Tetrahedron Vol. 40, No. 21, pp. 4161 to 4215, 1984
Printed in Great Britain.

0040–4020/84 $3.00 + .00
Pergamon Press Ltd.

TETRAHEDRON REPORT NUMBER R 174

MULTIPLY CHARGED CARBOCATIONS AND RELATED SPECIES IN SOLUTION

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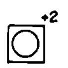
(*Received in the UK* 13 *February* 1984)

CONTENTS

INTRODUCTION

The amount of research on the generation, chemistry and nature of carbocations possessing one unit of charge has, of course, been enormous, with Saunders' work on equilibrium isotope effects[1] and Yannoni's and Myhre's work on the NMR of ions in the solid state at very low temperature[2] being notable recent examples. Research on carbocations with two or more charges, i.e. carbodications, carbotrications, etc. has lagged far behind primarily because there have been few suitable methods for making the ions so that they possess sufficient lifetimes for characterization. Fortunately, this state of affairs has changed dramatically in the last few years. This article will bring together and summarize what is known about these species.[3] No attempt will be made to discuss, except in a few pertinent cases, research on ions in the gas phase and theoretical studies, as these will be reviewed in a forthcoming publication.[4]

As polycations, both organic and inorganic, are remarkably diverse, it is worth spending a moment to give a working definition by which the species in this article were chosen. A recent book defines a carbocation as "any cation with an even number of electrons in which the charge may be formally located on one or more carbons."[5] This highly inclusive definition is easily extended to species with two or more positive charges. Here, of course, one must find a resonance structure of the appropriate species in which *all* charges are formally located on individual carbons. Thus ions **1** through **3** fulfil the requirements of the definition, while **4**–**6** do not. Nevertheless, many arbitrary choices were made and interesting exceptions to the rule will be found in this article, whereas certain other ions which obey the definition will not.



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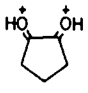

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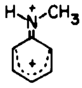

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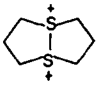

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Se_4^{+2}

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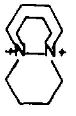

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General considerations

If one starts with a neutral molecule, there are only a few methods by which it can be converted into a multiply charged cation; these are: removal of electrons, either chemically or electrochemically; removal of anionic groups such as halides and tosylate; and addition of electrophiles such as H^+, NO_2^+ and a carbocation. If the result of this latter reaction is a cation rather than a carbocation, e.g. ROH_2^+, loss of a neutral molecule will yield a carbocation. For a carbodication, a combination of two of these reactions will yield the ion, for a carbotrication, three will be required, and so on. If the starting material is a carbocation, clearly only one of these reactions will be necessary to form the diion.

The above analysis is, of course, abstract in nature. There are a variety of reasons why a multiply charged ion will not form in a reaction or, if it does, will only have a transitory existence. Let us consider the formation of a carbodication from a neutral molecule; one has to introduce each unit charge in a separate step, i.e. sequentially. It is in general at least as difficult to introduce the second charge into the system as the first. Ionization potentials (Table 1) show this clearly. Electrochemical and thermochemical data, to be discussed later, also demonstrate this. Thus, the medium in which the desired sequential reactions are to occur may have sufficient power to bring about the first reaction, but not the second. Even if the second reaction is feasible, the intermediate produced in the first reaction may be too reactive for it to undergo the second, desirable reaction.

As inferred from the data (Table 1), multiply charged ions in general will have very large heats of formation (ΔH_f°). If one wants to prepare these ions in solution and prevent their decay, especially by charge separating reactions and by reaction with nucleophiles, it is necessary in effect to lower the ΔH_f°. This lowering can be an intrinsic property of the molecule. If, for example, the reactant possesses two half-filled nonbonding molecular orbitals (NBMOs), the first and second ionization potentials will be relatively small. Likewise, neutral molecules which have one filled antibonding MO will have small first

Table 1. Gas phase ionization energies for selected molecules

	Ionization energy (eV)		
		Ion formed	
Substrate RH	$RH^{+\cdot}$*	RH^{+2}†	$RH^{+3\cdot}$*
Benzene	9.44	26.1	44 ± 5
Toluene	8.82	24.2	42 ± 5
Naphthalene	8.12	22.8	40 ± 5, 41.2 ± 1.0‡
Biphenyl	8.5	22.1	—
Anthracene	7.75	21.3	—
Phenanthrene	8.10	23.1*	—
Methane	—	30.6§	—
Diphenylacetylene	8.85	23.3	—

* Ref. 6.
† Ref. 7.
‡ Ref. 8.
§ Ref. 9.

and second ionization potentials. Aromatic hydrocarbons with extended π systems should have lower ionization energies than ones with less extended π systems. If the desired ion possesses aromaticity, the stabilization brought about by this property also lowers the ΔH_f°. Spreading out charge over a large area is known from the laws of physics to help stabilize an entity. This is an especially important phenomenon here for it will help to reduce charge repulsion in the molecular system. This delocalization of charge can be brought about by inclusion of electron releasing substituents onto the molecular framework; the more of these groups that the molecule possesses, the better the delocalization will be. Geometry can also help in keeping the two or more charges away from each other. Ion pairing, a virtually unexplored phenomenon in this area of research, should also be effective. Solvation is undoubtedly the best way of delocalizing charge and stabilizing the ion. Again, this is especially important here because of charge repulsion. Thus one would want to use solvents that are known to solvate carbocations. Equally important one would want solvents of low nucleophilicity, free of troublesome nucleophiles such as water, to insure not only that the multiply charged ion survives but also to insure that any electrophilic intermediates formed on the way to the desired ion survive long enough to produce the desired ion. Finally, if the solvent also is functioning as a reactant, it should possess sufficient acid strength and/or oxidizing power to convert an intermediate into the desired product, e.g. $R^+ + H^+ \rightarrow RH^{+2}$ and $R^{+}\cdot \xrightarrow{-e} R^{+2}$.

How have multiply charged ions been characterized? In favorable cases the species have been isolated as stable salts which naturally makes characterization relatively easy. In the absence of isolation, the nature of the reactant and the mode of reaction in conjunction with ^1H- and ^{13}C-NMR spectroscopy have been used for ion characterization. As with carbocations, this has been the most widely used method of ion identification. Electronic spectroscopy has also been used on occasion. Thermochemical data, e.g. heats of reaction, redox potentials and pK_R^+ values, have also been extremely useful because the derived values for multiply charged carbocations are expected to be different than for an ion with one unit of charge. In favorable cases one can watch the multiply charged ion form sequentially from its predecessors.

CHEMICAL SYNTHESIS OF IONS

Monocyclic aromatic and antiaromatic ions and their benzo derivatives

The Hückel 4n+2 rule is certainly one of the most successful—and simple—predictors ever formulated in organic chemistry. In addition to neutral molecules, it is easily applied to ions including polyions. Neutral monocyclic species with 4n π electrons, i.e. antiaromatic ones, on loss of two electrons will yield aromatic dications. Aromatic molecules on loss of four electrons will yield another aromatic species, now with four units of positive charge. Several of these potentially aromatic multiply charged cations are shown below. Aromaticity, of course, is a property that will stabilize a molecule, whereas charge repulsion which may be severe here will destabilize it. *Ab initio* calculations bear this out.[10] The unsubstituted $C_4H_4^{+2}$ (**1**) and $C_8H_8^{+2}$ (**9**) are predicted to be weakly bound with exothermic charge separating reactions available to them. The $C_5H_5^{+3}$ (**7**), $C_6H_6^{+4}$ (**8**) and $C_9H_9^{+3}$ (**10**) ions are predicted to be strongly unbound with highly exothermic (> 150 Kcal/mol) fragmentation reactions available to them.

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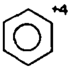

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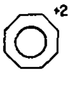

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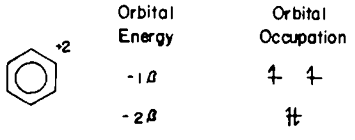
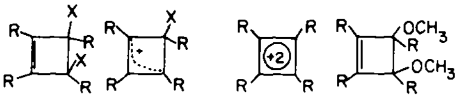
Antiaromatic ions, i.e. those obeying the Hückel 4n rule, may also be accessible. The prototype $C_6H_6^{+2}$ ion (**11**) is in addition to being antiaromatic predicted by Hund's first rule to have a triplet ground state. Sophisticated *ab initio* calculations, however, do not distinguish between a D_{6h} triplet and a singlet of lower symmetry as being the ground state.[11] One would also expect the antiaromatic character of the multiply charged ion to decrease as the ring size increases,[12] thus making these large ions potentially available for study.



11

Katz was undoubtedly the first person to attempt to prepare an aromatic dication. Treatment of the dichloride **12a** with silver hexafluoroantimonate in liquid SO_2 yielded the allylic ion **13a** rather than the desired tetramethylcyclobutadiene dication (**14a**).[13] Similar treatment of the dichloride or dibromide with $AlCl_3$ yielded the corresponding halocyclobutenyl ions **13a** and **13b**.[14] Farnum succeeded in preparing a dihydroxycyclobutadiene dication (**17**) by dissolution of **16** in H_2SO_4.[15] It was not possible at that time to decide which of several resonance structures is the major contributor to the actual structure. Freedman attempted to prepare the tetraphenylcyclobutadiene dication (**14b**) by treatment of the dibromide **12c** with Ag ion in benzene and dissolution in H_2SO_4.[16] Indeed the reactions did suggest the formation of a dication, two equivalents of silver bromide being formed in the former reaction and Br-free products in the latter. Treatment of the corresponding dichloride with stannic chloride in benzene generated what was thought to be the hexachlorostannate salt of the dication.[16] Subsequent X-ray crystallography of this material demonstrated it to be the chloroallylic ion **13d**.[17,18]

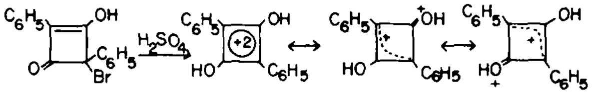
A breakthrough occurred in 1969 when Olah *et al.* treated the dichloride **12a** with SbF_5 in liquid SO_2 or SO_2ClF.[19] The initial product of the reaction, ion **13a**, underwent a slow ionization at $-75°$ to give tetramethylcyclobutadiene dication (**14a**) which was characterized by its NMR properties.[19] Note that the strong Lewis acid, SbF_5, and the weakly nucleophilic solvents, SO_2 and SO_2ClF, were used to bring about the desired transformation and stabilize the desired product. Perhaps the most revealing feature of the NMR data was the ^{13}C chemical shift of the ring C which occurred at a position predicted by the Spiesecke–Schneider relationship[20] for the unsubstituted cyclobutadiene dication. This relationship correlates ^{13}C shifts with π electron density, thus demonstrating in this instance that the observed species is dicationic. Quenching of the solution with $NaOCH_3/HOCH_3$ yielded a dimethoxycyclobutene (**15a**; mixture of *E* and *Z* isomers) which is also consistent with the dicationic nature of **14a**.



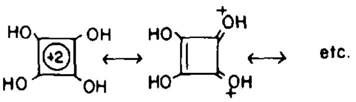
12 13 14 15

a) R=CH$_3$, X=Cl
b) R=CH$_3$, X=Br
c) R=C$_6$H$_5$, X=Br
d) R=C$_6$H$_5$, X=Cl

a) R=CH$_3$
b) R=C$_6$H$_5$
c) R=OH



16 17



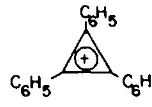
14c

Similar results were obtained when the tetraphenyldibromide **12c** was treated with SbF_5/SO_2 or $FSO_3H/SbF_5/SO_2$ at low temperature.[21] The resulting tetraphenylcyclobutadiene dication (**14b**), as with **14a**, was characterized by its ^1H- and ^{13}C-NMR properties, with Spiesecke–Schneider relationship again being obeyed. A notable discovery was that the phenyl rings of **14b** delocalize the positive charge to a greater extent than they do in the triphenylcyclopropenyl cation (**18**). This undoubtedly reflects the higher average charge density per carbon in **14b** when compared to **18** as well as charge repulsion in **14b** which does not exist in **18**.

In a subsequent full paper, in addition to **14a** and **14b**, the synthesis and characterization of 1,2-difluoro-3,4-diphenylcyclobutadiene dication (**19**) and 1,2-diphenylcyclobutadiene dication (**20**) were described.[22] These ions were also prepared by the ionization procedure used to synthesize **14a** and **14b** and were, as before, characterized by their NMR parameters. Interestingly the *ortho* carbons of both **19** and **20** were nonequivalent, indicating hindered rotation about the ring carbon of the 4-membered ring and the *ipso* carbon of the phenyl ring; hindered rotation was not observed in the tetraphenyl case (**14b**). In all the phenyl ions i.e. **14b**, **19** and **20**, the *para* carbons were quite deshielded; this can be attributed to a substantial resonance interaction between the 4- and 6-membered rings. For ion **20**, the ring hydrogens were also quite deshielded.

Olah and White have also prepared the tetrahydroxylcyclobutadiene dication (**14c**) by treatment of squaric acid with SbF_5/FSO_3H in liquid SO_2.[123] The proton NMR signal at 14.50 ppm is quite low and typical for protonated CO groups.[43] This species (**14c**) is best represented as a diprotonated diketone rather than as an aromatic cyclobutadiene dication.

The parent cyclobutadiene dication (**1**) is predicted by *ab initio* MO calculations to have a puckered (D_{2d}) ground state geometry 2.8 Kcal/mole lower in energy than the square planar (D_{4h}) form.[23a] Charge repulsion in **1** is also predicted to be more significant than Hückel aromaticity.[23b,c] Olah and Staral attempted to prepare this species by reaction of **21a** with SbF_5. The hoped-for ion was not observed. Instead the chlorocyclobutenyl ion **22a** was formed which, on heating, was converted into the fluorocyclobutenyl ion **24a**. One of the mechanisms that one can envision for this transformation involves **1**. Similar behavior was observed when the dimethyldichlorocyclobutene **21b** was treated with SbF_5. Here the conversion of chloro ion **22b** in the fluoro ion **24b** occurred at a lower temperature than it did in the case of **22a**. Thus, there is a critical interplay between the relative stability of the halocyclobutenyl cations and the aromatic dications and the nature and number of substituents that these ions possess, with tetrasubstitution favoring the dication and disubstitution favoring the monocation, except for the diphenyl case where extensive charge delocalization is possible. That the nature of the substituents is important in determining the stability of the dication was further born out by Hünig's synthesis and isolation of the tetraaminosubstituted dication **25**.[24a] It is interesting to note that the ring carbons of **25** are considerably less deshielded than those of **14a**, **14b**, **19** and **20**. Clearly a substantial amount of charge resides on the N atoms. It is questionable if this species should be called aromatic. Even in some of Olah's cyclobutadiene dications it is difficult to assess the extent of their aromaticity because deshielding, which is a criterion used to define aromaticity, is in fact an accumulated effect due both to charge and a dimagnetic ring current. Other cyclobutadiene dication salts have also been isolated.[24b]



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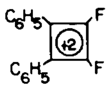

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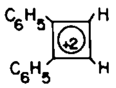

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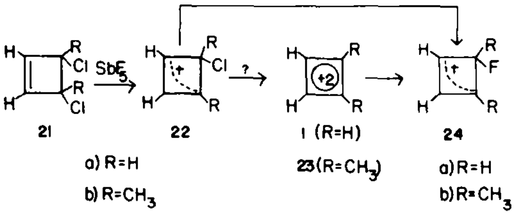

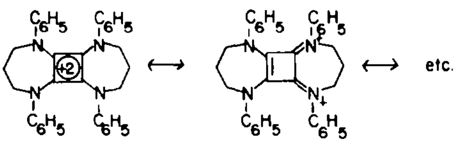

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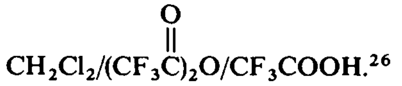
The mode of synthesis that Olah used to prepare cyclobutadiene dications is easily extended to benzocyclobutadiene dications. The ionization reaction, however, failed to produce the unsubstituted benzocyclobutadiene dication (**26a**) but did yield the dimethyl dication **26b**.[25] By comparison of the ^{13}C chemical shifts of **26b** with those of **14a**, **14b**, and **20**, these researchers concluded that **26b** possesses two units of positive charge and is aromatic.

