Superelectrophilic Nonclassical Carbocations

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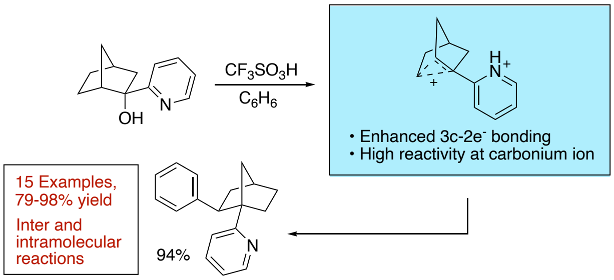


Abstract

The chemistry of dicationic and tricationic 2-norbornyl cations has been studied. A series of *N*-heterocyclic functionalized norborneol substrates were prepared and ionization of these compounds in superacid provided superelectrophilic species. These highly-charged 2-norbornyl cations were found to react with arene nucleophiles in high yields and stereoselectivity. DFT computational studies suggest that increasing positive charge on the structures tends to

enhance the degree of non-classical (or 3-center-2-electron) bonding through separation of the cationic charges.

Introduction

In 1949, Winstein and Trifan reported their solvolysis studies of norbornyl sulfonates and proposed the involvement of a carbonium ion intermediate **1**, the 2-norbornyl cation with 2-electron-3-center bonding or hypervalent bonding at carbon (Figure 1).[1] Evidence supporting nonclassical bonding became quite strong, include computational studies, a solid phase NMR spectrum taken at low temperature (5K), deuterium isotopic perturbation NMR studies, and even the X-ray crystal structure.[2,3] While many structural studies have been done related to the 2-norbornyl cation, there has been far less work utilizing these types of intermediates in synthetic methodologies. Of the synthetic methods reported, the vast majority involve relatively strong nucleophiles.[4] Only a few reports have described reactions involving these nonclassical ions with very weak nucleophiles such as arenes (Scheme 1). For example, List and coworkers described the Friedel-Crafts reaction of a 2-norbornyl trichloroacetimidate with imidodiphophorimidate catalyst.[5] Ionization to the 2-norbornyl cation provided an 80% yield of the product with 1,3,5-trimethoxybenzene. Macdonald et al. prepared the 2,2-

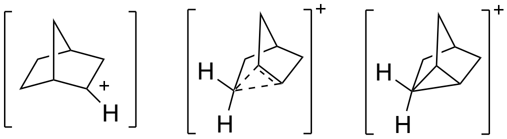
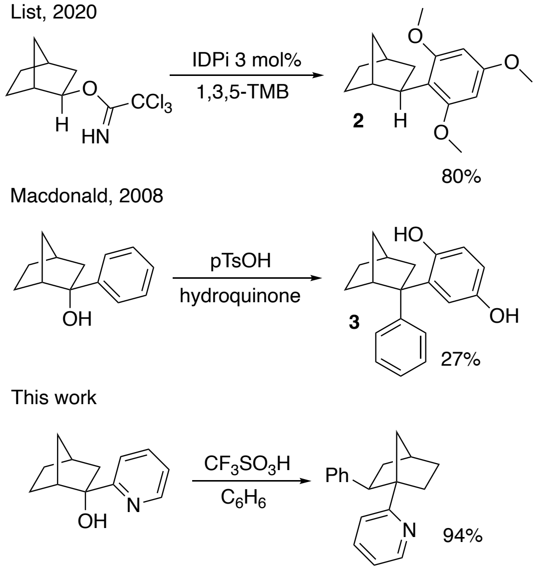


Figure 1. Representations of the 2-norbornyl cation (**1**).

Scheme 1.



