	55.1	43.3	156.8	126.5	46.4
C_6H_5	247.4	62.2	55.5	43.7	163.3	124.2	48.0
p-$C_6H_4(CF_3)$	234.4	65.8	54.7	44.0	180.4	117.8	48.5
3,5-$C_6H_4(CF_3)_2$	218.1	67.3	53.8	44.1	193.4	113.0	48.1

a) Parts per million relative to external TMS.

b) Multiplicity: s = singlet, d = doublet, t = triplet.

The sharp break in the plot of the C(5) chemical shifts *vs.* σ^+ (Figure 1) indicates that a dramatic change in the mechanism of charge transmission to C(5) occurs at the phenyl derivative ($\sigma^+ \sim 0$). Furthermore, the impressive reversal of the carbocation center chemical shifts to higher field for cations 1d and 1e reflect this change, and at the same time, implicate rehybridization of the carbocation center with increasing electron demand. The results are consistent with initial minimal charge delocalization to C(5) involving little structural and hybridizational change, followed by substantial electron supply involving dramatic changes in structure and hybridization with increasing demand of the cation center.

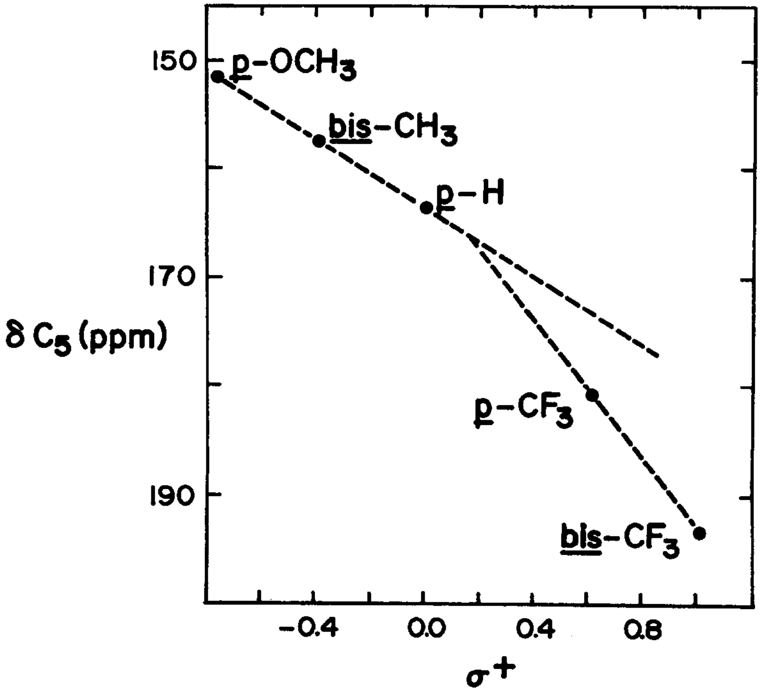


Figure 1. Graph of C(5) Chemical Shift in 2-Arylnorbornen-2-yl Cations *vs.* σ^+ Constants.

Brown points to the need for caution in extrapolating data from superacid media to solvolytic media.[2] We agree. However, a qualitative comparison of our carbocation data with his solvolysis data is nonetheless interesting. The solvolysis of the 2-arylnorbornen-2-yl *p*-nitrobenzoates reveals an increase in the *exo:endo* rate ratio for the 2-[3,5]*bis*(trifluoromethyl)phenyl derivatives[3] which Brown has interpreted as evidence for the onset of π-participation. Thus the onset of participation is observed in the cations generated in FSO_3H before it is observed in solvolysis (σ^+ 0 *vs.* +1.04). The results suggest that carbocations in FSO_3H can provide reasonable models for transition states in solvolysis provided the greater electron demand of the carbocation is taken into account.

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