Diprotonation of benzocyclobutenedione (**27**) with $FSO_3H/SbF_5/SO_2$ yielded what was formally a dihydroxybenzocyclobutadiene dication (**26c**). The lack of any substantial downfield shift of the ^{13}C resonances of **26c** when compared to those of **27** indicated that **26c** is better represented as a diprotonated diketone. It is interesting to note, however, that the OH chemical shift at 11.4 δ is considerably higher field than typical protonated ketones, suggesting some delocalization of charge.[43]

Dibenzocyclobutadiene dications are unlikely to be easily synthesized by the above ionization method because suitable precursors are not available. Removal of two electrons from biphenylene derivatives, however, represents a satisfactory alternative. Ronlan and Parker were able, for example, to generate and characterize $\mathbf{28b}^{+2}$ (two reversible one electron oxidations by cyclic voltametry and coulometry experiments) by anodic oxidation of **28b** in

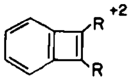


$$CH_2Cl_2/(CF_3\overset{\overset{\displaystyle O}{\|}}{C})_2O/CF_3COOH.^{26}$$

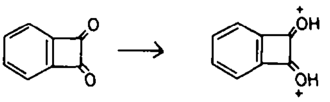
As indicated from UV-Vis spectroscopy, dissolution of **28b** in H_2SO_4 yielded the same dication

(λ_{max} 459 nm, ε 5.55×10^4). Anodic oxidation of the parent hydrocarbon **28a** in the same medium yielded ambiguous results because the second oxidation was irreversible.

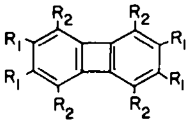
Olah has prepared several dibenzocyclobutadiene dications by oxidation of the neutral hydrocarbon with SbF_5 in SO_2ClF.[25b] Note that SbF_5 is functioning as an electron acceptor in these reactions. The ions **28a**$^{+2}$, **28c**$^{+2}$ and a mixture of **29**$^{+2}$ and **30**$^{+2}$ gave NMR spectra consistent with their dicationic character; the combined deshielding of ring carbons (compared to neutral molecules) for each ion was only compatible with a dication. Russian workers who also generated **28a**$^{+2}$ in the same manner as Olah came to the same conclusion.[27]



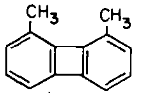
26
a) R = H
b) R = CH_3
c) R = OH



27 26c



28
a) $R_1 = R_2 = H$
b) $R_1 = OCH_3$, $R_2 = H$
c) $R_1 = H$, $R_2 = CH_3$



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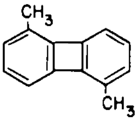
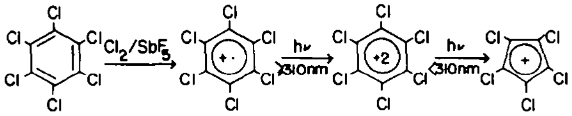


30

The simplest antiaromatic dication that one can image is the benzene dication (**11**). Although the parent dication has not yet been prepared in solution, the perchlorobenzene dication (**33**) has.[28] Treatment of hexachlorobenzene (**31**) with the powerful oxidizing agent Cl_2/SbF_5 at room temperature gave a deep purple solution of the radical cation **32**. After cooling to $\leqslant 77$ K, photolysis of the resulting rigid solution at $\geqslant 310$ nm resulted in the loss of a second electron and the formation of $C_6Cl_6^{+2}$ (**33**). The dication gave ESR signals characteristic of a triplet, i.e. 4 lines for the $\Delta m = 1$ transition with $D = 0.1012\ cm^{-1}$ and $E < 0.0003\ cm^{-1}$ and a $\Delta m = 2$ transition at half field. A Curie law plot was linear indicating that the observed triplet is the ground state of the species; this, of course, is what's expected from simple MO theory and Hund's first rule for the parent dication. Prolonged irradiation at < 310 nm converted **33** into the pentachlorocyclopentadienyl cation (**34**) which also has a triplet ground state. It is interesting to note that in converting **32** into **33** photolysis made the electron transfer reaction occur more easily. Although this technique has rarely been applied to this field of endeavor, it is well known in more traditional areas of photochemistry.[29] There is no reason why this technque cannot be used in the future to make a recalcitrant intermediate such as a radical cation undergo further electron transfer reactions to yield a carbodication and higher charged species.

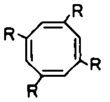


31 32 33 34

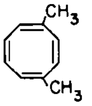
Although the potentially aromatic cyclooctatetraene dication (**9**) is unknown, several derivatives have been synthesized by Olah *et al.*[30] The ions, **35a**$^{+2}$, **35b**$^{+2}$, **36**$^{+2}$ and **37**$^{+2}$ were all prepared by oxidation of the corresponding neutral hydrocarbon with SbF_5 in SO_2ClF at $-78°$ and characterized by their ^1H- and ^{13}C-NMR parameters. Application of the Spiesecke–Schneider correlation[20] and comparison of the total ^{13}C deshielding with suitable model compounds demonstrated that these ions are planar, aromatic carbodications. It is interesting to note that the parent **9**—and several others—could not be prepared in agreement with the expectations of *ab initio* calculations.[10]

In these studies an interesting chemical transformation was observed when the solution

(SbF_5/SO_2ClF) of **35a**$^{+2}$ was warmed to −20°; the carbodication underwent an electrocyclic ring closure—formally forbidden—to give *cis*-2,3a,5,6a-tetramethyldihydropentalene dication (**38a**).[30] Although aromaticity is lost in this transformation, this effect is counterbalanced by relief of angle strain and probably charge repulsion. Interestingly, octamethylcyclooctatetraene (**39**) yielded permethyldihydropentalene dication (**38b**), undoubtedly via the undetected octamethylcyclooctatetraene dication.[31] Carbodication (**38b**) was also formed when octamethylsemibullvalene (**40**) and the tetramethylcyclobutadiene dimer (**41**) were treated with FSO_3H/SO_2. When **41** was treated with SbF_5/SO_2ClF at −78° or −10°, however, a new carbodication **42** was formed.[32] Here is an example where the selection of superacid and solvent, $FSO_3H:SbF_5$ in SO_2 versus SbF_5/SO_2ClF, was instrumental in bringing about different chemical transformations and stabilizing different ionic products.



35
a) $R=CH_3$
b) $R=C_6H_5$



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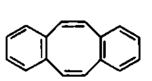

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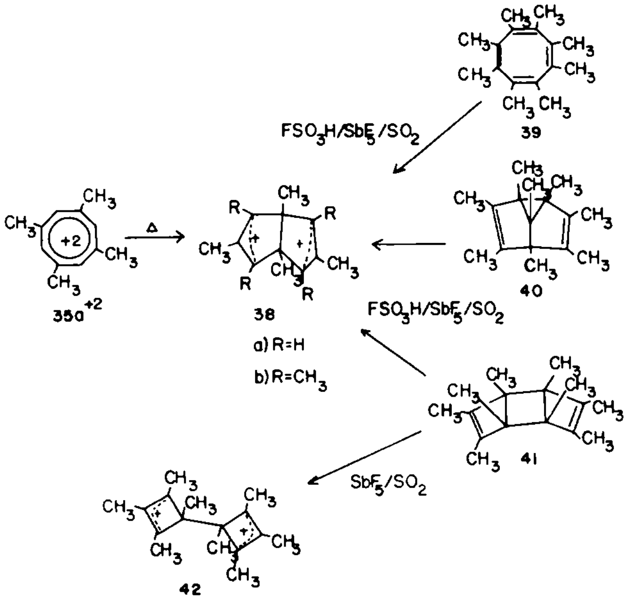


In an attempt to prepare the homo[15]annulenyl cation **44**, Schröder *et al.* treated [16]annulene (**43**) with the proton source, FSO_3H, in SO_2/CD_2Cl_2 at −80°.[33] To their surprise, ^1H- and ^{13}C-NMR spectroscopy indicated the formation of [16]annulene dication (**45**).[33] This species which possesses C_{2v} symmetry is distinctly aromatic because the three kinds of inner hydrogen appeared at δ 2.55, 4.10 and 4.48 ppm above tetramethylsilane (TMS) in the ^1H-NMR spectrum and the outer ones appeared 10.7 ppm below TMS; the Spiesecke–Schneider relationship was also found to be valid.[20] Although the mechanism for this transformation is unknown (loss of two electrons, diprotonation followed by loss of H_2, etc.), it is known that FSO_3H can function as an oxidizing agent as well as a proton source.[34]

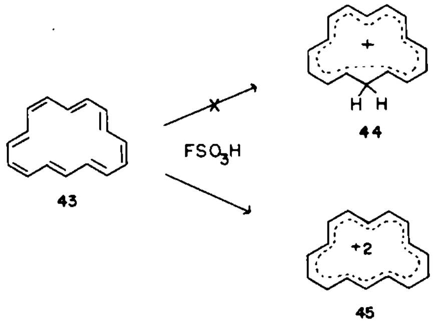
In a similar vein, the bridged aromatic [18]annulene (**46**) was oxidized to the "antiaromatic" [18]annulene dication (**47**) when treated with FSO_3H in SO_2ClF at −80° and then warmed to 0°.[35] This most interesting species was identified as an antiaromatic carbodication by its NMR characteristics and quenching studies. The C_{2v} dication yielded a ^{13}C-NMR spectrum in which the center of gravity for the annulene ring carbons was shifted downfield by 17.7 ppm, a deshielding value expected for a diion. Quenching with methanol at −80° generated the dimethoxyl adduct **48**,

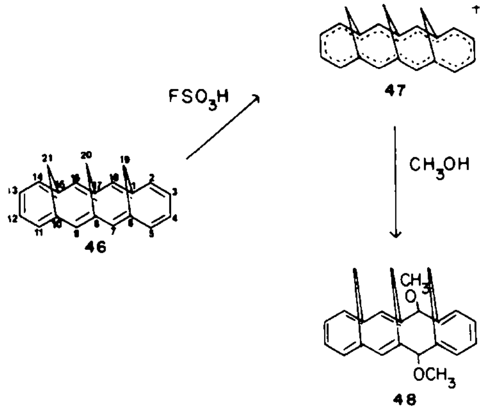
Table 2. ^{1}H-NMR comparison of **46** and **47**

Protons	Chemical shifts (p.p.m.)	
	46 in CD_2Cl_2*	**47** in $FSO_3H/SO_2ClF/CD_2Cl_2$†
H-19, 21 *exo* and *endo*	−0.45, 1.32 (AX System, J = 13.5 Hz)	4.35, 7.58 (AX System, J = 14.4 Hz)
H-20	0.53 (singlet)	8.25 (singlet)
H-2, 3, 4, 5 11, 12, 13, 14	6.70–7.70 (AA′XX′ System)	7.01–7.35 (AA′XX′ System)
H-7, 9, 16, 18	7.62 (singlet)	6.07 (singlet)

* Ref. 36.
† Ref. 35.

demonstrating the dicationic character of the observed species. In agreement with the predictions for a 4n π electron system, **47** possesses a paramagnetic ring current (Table 2): the annulene protons of **47** occur at approximately the same chemical shift as the corresponding protons of the neutral hydrocarbon **46**, a result attributed to counterbalancing effects of a downfield shift due to charge and an upfield shift due to the paramagnetic ring current, and the bridging protons of **47** many ppm's downfield from their neutral counterpart. It is interesting to note that this 4n system has a singlet ground state in contrast to that of the perchlorobenzene dication (**33**). A lack of planarity imposed on the π framework, unequal carbon carbon bond lengths, unequal substitution in **47** and ion pairing may contribute to this result.

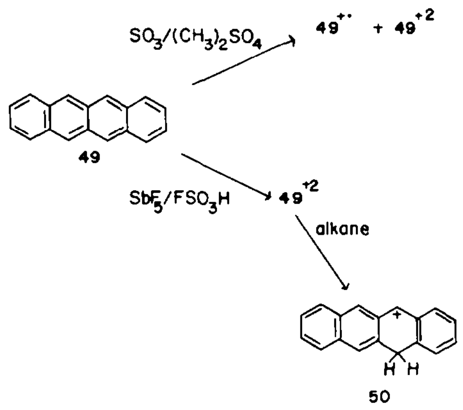


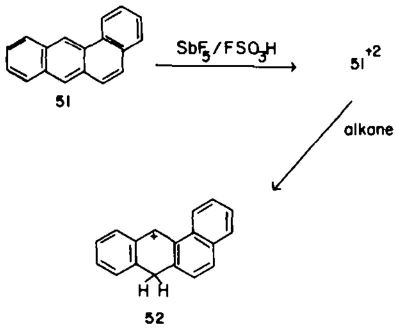


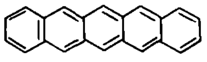
Polycyclic benzenoid hydrocarbons

A large number of carbodications have been generated by the chemical and electrochemical oxidation of polycyclic arenes. This section will deal with ions generated chemically; the electrochemically generated ones will be discussed later.

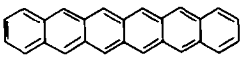
It was noted in 1959 that treatment of naphthacene (**49**) with SO_3 in dimethyl sulfate yielded a mixture of the naphthacene radical cation and dication.[37] The ions $\mathbf{49}^{+\cdot}$ and $\mathbf{49}^{+2}$ were identified by their UV-Vis spectra, the radical cation by comparison to its known absorption spectrum and the dication by its almost identical appearance to the spectrum of naphthacene dianion ($\mathbf{49}^{-2}$). Because of the symmetry characteristics of the π molecular orbitals of alternant hydrocarbons, the electronic spectra for a dication and dianion should be identical.[38] 1,2-Benzanthracene (**51**) also underwent a two electron oxidation to its carbodication $\mathbf{51}^{+2}$ in FSO_3H/SbF_5 and monoprotonation at C-9 and C-10 when treated with FSO_3H.[39] Naphthacene (**49**) behaved similarly, i.e. yielding the carbodication in FSO_3H/SbF_5 and undergoing monoprotonation at C-9 in FSO_3H. All ions were identified by UV-Vis absorption spectroscopy. When solution containing $\mathbf{49}^{+2}$ and $\mathbf{51}^{+2}$ were treated with an unspecified alkane, each was converted into a monoprotonated carbocation by hydride abstraction. This attests to the highly electrophilic nature of the dications. It would be worthwhile to repeat these experiments using NMR spectroscopy for ion identification in order to corroborate these results. Pentacene (**53**) in 96% H_2SO_4 and FSO_3H[40] and hexacene (**54**) in 96% H_2SO_4[41] both yielded the corresponding dication. In both cases the dications had electronic spectra very similar to the corresponding dianion.





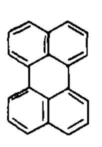


53



54

Brouwer and van Doorn have reported the proton NMR spectra of arene dications generated by treating perylene (**55**), naphthacene (**49**), and anthracene (**56a**) and its 9-chloro (**56b**), 9-bromo (**56c**), 9-methyl (**56d**), 9,10-dimethyl (**56e**), and 2,6-dimethyl (**56f**) derivatives in neat SbF_5 and SbF_5/SO_2ClF.[42] Only perylene (**55**) and naphthacene (**49**) yielded the carbodication in FSO_3H/SbF_5, while the anthracene dication (**56a**$^{+2}$) could also be prepared by treating 9,10-dibromo-9-10-dihydroanthracene with SbF_5. As expected the ring and Me hydrogens were deshielded when compared to the hydrocarbon values. 9,10-Anthroquinone generated a dication in FSO_3H/SbF_5.[43] The highly deshielded 13.8 δ chemical shift of the OH group suggests that this ion is best represented as a diprotonated ketone rather than the delocalized **56g**$^{+2}$.