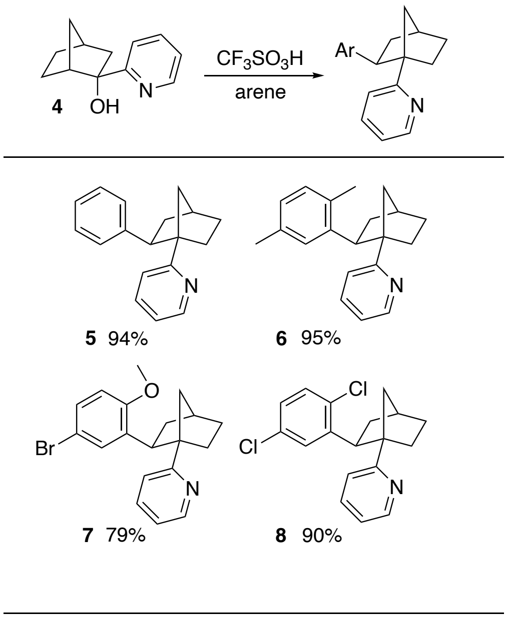
biarylnorbornane (**3**) as a scaffold for drug development.[6] This low yield conversion involves ionization of the alcohol precursor to generate the phenyl-substituted 2-norbornyl cation and subsequent electrophilic reaction with hydroquinone. Both examples (**2** and **3**) utilize activated arenes in the Friedel-Crafts reactions.

In 1964, Staskun reported the H_2SO_4 and $AlCl_3$-promoted cyclizations of β-ketoamides to provide quinolin-2-one products (Knorr cyclization).[7] With the need for excess acid in these conversions, he proposed a mechanism involving doubly-protonated (or ionized) species. Soon after, Olah recognized that conventional monocationic electrophiles may exhibit greatly enhanced reactivities if a second ionization occurs - producing reactive, dicationic intermediates called superelectrophiles.[8,9] These included superelectrophiles such as the protionitronium ion (NO_2H^{2+}) and the protonated acetyl ion (CH_3COH^{2+}).[8] Superelectrophilic activation has since been demonstrated for a wide variety of systems and it has been successfully used in many synthetic methodologies involving weak nucleophiles (including alkanes).[9] Other than theoretical studies involving carbonium dications done the Olah group and others,[10,11] there have been no reports describing the effects of superelectrophilic activation on nonclassical bonding or the chemical reactivities of these species. In this report, we describe our studies of multiply charged, or superelectrophilic, nonclassical ions. We have found that 2-norbornyl dicationic systems provide Friedel-Crafts products in high yields with benzene and related arenes. Theoretical calculations suggest that increasing charge on the systems tends to increase the importance of the nonclassical bonding within the ions.

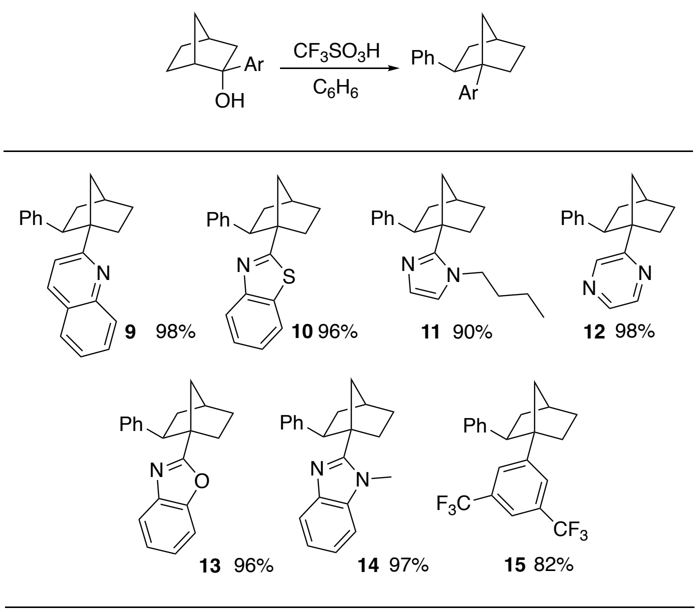
Results and Discussion

Our initial studies examined the chemistry of 2-(pyridin-2-yl)bicyclo[2.2.1]heptan-2-ol (**4**), prepared from 2-norcamphor and 2-lithiopyridine. When this substrate is reacted with benzene in the presence of superacidic CF_3SO_3H (triflic acid), the Friedel-Crafts product **5** is isolated in 94% yield (Scheme 2). The regiochemistry and stereochemistry of product **5** was verified by single crystal X-ray diffraction. Similar products (**6-7**) were obtained in high yields from *p*-xylene and *p*-bromoanisole. Despite being a moderately deactivated arene,[12]

Scheme 2. Products and isolated yields from the reactions of substrate **4** and related aryl-substituted norborneols.[a]



^{a}Reaction conditions: 1 mmol **5,** 10 mL $CHCl_3$, 5 mmol of C_6H_6, 0 °C, 0.5 mL CF_3SO_3H, 4 hrs.



