Direct Observation of 9-Benzonorbornenyl Cations

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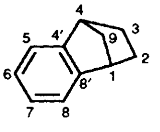
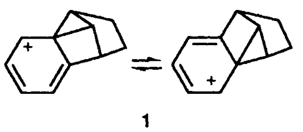
The 9-methyl-, 9-*p*-fluorophenyl and 9-hydroxy-benzonorbornenyl cations are prepared in superacid media and characterized by NMR spectroscopy and quenching experiments.

Bartlett and Giddings[1] demonstrated that *anti*-9-benzonorbornenyl brosylate undergoes acetolysis to give exclusively the corresponding unrearranged acetate. The acceleration of the ionization at C-9 by the fused benzene ring (6×10^5) is considerably inferior to the acceleration of ionization at C-7 of *anti*-7-norbornenyl tosylate by the double bond (10^{11}),[2] both relative to the rates of the corresponding saturated 7-norbornyl derivatives. The nature of the transition state in the solvolysis of 9-benzonorbornenyl brosylate could be **1** or **2**. Bartlett and Giddings discuss a symmetrical transition state **2**. This is supported by the study of substituent effects on the rate of solvolysis of 6- and 7-substituted 9-benzonorbornenyl brosylates by Tanida and coworkers.[3]





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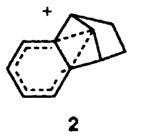

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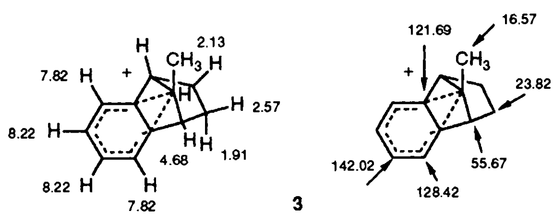
In this communication we report on the direct observation and characterization of the 9-methyl-, 9-*p*-fluorophenyl- and 9-hydroxy-benzonorbornenyl cations **3**, **4** and **5**. The conditions used for the preparation of the cations **3**, **4** and **5** are shown in Table 1.

Cation **3** is best generated at a temperature *ca.* −55 °C. Preparations at lower temperatures (−78 °C) yield mainly protonated 9-methylbenzonorbornen-9-ol and few cations. Temperatures higher than −50 °C lead to decomposition. Cation **4** is even more sensitive to changes in temperature and begins to decompose already at −90 °C.

On the assumption that the nature of the 9-benzonorbornenyl cation is represented by two rapidly equilibrating (fast on the NMR time-scale) homobenzylic cations **1**, the charge densities on carbons 5, 6, 7 and 8 should be the same and one would expect one ^{1}H NMR signal for the aromatic protons, respectively, one ^{13}C NMR signal for the aromatic carbons 5, 6, 7 and 8. In comparison with this, HMO- and OMEGA-calculations yield for the charge densities in the benzene ring of the symmetrical 9-benzonorbornenyl cation **2** q(C-6) =

Table 1

Cation	Precursor	Medium	T of preparation/°C	T of NMR measurement/°C
3	9-Methylbenzo-norbornen-9-ol	$FSO_3H–SO_2–SbF_5$	−55	−60
4	9-*p*-Fluorophenyl-benzonorbornen-9-ol	$FSO_3H–SO_2ClF–SO_2F_2$	−125	−95
5	9-Benzonorbornenone	$FSO_3H–SO_2ClF$	−110	−80



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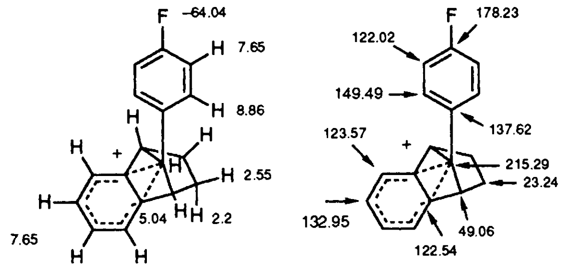

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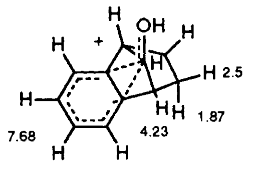

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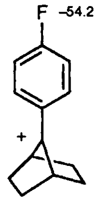

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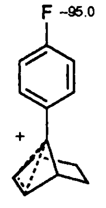

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q(C-7) > q(C-5) = q(C-8). In this case two ^{1}H NMR signals are expected for the aromatic protons and two ^{13}C NMR signals for the aromatic carbons 5, 6, 7 and 8.

The NMR chemical shifts (δ) of the ions are summarized in the formulae. Two signals of equal intensity are observed for the aromatic protons 5, 6, 7 and 8 of cation **3**. In the ^{13}C NMR spectrum of **3** we also observe for carbons 5, 6, 7 and 8 two signals of equal intensity. Thus, the experimental and theoretical data indicate a symmetrical interaction of type **2** for the 9-methylbenzonorbornenyl cation **3**. The ^{19}F chemical shifts of cations **4** and **6** indicate that ion **4** is stabilized relative to the norbornyl cation **6** by charge delocalization into the benzene ring. This stabilization is of course inferior to that caused by the anchimeric participation of the double bond in cation **7**. For ion **4** we observe again two ^{13}C NMR signals for the carbon atoms 5, 6, 7 and 8 which also indicates an anchimeric interaction of type **2**.

Quenching of the ions with MeOH-NaOMe at −100 °C yields in the case of ion **3** exclusively *anti*-ether (50%) and in the case of **4** a mixture of 73% *anti*- and 7% *syn*-ether. Molecular modelling shows that the reason for stereoselectivity in the quenching experiments must be the electronic interaction of C-9 and the benzene ring and not steric screening.

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References

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