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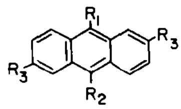
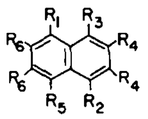


56

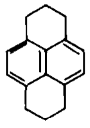
a) $R_1=R_2=R_3=H$
b) $R_1=Cl, R_2=R_3=H$
c) $R_1=Br, R_2=R_3=H$
d) $R_1=CH_3, R_2=R_3=H$
e) $R_1=R_2=CH_3, R_3=H$
f) $R_1=R_2=H, R_3=CH_3$
g) $R_1=R_2=OH, R_3=H$

The proton NMR spectra have also been recorded for the hexamethyl-, heptamethyl-, and octamethylnaphthalene dications, **57a**$^{+2}$, **57b**$^{+2}$ and **57c**$^{+2}$, respectively, in SbF_5/SO_2ClF.[44] The ring and Me hydrogens in the dications are not appreciably lower field than in the naphthalenes themselves. This can be attributed to compensating downfield shifts due to charge and upfield shifts due to the paramagnetic ring current brought about in these antiaromatic ions. The ring carbons on **57c**$^{+2}$, on the other hand, were considerably deshielded compared to its neutral counterpart as expected for a dicationic species. Olah and Streitwieser have recorded the ^{13}C-NMR spectra of 1,4,5,8-tetramethylnaphthalene dication (**57d**$^{+2}$) in SbF_5/SO_2ClF.[45] Surprisingly perhaps, the hexahydropyrene (**58**), which has an identical naphthalene substitution pattern as **57d**, and 1,2,3,4-tetramethylnaphthalene (**57e**) gave broad signals in the same medium, attributable to an equilibration of the paramagnetic radical cation and dication.[45] Of the three mechanisms which seem plausible for the equilibration: (1) disproportionation; $R^{+2}+R \rightleftharpoons 2R^{+\cdot}$; (2) electron transfer, $R^{+}+R^{+2} \rightleftharpoons R^{+2}+R^{+\cdot}$; and (3) electron transfer via an inorganic component X, $R^{+\cdot}+X \rightleftharpoons R^{+2}+X^{-\cdot}$, the disproportionation mechanism seems unlikely in these media as does the electron transfer mechanism. The nonalternant dibenzopyraclene (**59**) was not oxidized to a dication in SbF_5/SO_2ClF.[45] As with 9,10-anthroquinone, 1,4-naphthoquinone yielded in FSO_3H/SbF_5 a dication best represented as a diprotonated diketone.[43]



57

a) $R_1=R_2=H, R_3=R_4=R_5=R_6=CH_3$
b) $R_1=H, R_2=R_3=R_4=R_5=R_6=CH_3$
c) $R_1=R_2=R_3=R_4=R_5=R_6=CH_3$
d) $R_1=R_2=R_3=R_5=CH_3, R_4=R_6=H$
e) $R_1=R_5=R_6=H, R_2=R_3=R_4=CH_3$
f) $R_1=R_2=R_3=R_4=R_5=R_6=H$



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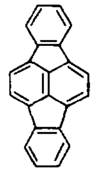
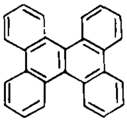


59

In a coup de grace Forsyth and Olah have looked at the behavior of 20 polycyclic benzenoid hydrocarbons in SbF_5/SO_2ClF.[46] They obtained ^{13}C-NMR data on the carbodications of naphthacene (**49**), 1,2-benzanthracene (**51**), pentacene (**53**), perylene (**55**), anthracene (**56a**), and octamethylnaphthalene (**57c**) as well as tetrabenznaphthalene (**60**), 1,2,5,6-dibenzanthracene (**61**), pyrene (**62**), 1,12-benzperylene (**63**), 1,2-benzpyrene (**64**) and 7,12-dimethylbenzanthracene (**65**). In all cases the ring carbon deshieldings were consistent with the observed ion being a carbodication. Picene (**66**) and 1,2,3,4-dibenzanthracene (**67**) yielded ^{13}C-NMR spectra in which the observed resonances were broad and some expected resonances were missing. This can be attributed to the rapid equilibration of the radical cations of **66** and **67** with the corresponding dications. It is interesting to note that, except for **60**, the energy of the highest occupied MO (E_{HOMO}) of both **66** and **67** is larger than for the hydrocarbons which yielded the carbodications readily. Not surprisingly, triphenylene (**68**), naphthalene (**57f**), phenanthrene (**69**), coronene (**70**) and chrysene (**71**), all of which have large E_{HOMO}'s, yielded radical cations exclusively in SbF_5/SO_2ClF (lack of ^{13}C-NMR signals); benzene was protonated to the benzenium ion by trace amounts of acid in the SbF_5.



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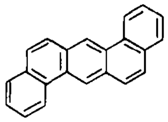

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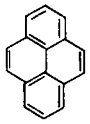

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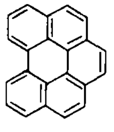

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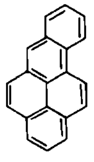

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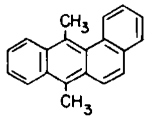

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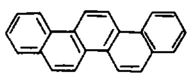

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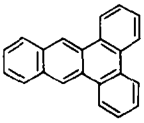

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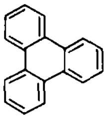

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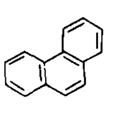

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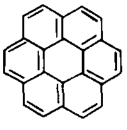

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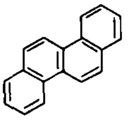
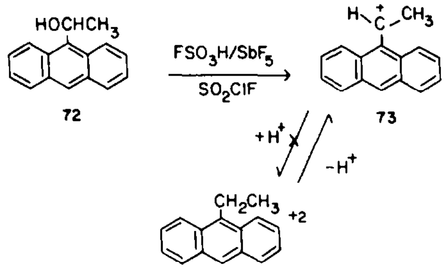


71

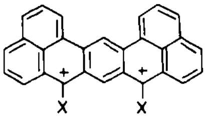
There is another method by which certain arene carbodications can, in principle, be made. If charge repulsion can be overcome, the protonation of a benzyllic cation will yield an alkyl-substituted arene dication. Such an approach has been attempted by Bodoev *et al.*[47] Dissolution of 1-(9-anthryl)ethanol (**72**) in $FSO_3H/SbF_5/SO_2ClF$ at $-90°$ yielded the benzyllic ion **73** which was stable at temperatures up to $-10°$; the carbodication (**74**) was not observed. When the experiment was repeated with FSO_3D, there was deuterium incorporation onto the Me group (via 9-vinylanthracene) and anthracene ring (except at C-10) but not at the cationic center, thus excluding the reversible formation of the dication. When the carbodication **74** was prepared in SbF_5/SO_2ClF and this solution diluted with

FSO_3H/SbF_5, the benzyllic ion **73** was formed irreversibly. Thus deprotonation is favored in this case. Similar experiments with 9,10-dimethylanthracene (**56e**) were unsuccessful, while those with octamethylnaphthalene (**57c**) demonstrated the facility of proton loss from its dication.

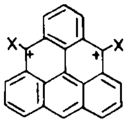


It is useful at this time to stop and consider what ^{1}H- and ^{13}C-NMR spectroscopies tell us about the nature of these polycyclic ions. First of all calculations show that the deshielding observed for ring carbons is dominated by the effect of charge although a small (upfield) effect due to ring currents is predicted.[48–50] Thus, the primary use of ^{13}C-NMR will continue to be, as it has up to now, to demonstrate that the observed species has two (or more) units of positive charge. The Spiesecke–Schneider relationship[20] will continue to be used successfully although, as noted recently,[51] the proportionality constant between chemical shift and charge is highly dependent on the molecular orbital method used. Because the ring current is expected to be small, it will be difficult to assess the antiaromaticity (or aromaticity) of the dications by ^{13}C-NMR spectroscopy alone. Fortunately these questions can be answered by ^{1}H-NMR spectroscopy. By calculating the downfield contribution due to charge alone in the carbodications of anthracene (**56a**),[50,52] tetracene (**49**),[52] 1,2,5,6-dibenzanthracene (**61**),[52] and perylene (**55**),[52] Müllen and Rabinovitz were able to demonstrate the existence of an upfield shift due to a paramagnetic ring current in these species. Thus these dications have antiaromatic character. Rabinovitz was also able, for a series of dications and dianions, to show that the magnitude of the paramagnetic ring current is inversely related to the energy difference of the HOMO and LUMO as predicted by theory.[53]

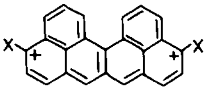
Even alternant non-Kekulé hydrocarbons are ones in which there are an even number of π electrons but in which it is not possible to draw a single Kekulé resonance structure. These systems ordinarily possess two nonbonding MO's in which two π electrons reside. This suggests that it should be relatively easy to prepare stable dications and dianions of these hydrocarbons. This has been borne out in the studies of Murata. He and his coworkers have been able to prepare the hydrocarbon dications **75a**[54] and **77a**[56] as well as the dihydroxy derivatives **75b**,[54] **76b**,[55] and **77b**[56] in D_2SO_4 and record their ^{1}H-NMR spectra; hydrocarbon dication **76a** could not be prepared.[55] As ^{13}C spectra were not recorded for these dications, it was not possible to assess the extent of charge delocalization in the ring systems of the dihydroxyderivatives **75b**, **76b** and **77b**.



75
a) X=H
b) X=OD



76
a) X=H
b) X=OD



77
a) X=H
b) X=OD

Diprotonation of arenes and annulenes

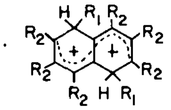
The diprotonation of an arene will in general be difficult because the reaction of the initially formed carbomonocation with a proton will be retarded because of electrostatic repulsion between the reacting particles. Nonetheless, if the acidity of the medium is made sufficiently large and the arene has a sufficient number of suitably placed electron releasing substituents, the charge repulsion can be overcome. As will be seen immediately below for the the diprotonation of arenes and in a later section on the protonation of carbocations, this approach has been successful.

Treatment of hexamethylnaphthalene (**57a**) and octamethylnaphthalene (**57c**) with $FSO_3H/SbF_5/SO_2ClF$ at low temperature yielded the carbodications **78a** and **78b**, respectively, which were characterized in the usual way by ^1H- and ^{13}C-NMR spectroscopy.[57] With the less acidic FSO_3H/SO_2ClF[58] only monoprotonation (at C-1) of these naphthalenes was observed. It is interesting to note that of the fifteen possible modes of diprotonation of naphthalene, only 1,5-addition occurs in these two hydrocarbons. Hückel theory suggest that 1,2- and 2,3-addition would be superior to 1,5.[57] There must be a subtle interplay of electronic, steric and strain effects in these systems to account for 1,5-addition.

Lammerstsma has also observed the diprotonation of an alkylated naphthalene; in this case the tetrasubstituted **58** yielded carbodication **79** in SbF_5/FSO_3H.[59] In FSO_3H, only monoprotonation at the β position was observed.

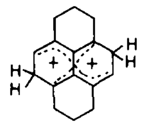
Diprotonation of di- and trimethylnaphthalenes has been observed when the acid is made even stronger still.[60] 2,7-Dimethyl-, 1,5-dimethyl-, and 1,3,5-trimethylnaphthalene in the strong HF/SbF_5[58] diluted with SO_2ClF gave the dications **80**, **81** and **83**, respectively, which were characterized by their NMR properties. As noted before, of the numerous diprotonation patterns which are possible for the naphthalenes, only one was observed in each case. The proton spectra of **81** and **83** were found to be temperature dependent. Analysis of this dependence suggested that the ions were in equilibrium with low concentrations of other dicationic forms. 1,3-Dimethyl- and 2,3-dimethylnaphthalene were not diprotonated in HF/SbF_5.

Another group has also looked at the NMR spectra of 1,5-dimethylnaphthalene in $FSO_3H/SbF_5/SO_2ClF$ and found only monoprotonation of the naphthalene skeleton.[61] This difference in behavior in supposedly the same medium can (perhaps) be explained by noting that diprotonation was observed when less than 30 vol. % of SO_2ClF was used[60] and monoprotonation when 50 vol. % was used,[61] with the ratio of HF to SbF_5 being 1 : 1 in both cases. It's not surprising that the amount of SO_2ClF in the acid medium effects its acidity.



78

a) $R_1=H, R_2=CH_3$
b) $R_1=R_2=CH_3$



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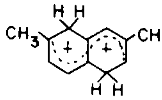

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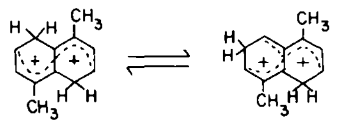
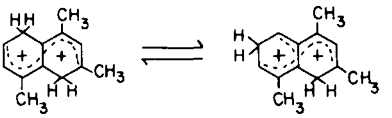
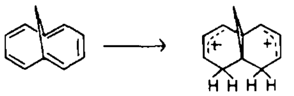


81 82

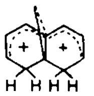


83 84

Another hydrocarbon which has ten π electrons has also been found to undergo diprotonation. On treatment with FSO_3H/SbF_5 in SO_2ClF at −120°, 1,6-methano[10]annulene (**85**) underwent diprotonation to give **86a**.[62] By a careful analysis of the ion's ^1H- and ^{13}C-NMR parameters and comparison to model compounds, the researchers were able to demonstrate that there is considerable charge delocalization into the 3-membered ring and the structure is better represented by the structure **86b**.



85 86a

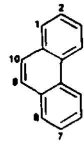


86b

Recently Laali and Cerfontain have protonated a series of phenanthrenes in FSO_3H/SbF_5 (1 : 1) in SO_2ClF/SO_2F_2 at −80°.[63] Phenanthrene (**69**) itself and monomethylderivatives were not diprotonated in this medium but several more highly methylated derivatives were. The results of these experiments are shown below (Table 3).

Table 3. Diprotonation of phenanthrenes

Location of Methyl groups	Location of Diprotonation
1,8	4,5
4,5	1,8
4,5-ethano	1,8
2,4,5,7	1,8
3,4,5,6	1,8 and 1,9

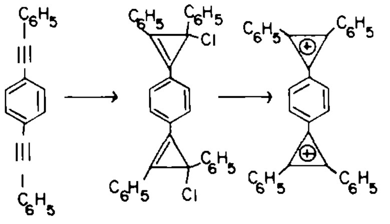


69

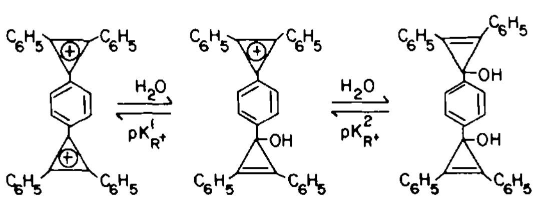
Nonbenzoid systems

There are, of course, a wide variety of aromatic nonbenzoid carbocations known. It would seem reasonable that one could link two or more of these ions together, either directly or through some intermediary such as a benzene ring, to form multiply charged cations. This approach has in fact been successfully applied to generate a wide variety of interesting multiply charged carbocations.

One would expect that methods which have successfully been used in the preparation of monocyclic ions could be extrapolated to carbodications. This was demonstrated to be true in the work of Eicher and Berneth.[64] Treatment of diacetylene **87**, first with phenylchlorocarbene and then with perchloric acid, yielded the carbodication diperchlorate **89**. A notable feature of this work was the determination of $pK^1_{R^+}$ and $pK^2_{R^+}$ (in ethanol water) associated with the reaction of the carbodication with H_2O to form monocation **90** and then with H_2O to form the neutral diol **91**. It is interesting to compare the values of -1.1 and $+3.5$ for $pK^1_{R^+}$ and $pK^2_{R^+}$, respectively, with the $+2.8$ value for the triphenylcyclopropenyl cation. It is slightly easier to ionize the diol **91** to form the monocation **90** than it is to form the triphenylcyclopropenyl cation from its neutral precursor. Ionization to yield the carbodication, however, takes a considerably greater acidity. This can be attributed, in part, to the introduction of a second charge into the system although structural and electronic effect could also be important.

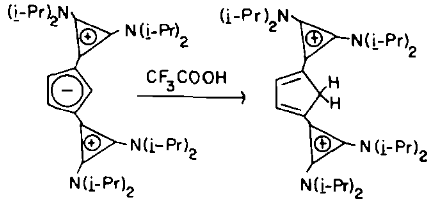


87 **88** **89**

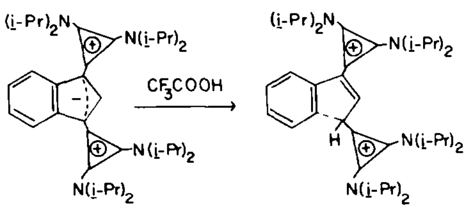


89 **90** **91**

The most widely used and successful method for placing two or more cyclopropenyl cations onto the same molecule involves the reaction of cyclopropenyl cations with anionic components. Yoshida, for example, has prepared the tripolar cations **92** and **94** by reacting the chlorocyclopropenyl cation **99a** with cyclopentadienyl and indenyl anions, respectively.[65] Dissolution of each of the carbocations in trifluoroacetic acid yields the carbodications **93** and **95**. Note that protonation of **92** yielded a fully conjugated carbodication, while protonation of **94** did not. In this latter case, the fully conjugated system would have included the "unstable' isoindene ring system.