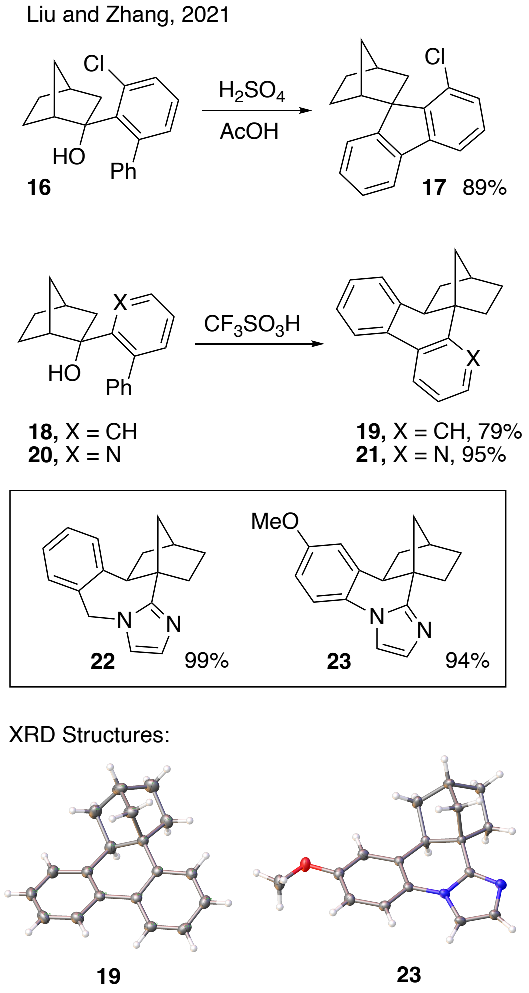
^{a}Reaction conditions: 1 mmol alcohol, 10 mL $CHCl_3$, 0 °C, 0.5 mL CF_3SO_3H, 4 hrs.

p-dichlorobenzene likewise gave the Friedel-Crafts product (**8**) in high yield. In all cases, nucleophilic attack leads to the exo stereoisomer with respect to the new aryl group.

With other *N*-heterocyclic systems, the arylation products are likewise prepared in good yields (Scheme 2). The norborneol substrates were typically prepared from deprotonation of the heterocycle with nBuLi and subsequent reaction with norcamphor. The pyrazinyl norborneol was prepared in low yield from lithium halogen exchange using iodopyrazine and nBuLi and subsequent reaction with norcamphor. Excellent product yields were obtained with benzene and triflic acid from the quinoline, benzothiazole, imidazole, pyrazine, benzoxazole, and benzimidazole systems (**9-14**). The *bis*-1,3-(trifluoromethyl)phenyl substrate gave an 82% yield of the phenylation product (**15**). In contrast, 2-(phenyl)bicyclo[2.2.1]heptan-2-ol provides a complex mixture of products from reaction with benzene in triflic acid. GCMS analysis shows at least 6 products of 248 m/z (the expected MW from a Friedel-Crafts reaction of the alcohol with benzene).