92 **93**

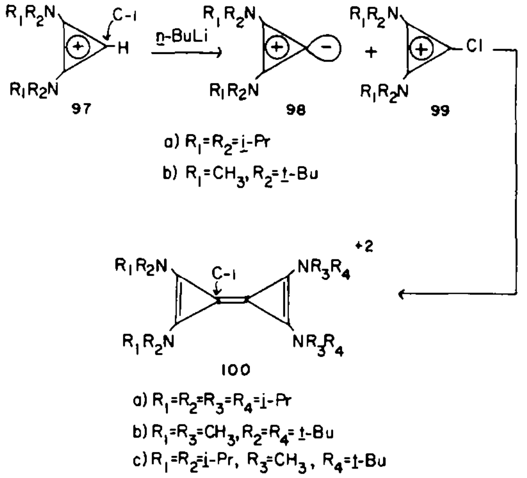


94 **95**

Trifulvalene (**96**) represents an ideal system in which to look for carbodications because Hückel theory predicts the molecule to have two electrons in an antibonding MO.[66] This expectation has been realized. Reaction of cyclopropenyl cation **97a**, first with butyllithium and then with chlorocyclopropenyl cation **99a**, yielded the tetraamino-substituted trifulvalene dication **100a**,[67] which was isolated as an air stable diperchlorate salt; it is also stable in both acidic and neutral solution. On the basis of Raman spectra the dication likely has a planar structure; ^1H and ^{13}C spectra also reveal two isopropyl signals which suggests hindered rotation about the carbon nitrogen bonds due to substantial double bond character in these bonds. The chemical shift of C-1 occurs at the rather unusual 89.6 ppm attesting to an unusual hydribization for this C. By comparison, C-1 of cyclopropenyl ion **97a** occurs at a lower field. Charge repulsion may be responsible for the difference in the C-1 chemical shift of the monocation and dication. Two other trifulvalenes, **100b** and **100c**, have also been prepared in a similar manner.[67]

Weiss and coworkers have also prepared **100a** via an analogous coupling of two cyclopropenyl fragments.[68] Interestingly, when these researchers treated the lithiocarbenoid **98a** with chlorodiphenylcyclopropenyl cation, the carbodication **101** is formed. Here the initially formed trifulvalene reacts with a second molecule of **98a**. In a subsequent publication Weiss and his students were able to prepare the carbotetracation **102** by reacting **98a** with trichlorocyclopropenyl cation.[69] This ion is one of the most highly charged "simple" carbocations prepared to date. ^{13}C-NMR studies on this molecule suggest that the diaminocyclopropenyl cation is as good an electron donor as a dialkylamino group.[69]

96



97

98

99

a) $R_1=R_2=i\text{-}Pr$

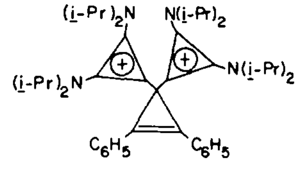
b) $R_1=CH_3, R_2=t\text{-}Bu$

100

a) $R_1=R_2=R_3=R_4=i\text{-}Pr$

b) $R_1=R_3=CH_3, R_2=R_4=t\text{-}Bu$

c) $R_1=R_2=i\text{-}Pr, R_3=CH_3, R_4=t\text{-}Bu$



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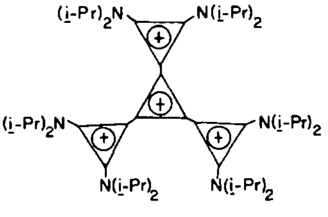
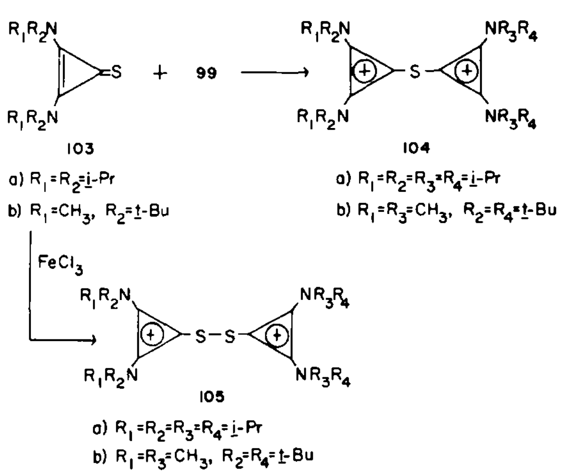


102

Sulfur-bridged dicyclopropenyl dications have been prepared by the reaction of the nucleophilic cyclopropenethiones **103a** and **103b** with the chlorocyclopropenyl cations **99a** and **99b**.[70] Oxidative coupling of the thiones with $FeCl_3$ gave the disulfides **105a** and **105b**. Although these latter dications were stable in acidic and neutral media, they reacted in aqueous bicarbonate to give the thiones and the aminocyclopropenyl cations **97a** and **97b**.[70] The mechanism of this transformation has not yet been investigated.



103

a) $R_1=R_2=i\text{-}Pr$

b) $R_1=CH_3, R_2=t\text{-}Bu$

104

a) $R_1=R_2=R_3=R_4=i\text{-}Pr$

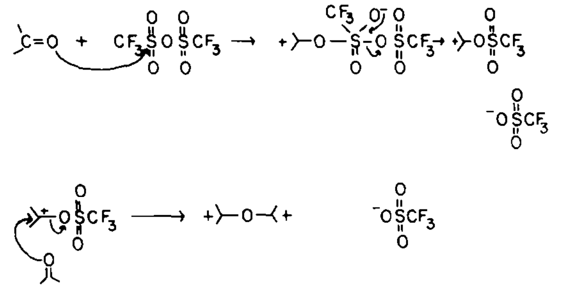
b) $R_1=R_3=CH_3, R_2=R_4=t\text{-}Bu$

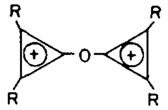
105

a) $R_1=R_2=R_3=R_4=i\text{-}Pr$

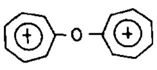
b) $R_1=R_3=CH_3, R_2=R_4=t\text{-}Bu$

Ketones which have highly polarized CO groups react with triflic anhydride in CH_2Cl_2 and CCl_4 to give ether dication salts which precipitate from solution.[71] The overall reaction which must involve two nucleophilic substitutions is facilitated by the high nucleophilic character of the CO group's O atom of cyclopropenones, cycloheptatrienones, annulenones and other "aromatic" ketones studied. These moisture sensitive materials give spectral properties consistent with their dicationic character. Not surprisingly these salts react with nucleophiles such as amines and water. The most reactive salt **106a** reacts even with ethyl ether to give **117**. Surprisingly, mixed dication ether salts could not be prepared by the triflic anhydride procedure.





106
a) R=n-Pr
b) R=C_6H_5
c) R=H



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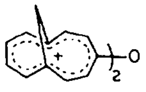

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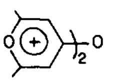

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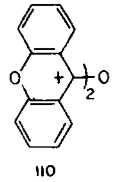

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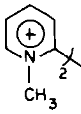

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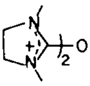

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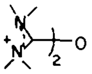

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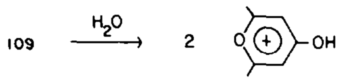

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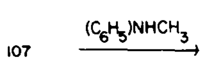

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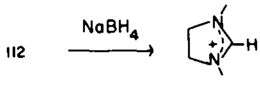

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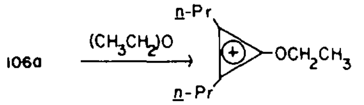
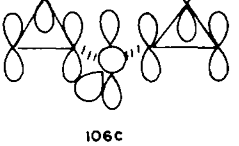
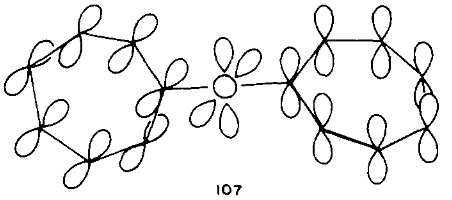


117

What are the structures of these ionic ethers? This was explored by Apeloig and Arad by molecular orbital methods.[72] One can imagine a structure in which the oxygen is bent (sp^2 hydridized) and the molecule planar overall. Here a nonbonding pair of 2p oxygen electrons will be delocalized into both rings; the second sp^2 nonbonding pair will not participate in this delocalization. If the O were bent but the two rings were orthogonal, both lone pairs could participate in conjugation, one pair to each ring. In this case, however, conjugation by the sp^2 pair would be less effective than by the 2p pair. A more effective overlap of orbitals would occur if the oxygen were linearlized, i.e. the O changed from sp^2 to sp hydridization. Here there would be two perpendicular 2p long pairs on O, each pair interacting effectively with one cationic ring. This linearization does not take place without a price, however, and that is the increase in energy associated with changing an sp^2 into a 2p lone pair. Thus there is a balance of effects at play here. Steric effects which may be significant in the planar structure should also not be neglected. The *ab initio* and MINDO/3 calculations suggest that the dicyclopropenyl dication **106c** will prefer to be planar with a bent oxygen, while dicycloheptatrienyl dication **107** will prefer to be perpendicular with a linear oxygen. Small barriers to rotation about carbon oxygen bonds are also predicted in both cases. It would be interesting to see the results of an ^{17}O-NMR study on these ions because it may help resolve the nature of the O atoms in these molecules.

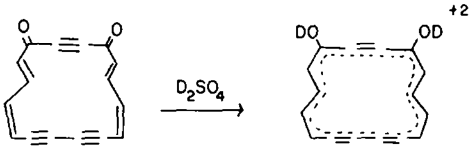


106c

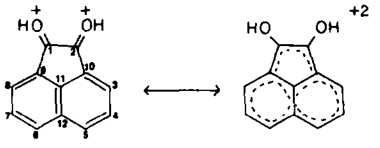


107

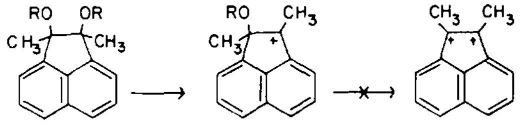
A continuing and perplexing question concerns the nature of the species produced by diprotonation of a cyclic conjugated diketone. Is the species a fully delocalized carbodication or merely a localized diprotonated diketone? In some cases, the answer is clear cut. Dissolution of diketone **118** in D_2SO_4 yielded an aromatic dication because the external vinyl hydrogens are deshielded by approximately 2.5 ppm when compared to the values for the diketone in $CDCl_3$ and the interior hydrogens are shifted upfield by +6.05 ppm.[73] Protonated acenaphthoquinone (**120**), on the other hand, which possesses no interior hydrogens is more difficult to assess. Acenaphthoquinone on protonation in $FSO_3H/SbF_5/SO_2$ yields a dication in which the naphthalene hydrogens are deshielded and the OH hydrogens are not observed.[74] Unlike OH hydrogens of simple localized protonated carbonyl compounds which appear at very low field,[43] phenolic or aromatic type OH hydrogens are ordinarily absent because of rapid exchange with protons in the acid medium. Thus, the absence of this signal suggests that **120b** is the better representation for the dication. This conclusion is also corroborated by ^{13}C chemical shift data: it is found that all the naphthalene ring carbons, except for C-9 and C-10 which are shifted upfield by 5.14 ppm, are shifted downfield, with C-11 by 34.40 ppm compared to its acenaphthoquinone value. C-1 and C-2 are, surprisingly, shifted upfield by 12.60 ppm; this was attributed to an increase in the C-1, C-2 π bond order.[74] Although the dication appears to be a fully delocalized carbodication, the hydroxyl groups still have a large influence in stabilizing the entity. When the dimethylacenaphthalene diol and ether **121** are treated with FSO_3H, FSO_3H/SbF_5 and HF/SbF_5, a monocation is produced, but not a dication.[75] The two Me groups cannot stabilize the acenaphthalene dication as effectively as two OH groups can.



118 119



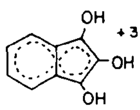
120a 120b



121 122 123

R=H or CH_3

The idea of generating new aromatic systems by the protonation of CO groups is easily extended to triketones. Indanetrione, for example, appears to give a delocalized carbotrication **124** when dissolved in $FSO_3H/SbF_5/SO_2$.[76] This conclusion is based, as in the case of acenaphthoquinone, on the deshielding of benzene hydrogens and lack of OH signal in the proton NMR spectrum of the ion and its ^{13}C-NMR characteristics. It is interesting to note that C-1,3 chemical shift in the ion is higher field than in the neutral precursor. This is attributed to the delocalization of charge over the entire molecule.[76] By way of contrast the C-1, C-3 signals for diprotonated 1,3-indanedione (**125**) are lower field than in the neutral precursor. Thus, a (significant) downfield shift of carbons bearing the O atoms is indicative of localized protonated carbonyls, while a small downfield or upfield shift is indicative of a delocalized aromatic structure. This conclusion is in direct contradiction to that made by Olah for diprotonated benzocyclobutenedione (**26c**) where a small shift was attributed to a localized nonaromatic structure.[25] The significance of the direction and magnitude of these shifts will obviously require further investigation.



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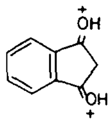
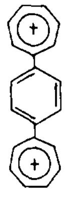


125

Several multiply charged cations containing two or more cycloheptatrienyl rings such as **126** through **129** have been prepared by Murray and Kaplan[77] and others[78] by reaction of the corresponding cycloheptatrienes with an appropriate amount of triphenylmethyl cation. The heptafulvalene dication **131**, which contains two linked 7-membered rings, has been prepared by Vol'pin *et al.* by reactions of dicycloheptatrienyl with an excess of PCl_5 in CCl_4;[79] in addition to **131**, a small amount of $C_7H_7^+$ (**132**) was also formed. When oxidized with H_2SO_4 or Br_2, **130** only yielded the monocyclic $C_7H_7^+$ (**132**). As with trifulvalene dication (**96**), the existence of this dication was anticipated from Hückel MO theory: the planar neutral hydrocarbon is predicted to have two antibonding electrons.[66b] It is questionable, however, whether this ion is planar, because one would expect severe interactions between hydrogens 2 and 2′ and 7 and 7′ in the completely planar form. It is interesting to note that attempts to prepare the carbodication **133** have been unsuccessful.[80]



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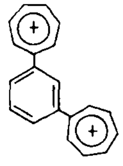

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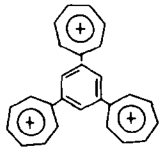

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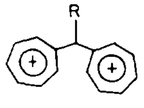
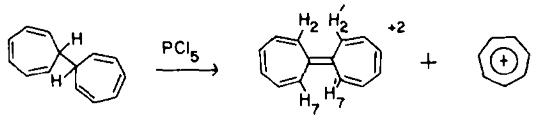


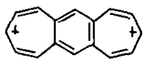
129

a) R=H

b) R=CH$_3$

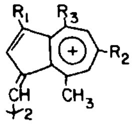


130 131 132



133

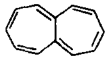
There are a variety of nonalternatant systems which contain fused odd-membered rings and many of these have been incorporated into multiply charged carbocations. The azulenodications **134a** and **134b**, for example, have been prepared by reaction of the corresponding azulene with glyoxal in the presence of acid.[81] When treated with hot methanol, **134b** underwent one electron reduction to give a radical cation;[82] the mechanism of this transformation is obscure.



134

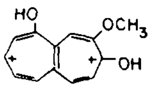
a) R$_1$=CH$_3$, R$_2$=H, R$_3$=i-Pr

b) R$_1$=H, R$_2$=R$_3$=CH$_3$

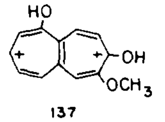


135

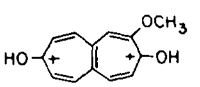
Heptalene (**135**) has Hückel MO characteristics similar to **96** and **131**[66b] and should yield a stable dication; *ab initio* calculations predict this entity to be a bound species.[83] Unfortunately, the parent carbodication has never been prepared.[84] Several heptalene diones are known, however, and they yield carbodications—**136**–**140**—when dissolved in FSO_3H.[85] By way of contrast dione **139** only yields a monocation when dissolved in CF_3COOH;[85b] CF_3COOH, of course, is a much weaker acid than FSO_3H. These ions appear to be dihydroxyheptalene dications because the observed average downfield shift of the ring hydrogens is in agreement with the Spiesecke–Schneider correlation.[20] This agreement may be fortuitous because the calculated charge densities are based on **135**$^{+2}$ and may not apply to these multiply substituted species.