Prompted by the results from intermolecular reactions, we sought to examine similar intramolecular conversions. A recent patent described an intramolecular reaction of the biaryl norborneols **16** (Scheme 3).[13] With H_2SO_4 and acetic acid, substrate **16** is reported to give the spirocycle **17** in 89% yield. This product is then used to prepare materials for use in organic luminescent devices. Similar reports have appeared in a family of patents.[14] Using a biphenyl

Scheme 3. Intramolecular reactions involving biaryl systems.



substrate (**18**), ionization in triflic acid gave the dihydrophenanthrene (**19**) product in 79% isolated yield. Analysis by NMR could not distinguish between a spirocyclic and the dihydrophenanthrene ring systems, however the structure of product **19** was confirmed by X-ray crystallography (see Supporting Information). Similar products were obtained from pyridyl (**20**) and imidazolyl substrates, to give cyclization products **21-23** respectively. Based on the present results, it is unclear if alcohol **16** actually provides the spirocycle **17**, as described in the 2021 patent. This system is very closely related to alcohol **18** - which gave the dihydrophenanthrene product **19**. While it is possible the different acid catalysts – H_2SO_4/AcOH vs. CF_3SO_3H – might generate different reaction manifolds, both alcohols are expected to ionize and produce similar aryl-substituted 2-norbornyl cations.

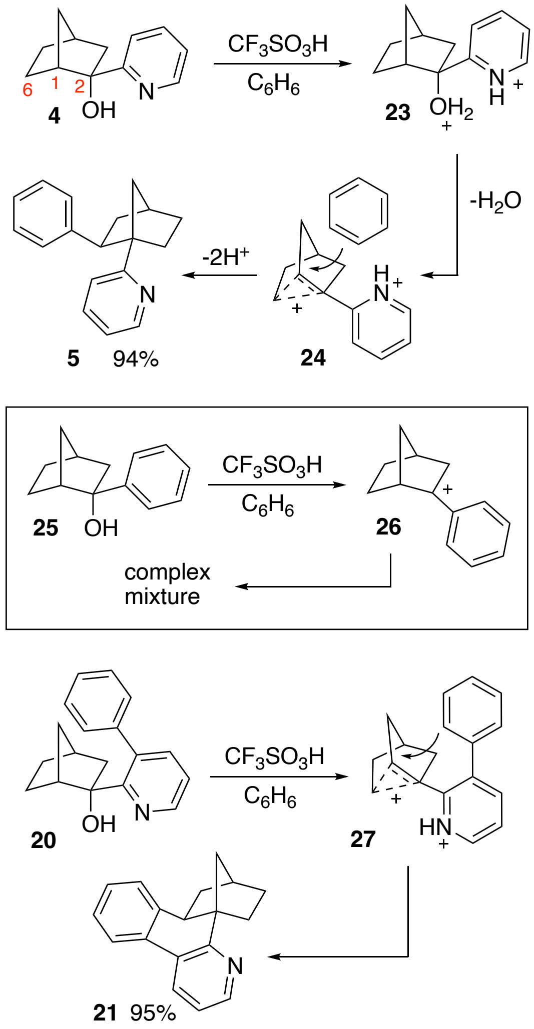
The observed transformations are consistent with the formation of 2-norbornyl dications - superelectrophilic species capable of reacting with weak nucleophiles (Scheme 4). In the case of compound **4**, ionization in superacid begins with protonation at the pyridyl and hydroxy groups to give the pyridinum-oxonium dication. The 2-norbornyl dication is generated from loss of water. A previous study by Olah and coworkers examined 2-aryl-2-norbornyl cations using NMR spectroscopy and applied the tool of increasing electron demand to this cationic system.[15] Based on ^{13}C NMR chemical shift patterns, they concluded "when the aryl group becomes less effective in delocalizing positive charge generated at the C(2) position, the neighboring C(1)- C(6) σ-bond begins to interact with the empty p orbital (electron deficient center), i.e. "the onset of σ-delocalization."" With ionization of compound **4**, the new carbocation center does not benefit from electron donation by the adjacent pyridinium ring.

Moreover, charge-charge repulsive effects should tend to favor the non-classical bonding or σ-delocalization. The non-classical bonding has the beneficial effect of separating the two positive charges – a favorable process seen in other highly charged carbocations.[16] Upon formation of the superelectrophilic 2-norbornyl cation (**24**), benzene reacts at the C(1) position instead of the C(2) position and this observation is consistent with transfer of positive charge to that site.