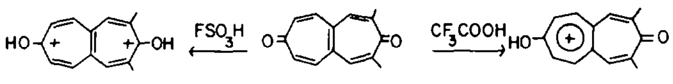
136



137

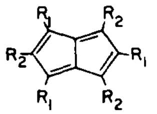


138



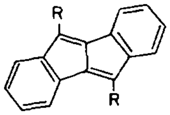
140 139 141

Pentalene (**142a**) is an even nonalternant hydrocarbon possessing a LUMO at $E = 0\beta$.[38] The hydrocarbon, therefore, should easily form a dianion which in fact was demonstrated by Katz.[86] The pentalene dication, on the other hand, is not known. The perchloro analogue **142b** has been reported,[87] but, owing to the lack of hydrogens, its dicationic nature has not been proven. Although pentalenes in general are not stable, 1,3,5-tri-t-butylpentalene (**142c**) is and it has been subjected to an electrochemical study. Anodic oxidation in acetonitrile yielded the stable radical cation, which was characterized by ESR spectroscopy, but not the dication.[88] This failure was attributed to the antiaromatic character of having two fused cyclopentadienyl cations. It is questionable, however, if one can extrapolate the behavior of a monocyclic system to a bicyclic one. Rabinovitz has generated the dibenzopentalene dications **143a** and **143b** by oxidation of the neutral hydrocarbons with SbF_5 in SO_2ClF.[89] The deshielding of the ring carbons of the two species is consistent with their dicationic character. The proton deshielding is larger than expected on the basis of charge alone. This extra deshielding is due to a diamagnetic ring current induced by the aromaticity of the two ions. Thus these pentalene dications, each of which has 14π electrons, are aromatic; this is consistent with a model in which the $4n+2\pi$ electrons exist at the periphery of each hydrocarbon dication. Because these "extended" pentalene dications have been prepared but the parent has not, charge repulsion must be quite significant in the latter, potentially aromatic dication. Attempts to prepare a different dibenzopentalene dication **145**, however, by protonation of the pentalenequinone **144** with FSO_3H failed.[90] Based on a lack of any deshielding by the ring protons and especially on the appearance of the oxygen containing protons at 15.53 ppm,[43] the dication is better formulated as a diprotonated diketone **145b**.



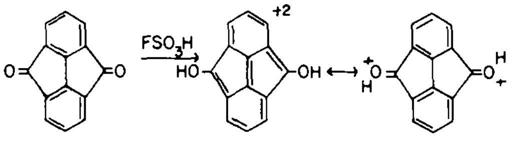
142

a) $R_1=R_2=H$
b) $R_1=R_2=Cl$
c) $R_1=t\text{-}Bu$, $R_2=H$



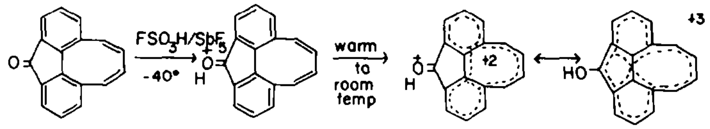
143

a) R=H
b) $R=CH_3$

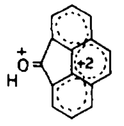


144 145a 145b

If one were to protonate cycloocta[def]fluorenone **146** and then subject this carbocation **147** to two one-electron oxidations, the resulting trication could be envisioned either as a dibenzocyclooctatetraene dication with a localized protonated carbonyl (**148a**) or as a nonalternant cycloocta[def]fluorenyl trication (**148b**).[91] If the former possibility were the true representation, the species might be expected to possess aromatic character. To explore these possibilities, Rabinovitz and Willner have prepared **146** and treated it with $SbF_5/FSO_3H/SO_2$ at $-40°$.[92] This indeed yielded the ion **147** which on warming to room temperature was transformed to a new species characterized as the aromatic **148a**. This conclusion was based on the comparison of ^{13}C- and ^1H-NMR parameters of it to its precursor and model compound **147** and to the protonated dication **149**, a species these researchers expected not to be aromatic ($12\pi e$ over the phenanthrene portion of the molecule). Ion **149**, it should be noted, was prepared in a manner similar to **148**.



146 147 148a 148b

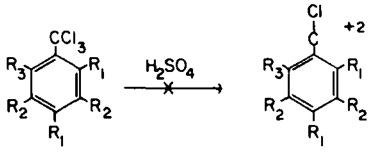


149

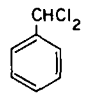
Dications stabilized by aryl substituents

The reaction which more than any other brought the subject of dications to the attention of the general chemical community was Hart's and Fish's reports on the conversion of trichloromethylarenes

150 into aryl chlorocarbene dications **151** in 100% H_2SO_4.[93] These conclusions which were based primarily on freezing point depression data were subsequently shown to be incorrect; no dications are formed in these reactions.[94] When **150a** is treated first with $SbCl_5$ and then with cycloheptatriene, dichloromethylbenzene (**152**) is formed.[95] Again there is no indication from these data for the formation of a dication in $SbCl_5$.



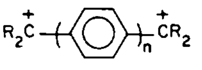
150 151



152

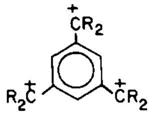
a) $R_1=R_2=R_3=H$
b) $R_1=R_3=CH_3$, $R_2=H$
c) $R_1=R_2=CH_3$, $R_3=H$

A variety of multiply charged cations containing triarylmethyl groups have been synthesized, primarily by ionization of diols with nonaqueous protic acids and halides with strong Lewis acids, and subjected to several interesting studies.[96-101] Several of these ions are shown below. The ease with which these ions are prepared can be attributed to a large degree to their nonplanar structures which aid in reducing charge repulsion.[99]



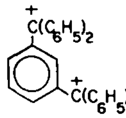
153

a) R = C_6H_5, n = 1
b) R = C_6H_5, n = 2
c) R = C_6H_5, n = 3
d) R = p$CH_3OC_6H_4$, n = 1

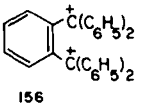


154

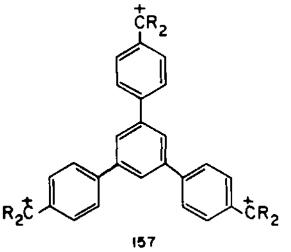
a) R = C_6H_5
b) R = p-biphenylyl



155

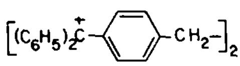


156



157

R = p-biphenylyl



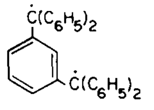
158

Hart and Fish have determined pK_{R+} and pK_{R+2} values for the systems **153a**, **153d**, **155** and **156** in aqueous sulfuric acid.[96] The results (Table 4) indicate that it is more difficult to put the second charge onto the molecule than the first and that having electron releasing substituents on the species of interest lowers the acidity required to generate the mono- and dications. Carbodication **156** is the hardest dication to generate probably because of the close proximity of the two carbon centers which possess most of the two units of charge.

Table 4

System	pK_{R+}	pK_{R+2}
156	—	−16.6
155	−7.9	−9.9
153a	−8.1	−10.5
153d	−3.1	−3.7

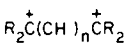
Dication **155** has been reduced electrochemically in an attempt to prepare the theoretically interesting *m*-xylylene biradical **159**; this failed.[100a] Other methods were found, however, to generate the triplet biradical.[100a,102,103]



159

The trityl dications **153a**, **153b** and **153c** undergo four reversible electrochemical reductions in benzonitrile to give ultimately the corresponding dianions.[100d] The resulting redox potentials were used along with calculated ionization potentials to determine the solvation enthalpies of the radical ions, $R^{+\cdot}$ and $R^{\cdot-}$, and diions, R^{+2} and R^{-2}. The results were in good agreement with the predictions of the Born equation, i.e. the positively charged species having the same solvation energy as the corresponding negatively charged ones and the diions having four times the solvation energy of the monoions.

Olah *et al.* have prepared a series of benzhydryl dications **160–164** (R = phenyl or aryl) by ionization of diols or dihalides with SbF_5 in SO_2ClF and characterized them by ^1H- and ^{13}C-NMR spectroscopy.[101] Attempts to prepare the methyl analogues of these species **160–163** (R = Me) and **165** failed. This is undoubtedly a consequence of lack of charge delocalization in the aliphatic dications. Interestingly, ion **166** in which the charges are separated by two methylene units could be prepared and characterized. Interestingly, dication **160c** has also been prepared and isolated as several crystalline salts.[104] In this example, of course, the four dimethylamino groups effectively remove the two positive charges from the adjacent C atoms.



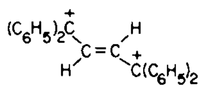
$R_2\overset{+}{C}(CH\ )_n\overset{+}{C}R_2$

160

a) $R = C_6H_5, n = 2$

b) $R = CH_3, n = 1$

c) $R = (CH_3)_2N$, n = 0



161

$R_2C{=}CR_2^{+2}$

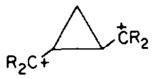
162

a) $R = C_6H_5$

b) $R = p\text{-}CH_3OC_6H_4$

c) $R = p\text{-}(CH_3)_2NC_6H_4$

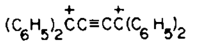
d) $R = CH_3$



163

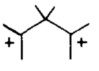
a) $R = C_6H_5$

b) $R = CH_3$

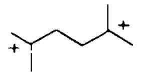


$(C_6H_5)_2\overset{+}{C}C{\equiv}C\overset{+}{C}(C_6H_5)_2$

164



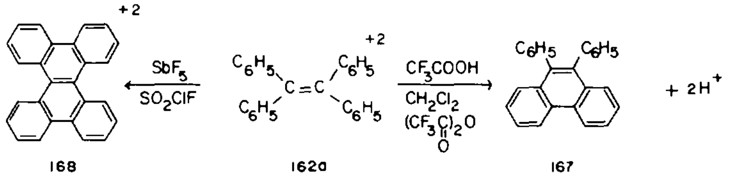
165



166

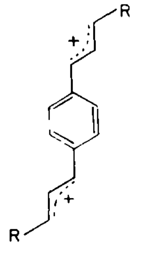
Carbodications **162b**[105] and **162c**[106] have also been synthesized electrochemically by anodic oxidation of the corresponding alkene in a variety of solvents and chemically by oxidation with Ag^+ in the case of **162c**[107] and with I_2/CCl_4 and light in the case of **162b**.[108] Dication **162b** (as its ICl_2^- salt) has been found to be decidedly nonplanar by X-ray crystallography.[108]

The tetraphenylethylene dication (**162a**) is chemically active. When generated electrochemically, it undergoes a first order reaction to give 9,10-diphenylanthracene (**167**).[105a] The activation parameters (E_a = 11.4 kcal/mol; $\Delta S\pm = -6$ cal/K-mol) have been determined for this cyclization.[105b] When generated in SbF_5/SO_2ClF, a series of cyclizations, deprotonations and electron oxidations yield **168** (dication of hydrocarbon **60**) as the observed product.[101]



168 162a 167

Several benzyllic dications are known.[101,109,110] A group of Russian workers, for example, have synthesized a series of diallyl carbodications **169** (R = aryl) and characterized them by a variety of techniques; no NMR data, however, were reported.[109] Olah and his students have synthesized and characterized in their usual way a series of 1,4-carbocations: **170a–170f** and **171a–171b**.[110] As already noted in several cases, when R = H or Me, stable carbodications were not observed. Attempts to prepare **171e** yielded instead the carbodication **172** which arises by a series of 1,2-hydride and methide shifts. Olah also found that the C-2 ^{13}C chemical shift of the aryl substituted norbornane dications correlated nicely with the C-1 ^{13}C chemical shift of aryl substituted cyclopentyl carbocations **173**. Thus one can conclude that there is no unusual interactions between the two charge centers in these dications. Finally, Olah has also prepared and characterized the p-xylylene dication **174**.[101]



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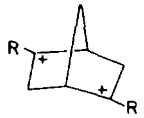
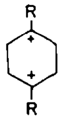


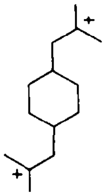
170

a) R=C_6H_5
b) R=4-$CH_3C_6H_4$
c) R=4-$CF_3C_6H_4$
d) R=3,5-$(CF_3)_2C_6H_3$
e) R=C_6F_5
f) R=OH
g) R=H
h) R=CH_3

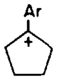


171

a) R=C_6H_5
b) R=4-$CH_3C_6H_4$
c) R=H
d) R=CH_3
e) R=n-Bu



172



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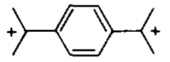
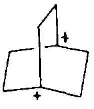


174

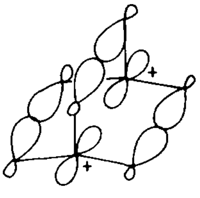
Aliphatic dications

In addition to several examples of purely aliphatic dications already mentioned, two others have been discussed in refereed journals. 1,4-Bicyclo(2.2.2)octane dication (**175**) has been prepared by ionization of the corresponding dichloride in SbF_5/SO_2 at −78° and characterized by its ^{1}H- and ^{13}C-NMR properties.[111] This dication in which the two charge centers are in close proximity is easily formed and remarkably stable, only decomposing slowing at temperatures above −60°. Its remarkable stability has been attributed to hyperconjugative interaction of the two cationic centers with the three bridging carbon carbon bonds.[111] This has the effect of delocalizing the two charges over the entire molecule, thus reducing charge repulsion.

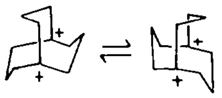
The 1,5-bicyclo(3.3.3)undecane dication (manxyl dication) (**177**) has also been prepared from the corresponding dichloride.[112] This carbodication has a temperature dependent ^{1}H-NMR spectrum which is attributable to the conformational process shown below.[112] Surprisingly, the structurally similar manxyl monocation (**178**) does not have a temperature dependent proton NMR spectrum.[112] Either the ring flipping is very slow here or so rapid that it cannot be retarded at the temperatures at which the NMR spectra were recorded. Also surprisingly, attempts to prepare carbodication **179** have failed.[3,113]



175



176



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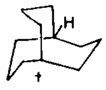

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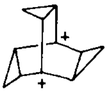
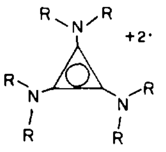


179

Stable radical dications

If a carbocation undergoes a one electron oxidation, a radical dication will be formed. Suitably placed electron releasing substituents should facilitate this oxidation. In fact, anodic oxidation of tris(dimethylamino)cyclopropenyl cation in dimethylformamide or dissolution of the ion in H_2SO_4 yields the stable radical cation **180a**.[114] The ESR spectrum of this paramagnetic species gave $a_H = 8.14$ gauss and $a_N = 7.51$ gauss and, owing to the large number of equivalent nitrogens (3) and hydrogens (18), had a very large spectral width of close to 200 gauss. Subsequently, stable salts of **180a** as well as **180b** and **180c** were prepared by oxidation of the appropriate cyclopropenyl cation with $SbCl_5$.[115] Oxidation with Br_2, NO^+ and NO_2^+ was also effective.[115]



180

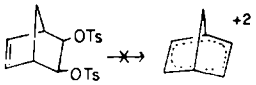
a) $R = CH_3$

b) $R = CH_2CH_3$

c) $R = -CH_2-CH_2-$

Attempted syntheses of bishomocyclobutenium dications

In 1969 Lambert and Holcomb reported their first attempt to prepare a bishomocyclobutenium dication (**182**) by solvolysis of a ditosylate (**181**).[116] The formation of the carbodication would require either the simultaneous departure of both tosyloxy groups or the sequential departure in which the loss of the second group occurs faster than the reaction of the intermediate cation with nucleophiles. The rate of solvolysis of *exo*-2,3-ditosylate **181** was compared to the rate of other unsaturated and saturated ditosylates and monotosylates and found to be faster than expected. One explanation, of course, for this rate acceleration is the formation of the "aromatic" dication, although other explanations such as the formation of a homoallylic monocation by a normal solvolysis are also plausible. These experiments illustrate the difficulty of deriving structural information from kinetic data alone. Subsequent detailed work by Lambert and Holcomb demonstrated that a bishomocyclobutenium dication is not formed in these solvolyses.[117] Later research on the solvolysis of ditosylates ruled out the formation of **183**, **184** and **185** during the course of these reactions.[118–120]



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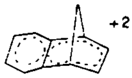

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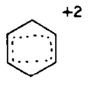

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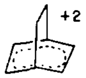


185

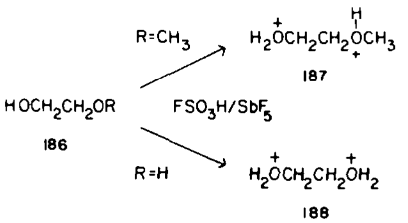
The effect of charge repulsion on the formation and stability of multiply charged cations

It would be remiss not to mention at least briefly other studies on the generation of multiply charged organic cations. Even though many of these reactions don't yield, by my definition, multiply charged carbocations, they present an informative comparison to the ones that do. Of interest is the comparative ease with which the ions are produced and their relative stability. Diols,[121] triols[121] and methoxyalcohols[122] in which the OH and OMe groups are on adjacent carbons are easily protonated at each basic site in $FSO_3H/SbF_5/SO_2$. The charge centers are four atoms removed from one another which is comparable to the closest approach in simple aliphatic carbodications.