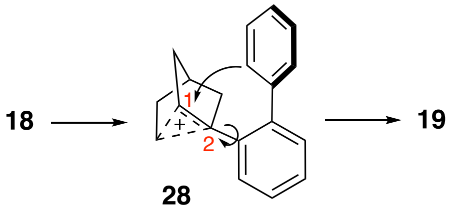
When the phenyl-substituted norborneol (**25**) is reacted with triflic acid and benzene, a complex mixture is obtained. It is notable that Macdonald obtained the substitution product **3**, albeit in low yield, with the arene nucleophile. Nucleophilic attack occurred at the C(2) position, suggesting less transfer of charge to the C(1) and σ-delocalization. In contrast to the phenyl-substituted norborneol, a bis(3,5-(trifluoromethyl)phenyl-substituted norborneol provides the Friedel-Crafts product (**15**, Scheme 2) in 82%. Nucleophilic attack by benzene occurs at the C(1) position which indicates an increasing amount of non-classical bonding and positive charge development at C(1). These results are in accord with Olah's NMR study of 2-aryl-2-norbornyl cations, where it was observed that C(1) is modestly deshielded in the case of the bis(3,5-(trifluoromethyl)phenyl-substituted norbornyl cation (δ 66.2) versus the phenyl-substituted norbornyl cation (δ 59.8). Like the pyridinium ring, the bis(3,5-(trifluoromethyl)phenyl is less effective at stabilizing the carbocation through π-electron donation compared to the phenyl group. This creates increased electron demand and an increasing degree of non-classical bonding.

With the biaryl norborneol (**20**), ionization in superacid gives the expected dicationic 2-norboryl ion (**27**) and cyclization occurs rapidly at the C(1) position to give product **21** (Scheme

Scheme 4. Proposed mechanisms for the reactions of substituted norborneols.



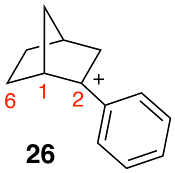
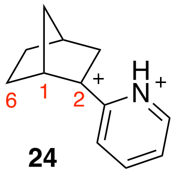
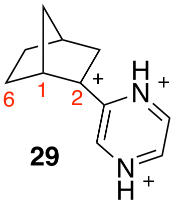
4). Similar dicationic 2-norboryl ions are proposed for the imidazole derivatives leading to products **22** and **23**. Interestingly, the biphenyl-substituted norborneol (**18**) provides a good yield of the cyclization product **19** from a Friedel-Crafts reaction at C(1). This product necessitates the involvement of σ-delocalization and at least some positive charge at C(1). This



can be understood as a consequence of C-C bond rotation between C(2) and the aryl ring – preventing conjugation between the empty p-orbital at C(2) and the aryl group π-system. Rotation of the bond (**28**) leads to an increasing degree of σ-delocalization and positive charge formation at C(1). The ortho-phenyl group is then ideally positioned to form the new C-C bond at C(1).

In order to further understand the impact of neighboring cationic charge on the structure of these ions and nonclassical bonding, DFT calculations have been done.[17] Calculations were carried out at the IEFPMC(H_2O)/M06-2X/6-311++G(d,p) level of theory (Table 1). With variation of the aryl substituent group, an increasing amount of charge can be placed on the 2-norbornyl cation. Progressing from the mono- to di- to tricationic structures (**26** -> **24** -> **29**) shows evidence of increasing participation of the C(1)-C(6) σ-bond in stabilization of the carbocation center. For example, C(1)-C(6) bond distance lengthens from 1.594 to 1.863 to 1.939 Å from the mono- to the tricationic structure (**26** -> **24** -> **29**). The lengthening of this bond suggests removal of electron density from C(1) and the development of positive charge at that carbon, which is consistent with the observed Friedel-Crafts chemistry. In the same series, C(6) draws closer to C(2), indicating a stronger bonding interaction. From the mono- to the tricationic structure (**26** -> **24** -> **29**), the C(2)-C(6) bond

Table 1. Calculated bond lengths, Å, and bond angles for ions **26**, **24**, and **29** (IEFPPMC(H2O)/M06-2X/6-311++G(d,p) level of theory).