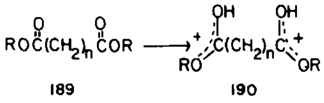
A variety of diacids[123–125] and diesters,[124,126–128] including oxalic acid and diethyl oxalate, are also diprotonated in $FSO_3H/SbF_5/SO_2$, $FSO_3H/SbF_5/SO_2ClF$ and HF/SbF_5. In these cases, each charge is delocalized via resonance over a carboxyl function group, thus stabilizing the ions by charge dispersion. Interestingly several of the diprotonated aliphatic diacids[123] and all three diprotonated benzene dicarboxylic acids[125] dehydrate to give dications which have an acylium ion at one end of the molecule and a protonated carboxylic acid at the other end. In the aliphatic cases, the ease with which the dehydration occurs depends on the number of methylene groups separating the charge centers.[123] When $n = 0$ and 1, no dehydration occurs; when $n = 2$, it occurs reversibly; and, when $n > 2$, it occurs irreversibly. This contrasting behavior must be a consequence of charge repulsion.

Another interesting aspect of multiprotonation was reported by Bruck and Rabinovitz.[128] When they treated a series of aromatic esters in which a benzene ring was substituted with from one to six carbomethoxy groups with $FSO_3H/SbF_5/SO_2$, protonation of the molecules occurred. From proton NMR spectral data, it was concluded that each molecule was protonated on the carbonyl group of each ester linkage. Thus as many as six positive charges (on the hexacarbomethoxybenzene) were placed on one of these molecules.

Di- and triketones,[43,124,126,127,129] methoxyaldehydes,[130] and methoxyketones[121] are also protonated on each CO group in superacid media. 2,3-Butanedione[129] and 2,4-pentanedione[124,127] are diprotonated in $FSO_3H/SbF/SO_2$ and HF/SbF_5, respectively. Replacing one or both methyl groups with CF_3 yields ketones which are only monoprotonated in HF/SbF_5.[124] Perfluoromethyl, not surprisingly, destabilizes the cationic centers.



$HOCH_2CH_2OR$ 186; $H_2\overset{+}{O}CH_2CH_2\overset{+}{O}(H)CH_3$ 187; $H_2\overset{+}{O}CH_2CH_2\overset{+}{O}H_2$ 188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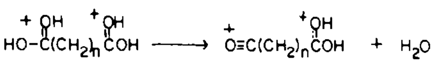
R=H or CH_2CH_3, n≥0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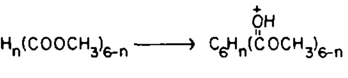
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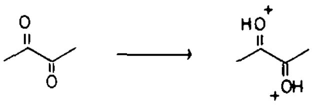
n=0-5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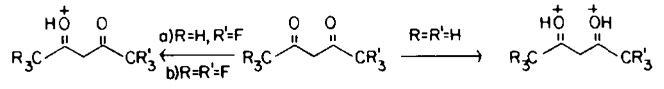
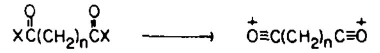


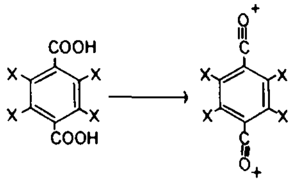
196 197 198

Diacylium ions can be made by ionization of aliphatic dicarboxylic acid fluorides with SbF_5 in $FCCl_2CF_2Cl$[131] and chlorides in 11.5 mol % SbF_5/FSO_3H.[127] A distinctive charge repulsion effect is observed in these reactions. In the former medium only when the number of methylene groups (n) separating the carbonyl fluoride groups is three or greater is the diacylium ion formed.[131] In the latter medium, when n is greater than five, the dication is formed irreversibly, when it's between 3 and 5, an equilibrium concentration of the dication is produced, and lastly, when n is equal to 2, only ionization at one end of molecule is observed.[127] Diacylium ions have also been generated by the reaction of aromatic dicarboxylic acids with SO_3.[132]


199 200

a) X=F

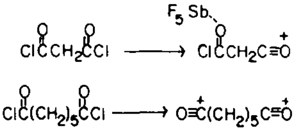
b) X=Cl


201 202

X=Br or Cl

In a very informative paper Larsen and Bouis have reported in detail the heats of reaction associated with the generation of a variety of dications.[127] These ions were also generated independently in a variety of strong acids and at various temperatures and identified by proton NMR spectroscopy. Below are summarized the salient results of this investigation.

The heats of reaction, corrected for heats of solution, have been measured for the ionization of a series of aliphatic diacid chlorides in 11.5% SbF_5 in FSO_3H.[127] When the number of methylene groups separating the two ends of the molecules is five or greater, the diacylium dications are formed exclusively and the heats of reaction are identical. Thus the relative stabilities of these diacrylium ions are identical and charge repulsion effects must be very small in these dications. When the number of methylenes is two or three, the diacylium ions are formed reversibly, in the former case in equilibrium with the monoacylium ion and in the latter in equilibrium with the diacid chloride. When there is only one methylene group between the ends of the molecule, only the monoacylium ion is formed. Quite interestingly, the heat of reaction for generating a diacylium dication is only slightly more exothermic than generating the monoacylium ion. It appears that most of the heat associated with removal of a chloride belongs to the heat of complexation of the SbF_5 with the CO group.



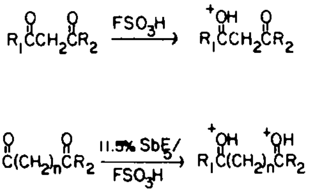
$$ClC(O)CH_2C(O)Cl \longrightarrow ClC(O\cdots SbF_5)CH_2C\equiv\overset{+}{O}$$

$$ClC(O)(CH_2)_5C(O)Cl \longrightarrow O\equiv\overset{+}{C}(CH_2)_5C\equiv\overset{+}{O}$$

ΔH= −35.1±0.5 Kcal/mole

ΔH= −41.2±0.3 Kcal/mole

Larsen and Bouis have protonated a series of diketones in H_2SO_4, FSO_3H, 11.5% SbF_5 in FSO_3H and 1 : 1 SbF_5/FSO_3H in SO_2 (listed in order of increasing acid strength).[127] Not surprisingly, monocations are formed in the weaker acids and dications in the strong ones. Furthermore, in stronger acids dications are favored at low temperatures (−60°) and monocations at higher temperatures (⩾10°). The measured and corrected heats of reactions are quite informative. For example, the heat liberated in diprotonation of a diketone such as 2,5-hexanedione is somewhat less (*ca* 5.5 Kcal/mol) than twice the heat liberated in the protonation of acetone and 2-pentanone. This destabilization of the dications is due to charge repulsion. Another interesting result is obtained by comparison of phenyl and alkyl substituted *β*-diketones. As one would expect on the basis of charge delocalization, mono- and diphenyl *β*-diketones are diprotonated more easily than aliphatic analogues. Surprisingly, mono- and diprotonation of the phenyl ketones liberates less heat than the same reactions of alkyl ketones. Ground state interactions in the phenyl compounds, steric inhibition to solvation and ion size are effects which may explain these unusual results.



$$R_1C(O)CH_2C(O)R_2 \xrightarrow{FSO_3H} R_1C(\overset{+}{O}H)CH_2C(O)R_2$$

$$R_1C(O)(CH_2)_nC(O)R_2 \xrightarrow[FSO_3H]{11.5\%\ SbF_5/} R_1C(\overset{+}{O}H)(CH_2)_nC(\overset{+}{O}H)R_2$$

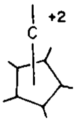
ΔH(Kcal/mole)	
−24.0	$R_1=R_2=CH_3$
−22.2	$R_1=C_6H_5$, $R_2=CH_3$
−18.6	$R_1=R_2=C_6H_5$
−39.2	$R_1=R_2=CH_3$, n=2
−36.4	$R_1=C_6H_5$, $R_2=CH_3$, n=1
−34.7	$R_1=R_2=C_6H_5$, n=1

Diprotonation of diesters is easier to accomplish than of comparable diketones.[127] Charge delocalization is undoubtedly more effective in a carboalkoxy group than in a simple CO group. Measured heats of diprotonation of diesters demonstrate that charge repulsion is negligible when the number of methylene groups separating the ends of the molecule is as low as two. Contrast this to the diacid chloride examples where a minimum of five methylene groups was required to form the diacylium dication. Diprotonation of diesters is less exothermic than diprotonation of comparable diketones. Thus, as noted in the comparison of alkyl and aryl ketones, generation of the most stable ion does not liberate the most heat.

Diethyl fumarate and diethyl maleate are monoprotonated in fluorosulfonic acid and diprotonated in 11.5% SbF_5/FSO_3H.[127] Comparison of their ^1H-NMR spectra and heats of reaction with the saturated analogue, diethyl succinate, demonstrates that the ethylene linkage in the two unsaturated esters has a considerable destabilizing effect.

Pyramidal dications

There has been great excitement in the organic community ever since Hogeveen's and Kwant's initial report on the synthesis and characterization of the polyhedral carbodication, $C_6(CH_3)_6^{+2}$ (**203**).[133a] Unlike organic molecules where polyhedral structures are to date unusual, they are quite common amongst inorganic materials such as boranes—B_5H_9 (**204**), for example—carboranes and metal CO clusters.[134–136] The structures **205a** and **205b**, for example, which are closely related to **203**, have recently been reported.[137]



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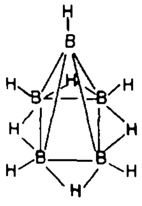

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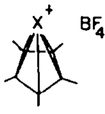
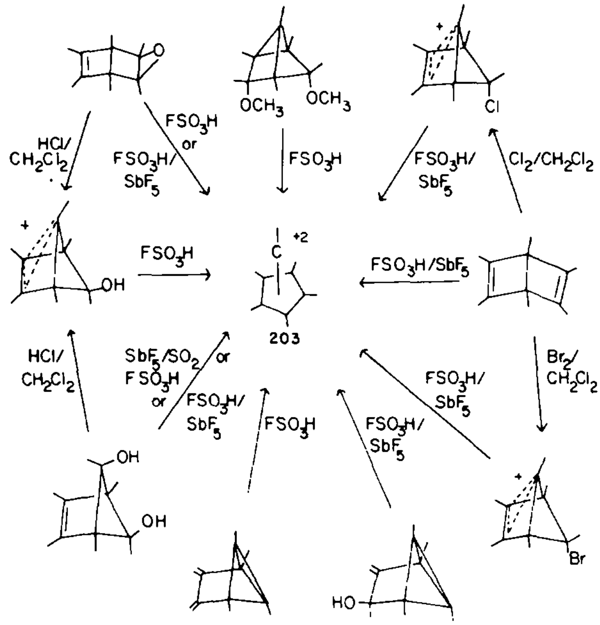


205

a) X=Sn

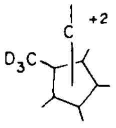
b) X=Ge

The dicationic nature of **203**, which has been generated from an amazing number of precursors,[133,138] is demonstrated by its mode of synthesis. All the precursors are so constituted that they can undergo a sequence of two reactions involving addition of positively charged electrophiles such as H^+ and Cl^+ and/or the loss of nucleophiles such as Cl^-, H_2O and $HOCH_3$. Secondly, when the ion is quenched with $LiAlH_4$, ^-OMe and ^-OH, the isolated products correspond to the addition of two hydrides, methoxides and hydroxides, respectively, to **203**.[133] Finally, when the ion is treated with hydride donors such as isopentane, monocationic products are produced.[133]



Carbodication **203**, which has very simple temperature independent NMR spectra [^{1}H-NMR: δ 2.14 (1 CH_3), 2.83 (5 CH_3); ^{13}C-NMR: 126.4 (5C, 5-membered ring), 22.1 (1C, apical), 10.2 (5 $\underline{C}H_3$), -2.5 (1 $\underline{C}H_3$)],[138] is stable from $-140°$ to $+40°$.[133a] The NMR spectra are consistent either with the nonclassical structure **203** or with a set of equilibrating classical ones with a low energy of activation. Its unusual NMR spectra, notably the carbon resonance at -2.5 δ, its thermal stability, its lack of any significant absorption above 200 nm expected for cyclopropylcarbinyl cations[139] and its lack of carbonylation with pivaloyl cation also expected for a cyclopropylcarbinyl cation[133c] are all consistent with the nonclassical structure. MO calculations are also consistent with this formulation.[140] Furthermore, when generated in deuterated media, very little deuterium is incorporated into the ion's structure as one might expect for a classical ion undergoing deprotonation followed by reprotonation.[133c] It's hard to see how the nonclassical dication could undergo this reaction.

This carbodication has recently been subjected[141] to Saunders' D-induced isotopic perturbation test[1] which distinguishes equilibrating structures from nonclassical ones. Model studies have shown that large splittings of up to 100 ppm in the ^{13}C-NMR spectra are observed for equilibrating classical structures and small splittings of less than 2 ppm for frozen and nonclassical structures. Ions **206** and **207** showed splittings of considerably less than 1 ppm consistent with a nonclassical structure for **203**. The only criticism which one might make with the study, and one acknowledged by the authors of this work, is that the model compounds that Saunders used bear little relationship to the possible structures here.



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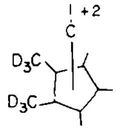
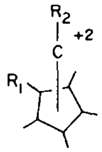


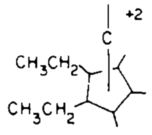
207

Other pyramidal carbodications in which one or two Me groups are replaced by Et or i-Pr have been synthesized[138] by procedures analogous to ones used to prepare the permethyldication **203**. The NMR spectra of these ions are similar to that of **203** implying that they also have nonclassical pyramidal structures.



208

a) $R_1=CH_2CH_3$, $R_2=CH_3$
b) $R_1=CH_3$, $R_2=CH_2CH_3$
c) $R_1=$i-Pr, $R_2=CH_3$
d) $R_1=CH_3$, $R_2=$i-Pr



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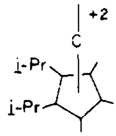
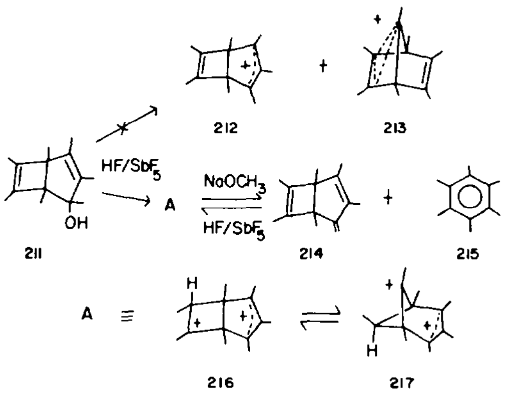
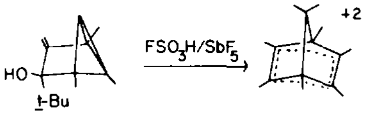


210

Other carbodications are also available from structurally similar starting materials.[142] For example, when alcohol **211** is treated with HF/SbF$_5$ in SO$_2$ClF at $-125°$, an ion which we shall call *A* is formed; *A* is not the carbocations **212** or **213**. Ion *A* gives a broad singlet in its ^{1}H-NMR spectrum at 3.08 δ and resonances at 165.1 δ (singlet) and 21.4 δ (q, J_{CH} = 138 Hz) in its ^{13}C-NMR spectrum. When quenched at $-95°$ with NaOCH$_3$/CH$_3$OH, *A* yields primarily alkene **214**, which regenerates *A* in HF/SbF$_5$, and hexamethylbenzene. Independent synthesis shows *A* not to be the heptamethyltropylium ion and, on the basis of calculated weighted-average chemical shifts, not to be several equilibrating monocations. Further comparisons of the chemical shifts with model compounds demonstrate *A* is likely an equilibrium mixture of **216** and **217**.