Calculated Structural Parameters	 **26**	 **24**	 **29**
C(1)-C(2)	1.465	1.396	1.412
C(1)-C(6)	1.594	1.863	1.939
C(2)-C(6)	2.344	1.841	1.733
C(2)-C(ring)	1.416	1.483	1.483
C(6)-C(1)-C(2) bond angle	100°	67°	60°

length decreases from 2.344 to 1.841 to 1.733 Å. The slight lengthening of the C(2)-C(ring) bond – with the charged rings - is consistent with the decrease in π-electron donation from the aryl ring to the carbocation site at C(2). It is also notable that the C(6)-C(1)-C2) bond angle decreases dramatically from 100° to 67° to 60° with increasing charge. All of these structural parameters suggest the nonclassical bonding is enhanced with adjacent cationic charge.

The energetics of the reaction were also study by DFT calculations (Figure 2). For the ionization of the phenyl-substituted norborneol, the monocationic 2-norbornyl cation **26** is generated**.** The lowest energy pathway involves formation of a π-complex at the 2-position in a reaction with benzene. The transition state leading to the σ-complex is located 20.8 kcal•mol^{-1} above the π-complex – a late transition state with the forming C-C bond at 1.88 Å in length. Formation of the monocationic σ-complex is slightly endergonic. In the case of the pyridyl-substituted norborneol, the dicationic 2-norboryl cation **24** is generated. This involves cleavage of the C-O bond with a transition state that is 8.7 kcal•mol^{-1} above the oxonium dication. The longer C-O bond distance at the transition state - compared to the monocationic system – is the consequence of the more highly electrophilic carbocation center with the dication. Upon formation of dication **24**, the lowest energy pathway leads to the π-complex at the C(1) position. The transition state leading to the σ-complex is located 5.7 kcal•mol^{-1} above the π-complex – an early transition state with the forming C-C bond at 2.41 Å in length. For comparison purposes, formation of the σ-complex at the 2-position was also calculated. This transition state is found 11.0 kcal/mol above the dicationic π-complex (see Supporting

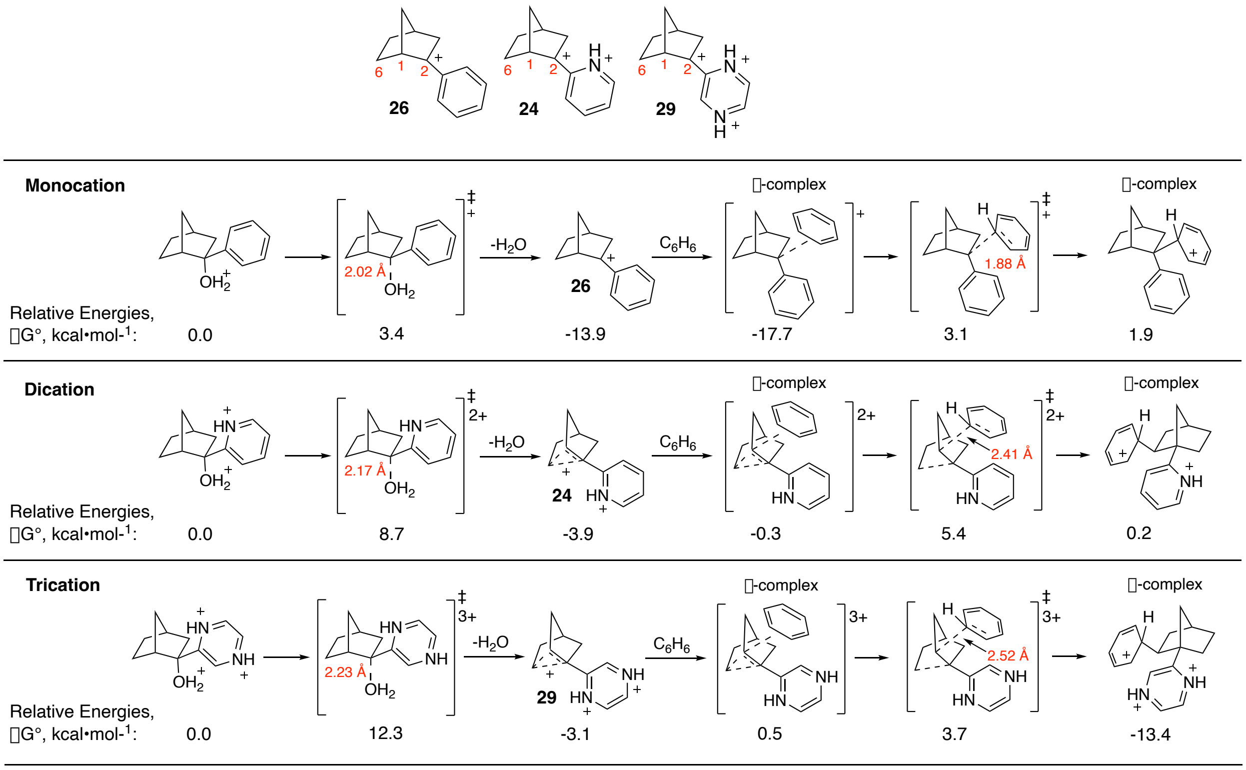


Figure 2. DFT calculated structures and energies for steps involving ions.

Information for details). The lowest energy path involves formation of the σ-complex at the 1-position (5.7 kcal/mol above the π-complex), which is in accord with the experimental observation of nucleophilic attack occurring at the site of σ-delocalization (at the non-classical ion).

For the ionization of the pyrazinyl-substituted norborneol, the tricationic 2-norbornyl cation **29** is generated**.** Cleavage of the oxonium C-O bond occurs with a transition state located 12.3 kcal•mol^{-1} above the oxonium dication. The long C-O bond distance (2.23 Å) is indicative of a late transition state and a highly electrophilic carbocation center. Again, the nonclassical bonding in **29** leads to nucleophilic attack at the C(1) position. The transition state leading to the σ-complex is located just 3.2 kcal•mol^{-1} above the π-complex with the forming C-C bond 2.52 Å in length. The σ-complex forms in an exergonic step and this structure benefits from the separation of cationic charges. Again for comparison, the formation of a σ-complex at the 2-position was calculated. This transition state is found 12.2 kcal/mol above the tricationic π-complex (see Supporting Information for details). The lowest energy path involves formation of the σ-complex at the 1-position (3.2 kcal/mol above the π-complex), which is in accord with the experimental observation of nucleophilic attack occurring at the site of σ-delocalization (at the non-classical ion).

Through the series of 2-norbornyl cations, the monocationic system reacts at the 2-position while the di- and tricationic systems react at the 1-position. This is consistent with an increasing degree of non-classical bonding with the multiply charged systems and the movement of positive charge from the 2-position to the 1-position. Besides increasing the degree of non-classical bonding, the added charge also enhances the electrophilic reactivity of the carbocation system, essentially generating a superelectrophilic carbonium ion site. This was demonstrated in the Friedel-Crafts reactions with arenes such as benzene and *p*-dichlorobenzene at the superelectrophilic carbonium site of the dicationic systems – contrasted with the previously reported chemistry showing reactions with only electron rich arenes at the monocationic systems.[5,6]

Conclusion

In summary, this work presents evidence that non-classical bonding may be enhanced by electrostatic effects. When the 2-norbornyl cation is adjacent to cationic groups, there is an increasing degree of σ-delocalization. This creates a superelectrophilic carbonium ion which has been shown to react with arenes in high yields and excellent regioselectivities. A similar impact is expected with strongly electron-withdrawing groups that are uncharged.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at …. Experimental procedures and characterization data for all compounds; ^{1}H and ^{13}C NMR spectra; computational methods and results; X-ray diffraction data for compounds **5**, **19,** and **23**.

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Author Contributions

This manuscript was written with significant contributions from all authors.

Notes

The authors declare that they have no competing interests that could have influenced the work reported within this manuscript.

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Dedication

This manuscript is dedicated to the memory of Professor George A. Olah, whose work with carbocations and non-classical bonding continues to inspire the scientific community.

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