Similar experiments by Hogeveen and his group showed that when alcohol **218** is treated with FSO$_3$H/SbF$_5$, ion **219** is formed by a deep seated rearrangement.[142] This bishomoaromatic carbodication, of course, is similar to the ones Lambert attempted to prepare by solvolytic means.[116–120]



218 219

ELECTROCHEMICAL SYNTHESIS OF IONS

General comments

In addition to chemical methods, electrochemical oxidation, i.e. anodic oxidation, represents the second most powerful procedure for the synthesis of multiply charged carbocations. Several syntheses using this technique have already been described in this article. It may surprise many that the electrochemical generation of multiply charged ions is a well developed technique and has been summarized in numerous reviews and books.[143] No attempt will be made to review again this vast amount of work, but several salient features of this work, which should be of interest to the organic chemical community, will be described.

Of the numerous electrochemical techniques which have been developed to generate and study ionic species, cyclic voltammetry and coulometry are the ones most widely used and useful.[143d,j,k] Cyclic voltammetry involves the application of a potential, which is varied linearly in time (10 mV/sec to 10 kV/sec), to a stationery electrode in an unstirred solution.[143j] At a predetermined value, usually before solvent oxidation or reduction, the potential is stopped and then swept in the reverse direction. Thus, species at the electrode surface are oxidized when the potential is swept in one direction and reduced when swept in the other. The oxidation and reduction reactions, of course, are detected by the generation of a current. A cyclic voltammogram then is a plot of current, either cathodic or anodic, versus potential. In plotting the data, it is customary that oxidations are drawn in one direction, usually from right to left, and the subsequent reduction from left to right. Ordinarily, diffusion to and from the vicinity of the electrode is not important in this technique, in fact it is to be avoided, and only species within a fraction of a millimeter of the electrode surface are electroactive.

If a species is oxidized and the resultant radical cation is long-lived, the radical cation will be reduced when the potential is reversed and the resultant oxidation reduction (redox) couple is said to be reversible. Various tests have been developed to elucidate if a redox couple is truly reversible. The reader is referred elsewhere for a discussion of these tests.[143j,144] On the other hand, the radical cation may be unstable and undergo intra- and/or intermolecular reactions. If the rate of reaction is faster than the potential sweep rate, there will be no radical cation in the vicinity of the electrode at the potential required for its reduction and no reduction peak will be observed. Obviously this situation corresponds to an irreversible oxidation. Under these circumstances, the decomposition product(s) may also be oxidized or reduced because they are still in close proximity to the electrode surface. Because the potential sweep rate and temperature can be varied, it may be possible to outrace the decomposition reaction and have radical cation in the neighbourhood of the electrode surface at the potential needed to reduce it. Therefore, it may be possible to turn an irreversible process into a reversible one by increasing the sweep rate and/or lowering the temperature. Kinetic data is potentially also available from this type of experiment.

If one wants to prepare a dication, it stands to reason that the electrogenerated radical cation must be sufficiently long lived so that when the potential for its oxidation is reached, it will be there to react. If the resultant dication is long lived, it will be reduced to the radical cation on the reverse sweep and the radical cation in turn reduced to the neutral substrate. Ideally one will then see two reversible redox couples, the first for $R \underset{-e}{\overset{-e}{\rightleftharpoons}} R^{+\cdot}$ and the second for $R^{+\cdot} \underset{+e}{\overset{-e}{\rightleftharpoons}} R^{+2}$ (Fig. 1). If the couples are truly reversible, the measured potentials have thermodynamic significance and one can calculate, for example, the equilibrium constant for the dispropotionation reaction: $R + R^{+2} \rightleftharpoons 2R^{+\cdot}$.

Solvent selection is extremely important in these experiments. The solvent, of course, should not react with the substrate of interest. If one wanted to oxidize anthracene, for example, but it was protonated irreversibly in the solvent of choice, one would be looking at the electrochemistry of a completely different species. The solvent should be polar in order to dissolve an electrolyte required for good solution conductivity and the solvent should possess low nucleophilicity because the generated

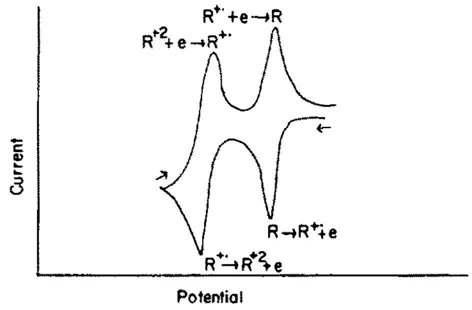
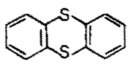


Fig. 1. Cyclic voltammogram of two reversible, one electron oxidations.

radical cations and dications will, in general, be highly reactive with nucleophiles. The solvent must also be electroinactive in the potential region where the radical cations and dications are generated. For these reasons acetonitrile has been found, for example, to be a good electrochemical solvent, while benzene has not.

The electrolyte, the ionic component in solution required for the generation of a current, must also be carefully selected. The ionic compound must be sufficiently soluble in the organic solvent to generate a current, it must be electroinactive in the potential region of interest, and the anion must be poorly nucleophilic so as not to react with the generated radical cations and dications. Tetra-n-butylammonium perchlorate, hexafluorophosphate and tetrafluoroborate have all been used successfully as electrolytes in anodic oxidation experiments.

Residual impurities such as water have a disasterous effect on these experiments for two reasons. Firstly, radical cations and dications are highly reactive with water. If one is attempting to generate a dication, but the radical cation reacts with water, the dication cannot be prepared. Even if the dication can be prepared but it reacts rapidly with water, a reversible oxidation reduction couple cannot be obtained. Secondly, one is dealing with low concentrations of substrate and even lower concentrations of generated ions. Even very low concentrations of nucleophilic impurities will destroy electrogenerated ions. In a remarkable breakthrough Hammerich and Parker have shown that addition of active neutral alumina to the electrolyte solution removes these impurities and leads to well behaved cyclic voltammograms.[145] These workers found reversible one and two electron oxidations for **220**, **221** and **222** in several solvents including CH_3CN and CH_2Cl_2. The use of trifluoroacetic acid and trifluoroacetic anhydride in CH_2Cl_2 has also proven effective in removing solvent impurities.[145]



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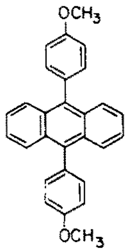

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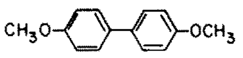
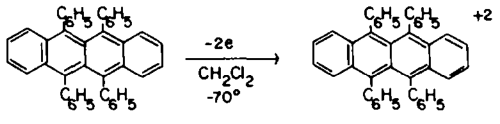


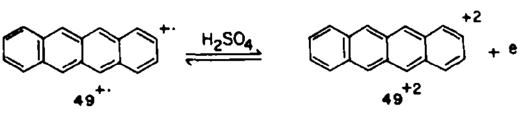
222

In a coulometry experiment exhaustive electrolysis is carried at a constant potential. It is possible to generate via this technique sufficient product for isolation and characterization, although the presence of the electrolyte sometimes makes isolation difficult to accomplish. The time scale in the coulometric experiment is much longer than for the cyclic voltammetric experiment. Ions that are long-lived on the cyclic voltammetry time scale may be far too short-lived to survive exhaustive electrolysis. Radical cations and dications must have essentially infinite lifetimes to survive these conditions. In addition to generating large amounts of product by coulometry, one can also determine the n value, which is the ratio of the Faradays of electricity generated per mol of reactant consumed. This quantity is helpful in elucidating the nature of the electrochemical product. For example, if one were performing the experiment at a potential where a radical cation is formed and it is stable, n = 1 is expected; if a dication is formed and it is stable, n = 2 is expected. If the ionic products react, however, other n values are possible depending on the electrochemical activities of the products.

Below are shown several representative electrochemical reactions known to generate carbodications. The success of these experiments depended on the same factors which were important in the chemical synthesis of carbodications, i.e. proper selection of solvent, reaction conditions and substrate.



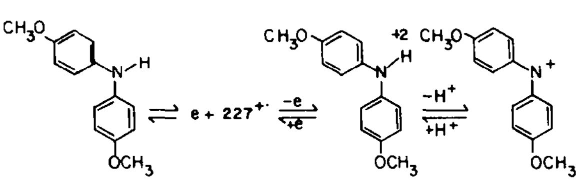
223 224



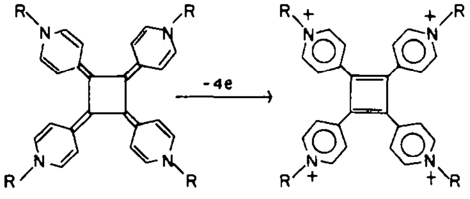
$49^{+\cdot}$ 49^{+2}

$(C_6H_5)_3C^+ \underset{+e}{\overset{-e}{\rightleftharpoons}} (C_6H_5)_3C^{+2\cdot} + e$

225 226

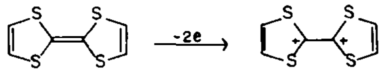


227 228 229

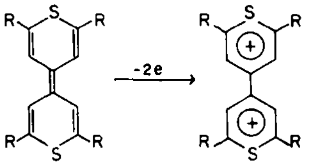


230 231

$R = CO_2C_2H_5$

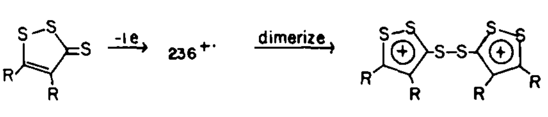


232 233



234 235

a) R=H
b) $R=C_6H_5$
c) $R=CH_3$



236 237

$R = p\text{-}CH_3OC_6H_5$

Rubrene (**223**), a molecule with an extended π system and four stabilizing phenyl substituents, yielded the carbodication **224** when subjected to cyclic voltametry at −70° in CH_2Cl_2.[146] Lowering the temperature suppressed competing and undesirable nucleophilic reactions.[146]

The experiment need not begin with an uncharged substrate. Naphthacene (**49**), for example, on dissolution in sulfuric acid yielded the radical cation $\mathbf{49}^{+\cdot}$. When this species is oxidized electrochemically, the radical cation yielded the carbodication $\mathbf{49}^{+2}$ reversibly.[147] Sulfuric acid in this experiment not only served as an oxidizing agent to generate $49^{+\cdot}$ but also as a nonnucleophilic medium necessary to stabilize $\mathbf{49}^{+2}$. The trityl cation (**225**) in this medium generated the interesting trityl radical dication (**226**) reversibly.[147]

Interesting species other than multiply charged carbodications can be generated in these experiments. Cyclic voltammetry of di-*p*-anisylamine (**227**) in CH_2Cl_2/Al_2O_3 generated the amine dication **228** in two reversible steps.[148] The dication in turn lost a proton reversibly to give the di-*p*-anisylnitrenium ion (**229**) which has a lifetime of approximately 1 second at room temperature in this medium.[148] Although not explored in this work, it should be possible to estimate the pKa of the amine dication **228** by suitable electrochemical experiments.

In a similar vein, a stable "cyclobutadiene" was prepared electrochemically.[149] Radialene **230** underwent four reversible one electron oxidations to yield the antiaromatic species **231**.[149] Presumably the driving force for each of the four oxidations is the formation of an aromatic pyridinium ion. Although this work is certainly interesting, it is questionable whether these N-stabilized ions should be called carbocations.

Sulfur-stabilized carbocations such as the tetrathiofulvalene dication **233** are very common and have been prepared frequently by anodic oxidation of the neutral species.[143c,f] Se and Te analogues are also known.[143c,f] The interest in tetrathiofulvalenes and Se and Te analogues and their electrochemistry stems in part from their use in the synthesis of organic superconductors.[150]

Many other sulfur stabilized multiply charged cations are known. Take, for instance, the aromatic dithiopyrilium dications **235a**–**235c** which have all been prepared electrochemically.[151] The parent **235a** has also been prepared by a more traditional route.[152]

Dications have also been prepared by the dimerization of radical cations i.e. $2R^{+\cdot} \rightarrow R-R^{+2}$. The conversion of **103** into the dication **105** using iron trichloride undoubtedly proceeded in this fashion. Likewise, anodic oxidation of the monomeric thione **236**, which produced the dication **237**, certainly occurred by dimerization of the radical cation $\mathbf{236}^{+\cdot}$.[153]

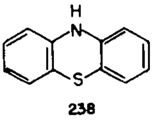
The above examples hopefully give a flavour of how electrochemistry can be useful in the study of multiply charged cations. The sections which follow will explore several additional topics in somewhat more detail.

Electrochemistry in liquid sulfur dioxide

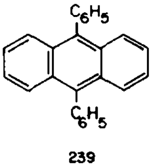
In a recent development Tinker and Bard have found liquid SO_2 to be an excellent solvent for making, electrochemically, stable solutions of radical cations and dications.[154] The molecules studied in their original publication were thianthrene (**220**), phenothiazine (**238**), and 9,10-diphenylanthracene (**239**).[154]

It is perhaps surprising that researchers had not, prior to this work, used SO_2 as an electrochemical solvent because the medium has several desirable properties. Because SO_2 boils at −10°, all experiments must be performed below this temperature, thus suppressing reactions of the electrogenerated species with the solvent and any impurities present. The medium has a reasonable dielectric constant, is poorly nucleophilic and solubilizes a great many organic compounds. Furthermore, being a gas at room temperature, it is easy to manipulate and easy to remove if it is desired to isolate a product.

The behavior of **220**, **238** and **239** in liquid SO_2 was similar. Thianthrene (Th) (**220**), for example, at −40° gave two reversible waves by cyclic voltammetry. The 0.58 V potential difference between the two redox couples yielded a value of 4.4×10^{-12} for the equilibrium (disproportionation) constant for the reaction: $2Th^{+\cdot} \rightleftharpoons Th^{+2} + Th$. In a solution originally containing only $Th^{+\cdot}$, the amount of dication Th^{+2} and neutral Th is exceedingly low. Controlled potential coulometry at a voltage sufficient to form $Th^{+\cdot}$ but not sufficient to form Th^{+2} yielded an n value of 0.99, as expected. Voltammetric reduction of this solution demonstrated that $Th^{+\cdot}$ is stable for several hours. Coulometry at a voltage where Th^{+2} is formed yielded an n value of 1.98. The solution of Th^{+2} formed in this way is stable for at least 2 hr. Experiments with phenothiazine (**238**) demonstrated that it yielded stable solutions of the radical cation and dication in liquid SO_2. 9,10-Diphenylanthracene (**239**) underwent two reversible one electron oxidations when studied by cyclic voltammetry. The dication was found, however, not to be stable on the coulometric time scale.



238



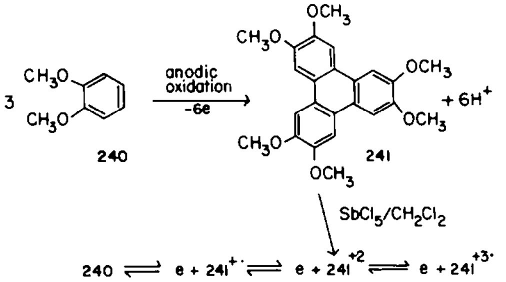
239

Oxidation of methoxy substituted aromatics

Generation of a dication possessing a triplet ground state. Parker and his students have studied extensively the electrochemistry of aromatic compounds with OMe substituents,[26,105,155] because the molecules are good candidates for the synthesis of stable carbodications. One of Parker's more interesting studies in this area involved the anodic oxidation of veratrole (**240**) and the hexamethoxytriphenylene **241**.[156]

Cyclic voltammetric studies of veratrole (**240**) in CH_2Cl_2 containing 10% trifluoroacetic acid demonstrated that the molecule underwent an unusual oxidative trimerization to give the triphenylene **241**. This species (**241**) when subjected to cyclic voltammetry in trifluoroacetic acid at room temperature underwent two one electron oxidations to give the triphenylene dication $\mathbf{241}^{+2}$. When the cyclic voltammetry was carried out on the electron rich **241** at −70° in a 1 : 1 mixture of trifluoroacetic acid and fluorosulfonic acid, a third (reversible) oxidation was observed, corresponding to the generation of the radical trications $\mathbf{241}^{+3\cdot}$. The low temperature, the weakly nucleophilic solvent and the presence of six electron releasing methoxy groups were undoubtedly significant in stabilizing the carbotrication. It would be interesting to see if this trication could also be prepared chemically in a superacid medium.

The MO's of triphenylene are such that removal of two π electrons from the highest occupied orbitals should yield a dication possessing a triplet ground state.[38] Although the prediction has never been verified for the parent substrate, it has for the triphenylene **241**.[156] Dissolution of this compound in the oxidizing medium $SbCl_5/CH_2Cl_2$ at an unspecified low temperature and cooling to −196° yielded a frozen solution giving an ESR spectrum characteristic of a triplet with $D = 0.038\ \text{cm}^{-1}$ and $E \sim 0\ \text{cm}^{-1}$. The D value is similar to that observed for the triplet state of the triphenylene dianion[157] and an E value of zero is expected for a species having trigonal symmetry. As no temperature dependent studies were reported, it is not known whether the triplet is the ground state of the molecule.

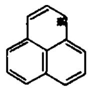


Multistage redox systems

Electrochemical techniques are not only well suited for the synthesis of cationic species in polar solvent but also the corresponding anionic species in the same medium. These multistage redox reactions can rarely be done using traditional chemical reagents. One reason for this difference lies, of course, in the short time scales associated with electrochemical techniques. Much of this work has been summarized in Deuchert's and Hünig's review article on multistage redox systems.[143i]

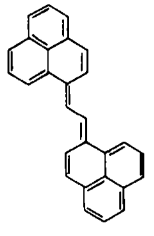
Polycyclic aromatic hydrocarbons are excellent candidates for multistage redox behavior because they possess high lying highest occupied molecular orbitals required for the easy oxidation of the molecule and low lying unoccupied molecular orbitals required for easy reduction. The phenalenyl ring system (**242**) is particularly well suited for this purpose because it has a nonbonding MO;[38] the cation, radical and anion should all be easy to generate and be stable because of extensive delocalization of the positive or negative charge or the odd electron. This has been amply demonstrated.[158] If one were to link two of these units together in the proper fashion, it should be possible to generate a dication and a dianion, all connected through four one electron redox steps. Murata and his students have recently prepared hydrocarbon **243**, which does possess two phenalenyl fragments, and have shown that the hydrocarbon undergoes four redox reactions in dimethylformamide,[159] yielding in the extremes a dication and a dianion. A notable finding of this study was the low oxidation and reduction potentials of **243**, which are attributable to the exceptional ability of the phenalenyl system to stabilize its three oxidation states. The cumulene analogue **244** also behaved similarly to **243**.[160]

When **243** and **244** are treated separately with molten $NaCl/AlCl_3$, they are converted into pentaleno[1,2,3-cd : 4,5,6-c'd']diphenalene (**245**) in low yield.[161] When treated with H_2SO_4, this nonbenzenoid aromatic hydrocarbon is converted into the carbodication **246** which contains two insulated phenalenyl carbocation units. When subjected to cyclic voltammetry in dimethylformamide at −50°, **245** underwent oxidation to a dication and reduction to dianion similar to that already noted for **243** and **244**. Note that the diionic species $\mathbf{245}^{+2}$ and $\mathbf{245}^{-2}$ can be pictured as having two phenalenyl units linked together by a double bond.

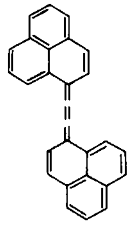


242

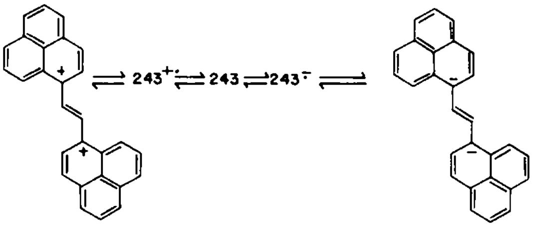
* = +, −, or ·



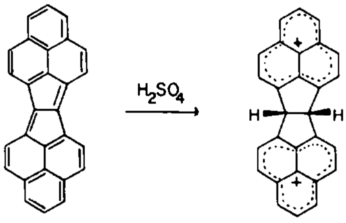
243



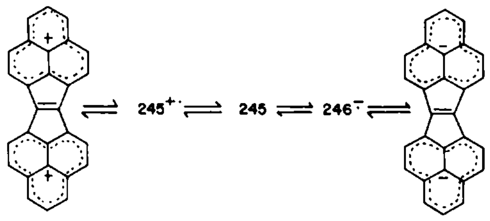
244



243^{+2} 243^{-2}

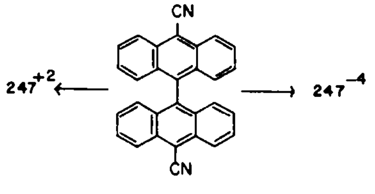


245 246



245^{+2} 245^{-2}

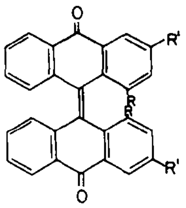
The above phenalenes all undergo a total of four one-electron oxidations. A molecule is known which undergoes a remarkable six one-electron oxidations. Cyclic voltammetric studies of 10,10′-dicyano-9,9′-bianthryl (**247**) in "super pure" propionitrile demonstrated that the molecule undergoes four reversible reductions to yield a tetraanion and two reversible oxidations to give a carbodication.[162] A third oxidation wave was observed but it was irreversible, and the formation of the trication radical was not investigated further. One can attribute the large number of redox steps to the fact that **247** consists of two weakly interacting anthracene units, each of which can hold either one positive charge or two negative charges. As charge builds up in the molecule, additional twisting of the rings will help to relieve charge repulsion. Careful consideration of the redox potentials demonstrated that twisting is substantial in the carbodication.[162]



247

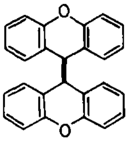
Some molecules structurally similar to **247** exist in two stable conformational forms. Bianthrone (**248a**), for example, exists in a stable form *A* in which each anthrone ring is folded, one up and one down.[163] When the *A* form of **248a** is heated, it is converted into the thermodynamically less stable form *B* in which each anthrone ring is planar but the rings are twisted from one another about the 9,9′ bond.

Because **248a** can exist as two conformation isomers (conformers), this can lead to interesting electrochemistry of the substrate because the rate of conversion of one conformer into the other will depend on the oxidation state of the electrogenerated species. It is possible to investigate the chemical behavior of neutral and charged entities that cannot be made any other way.



248

a) R=R'=H
b) R=CH_3, R'=H
c) R=H, R'=CH_3
d) R=H, R'=OCH_3



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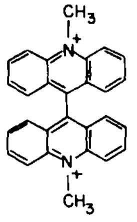
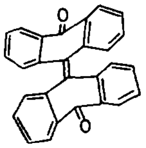
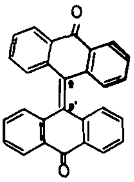


250



248a
Form A



248a
Form B

When bianthrone (**248a**) in its stable *A* form is subjected to cyclic voltammetry in benzonitrile at 21°, it undergoes an irreversible two electron reduction to give the dianion of form *B*, i.e. B^{-2}.[163] Clearly at the dianion stage conformer *B* is more stable than *A*. If the potential is now swept in the opposite direction, B^{-2} is oxidized in two one electron steps to give neutral *B*. At this point, of course, *B* being less stable than form *A* is converted back into *A*. If the potential sweep rate is made fast enough, however, the conversion of *B* into *A* can be outraced and the reduction of *B* into $B^{-\cdot}$ and B^{-2} or the reversible one electron oxidation of *B* into $B^{+\cdot}$ and then B^{+2} can be observed. Similar behavior was also observed for 1,1'-dimethylbianthrone (**248b**), 3,3'-dimethylbianthrone (**248c**) and 3,3-dimethoxybianthrone (**248d**). Dixanthylene (**249**) behaved similarly but, owing to the very rapid conversion of its *B* form into its *A* form, cyclic voltammetry was performed at −94°.

Behavior of bianthrone

$$A \rightarrow B^{-2}$$

$$B^{-2} \rightleftharpoons B^{-\cdot} + e$$

$$B^{-\cdot} \rightleftharpoons B + e$$

$$B \rightarrow A$$

$$B \rightleftharpoons B^{+\cdot} + e$$

$$B^{+} \rightleftharpoons B^{+2} + e.$$

For molecules **248a**, **248b** and **248c** it was also possible to enter the conformer *B* manifold by oxidation of the stable *A* form into B^{+2}, although products other than B^{+2} were produced in the oxidation.[163] Only with the methoxy substituted **248d** was the dication B^{+2} formed cleanly.

Lucigenin (**250**) is a stable dication existing exclusively in a conformer of type *B*. On reduction, lucigenin (**250**), i.e. B^{+2}, is first reduced to $B^{+\cdot}$ and then to *B* where it is converted into the more stable conformer *A* at rate 100 times greater than for the same interconversion in the bianthrone reaction.[164] By performing cyclic voltammetric experiments at −14° in dimethylformamide it was possible to detect the reversible one electron reductions of *B* to $B^{-\cdot}$ and B^{-2}, although the reduction and oxidation peaks of conformer A are prominent and the oxidation peak for $B \rightarrow B^{+2} + 2e$ barely detectable.[164] At this temperature the conversion of B into A is still sufficiently rapid for A to be detected electrochemically. When the experiment was run at $-60°$, however, the peaks associated with conformer A are almost completely suppressed and the oxidation peak for $B \rightarrow B^{+2}$ is significant.

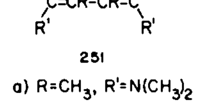
Behavior of lucigenin

$$B^{+2} \xrightarrow{+2e} B$$
$$B \rightarrow A$$
$$B + e \rightleftharpoons B^{\cdot-}$$
$$B^{\cdot-} + e \rightleftharpoons B^{-2}$$
$$A \rightarrow A^{-2}.$$

Disproportionation constants

Simple Hückel theory suggests that the energy required to remove a π electron from an aromatic hydrocarbon, i.e. the energy for $R \rightarrow R^{+\cdot} + e$, will be identical to energy required to remove an electron from its radical cation to form a carbodication. Hückel theory, as is well known, neglects electron electron charge repulsion which will be approximately five electron volts in this case. Thus removal of the first electron alleviates electron repulsion between the two electron in the highest occupied MO that will not exist when the second electron is removed. One can conclude from this analysis that the second ionization potential will be higher in energy than the first, and this has been amply demonstrated in the gas phase (Table 1). Of course, the MO energies and the geometry of the radical cation (and carbodication) may be different than for the neutral species. This will also have the effect of making the two ionization potentials different from one another.

In solution, the same trend is ordinarily observed, i.e. the second oxidation potential being larger than the first. In many cases, however, removal of the second electron is not much more energetic than removal of the first.[143i,j,k] It is even found occasionally that removal of the second electron occurs more easily than removal of the first.[165] This has been demonstrated for compounds **251a** and **251b**.[165] Cyclic voltammetry on the butadiene **251a** in acetonitrile, for example, showed that the molecule underwent a single, reversible, two-electron oxidation; butadiene **251b** behaved similarly. When **251a** was oxidized coulometrically until one electron per molecule had been removed, the solution yielded no ESR signal for the expected radical cation indicating that once formed the radical cation had completely disproportionated into **251a** and its dication **251a**$^{+2}$. When **251b** was subjected in a like manner, only 10% of the anticipated ESR signal of the radical cation was observed. Under the assumption that 10^{-6} M of **251a**$^{+\cdot}$ could be detected by ESR, the oxidation potential for **251a**$^{+\cdot}$ $\rightarrow$ **251a**$^{+2}$ $+ e$ was estimated to be at least 0.24 V less than for **251a** $\rightarrow$ **251a**$^{+\cdot} + e$; for **251b**, the second oxidation potential was estimated to be 0.08 V less than the first, From these numbers, it is possible to calculate the numerical value of the disproportion constant for the reaction $2R^{+\cdot} \rightleftharpoons R + R^{+2}$ (Table 5). The ability of the four dimethylamino groups in **251a** and **251b** to stabilize the unit charges in the cationic states is clearly responsible for explaining these results.



251

a) $R = CH_3$, $R' = N(CH_3)_2$
b) $R = H$, $R' = N(CH_3)_2$
c) $R = H$, $R' = CH_3$
d) $R = H$, $R' = C_6H_5$

Structural factors in some cases are important in determining the relative values of the first and second oxidation potentials as reflected in their disproportionation equilibrium constants. Consider the conjugated dienes **252** which have been studied in detail by Hünig and his students.[143i] In the molecules where $R = H$, as the number of ethylene units separating the six membered rings increases, K_{dis} also increases (Table 6). One explanation for this trend is as follows: As the size of the radical cation increases, its positive charge is dispersed over a larger area; as a result coulombic repulsion associated

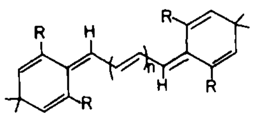
Table 5. K_{dis} values for butadienes

Compound	K_{dis}
251a	$>10^4$
251b	25
251c	9.1×10^{-4}
251d	1.9×10^{-4}

Table 6. K_{dis} values for polyenes

		K_{dis}	
Compound	n	R = H	R = CH_3
252	1	3.3×10^{-9}	4.0×10^{-2}
252	2	4.0×10^{-6}	1.2×10^{-2}
252	3	5.0×10^{-4}	7.1×10^{-3}
252	4	5.0×10^{-2}	0.25

with bringing together two radical cations will be reduced, thus facilitating the disproportionation reaction. Interestingly, this trend is not observed for those molecules where there are methyl groups on the six membered rings (**252**, R = CH_3). Noteworthy, though, are the consistently larger K_{dis} values for the molecules which have these Me groups.



252

Disproportionation constants have also been determined by Parker *et al.* for compounds **220**, **221** and **222** in a wide variety of solvents.[145] Solvent has a profound effect on these equilibria (Table 7); the K_{dis} values vary by 38,000 for **220**, for example. The first oxidation potentials were found not to be very solvent dependent which means that the disproportionation equilibria (K_{dis}) are largely determined by the much more variable second oxidation potentials. Thus changes in solvation in going from the neutral molecule to the radical cation are relatively unimportant, while they are much more so for the reactions forming the dications. Ion pairing which should be more significant in the higher charged dications may also contribute to these results.

Reactions of electrochemically generated carbodications

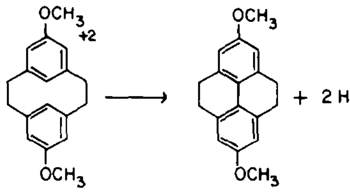
In most cases the method by which a multiply charged carbodication is prepared will have little bearing on its chemical fate. Nonetheless several reactions are associated with electrochemistry (and electrochemists) and some of these will be discussed in this section. In a previous section the cyclization of the electrochemically generated tetraphenylethylene dication (**162a**) was described.[105] Several other typical reactions are summarized below. The reader is referred to the indicated references for more details.

Table 7. Solvent effects on K_{dis}

	Compound		
Solvent	**220** ($K_{dis} \times 10^{12}$)	**221** ($K_{dis} \times 10^{6}$)	**222** ($K_{dis} \times 10^{7}$)
CH_3CN*	2.3×10^3	1.9×10^2	2.7×10^2
CH_3CH_2CN*	1.0×10^4	6.0×10^2	2.7×10^2
$(CH_3)_2CHCN$*	7.6×10^4	1.9×10^3	1.8×10^2
C_6H_5CN*	4.9×10^3	1.3×10^2	5.6×10^1
CH_3NO_2*	1.0×10^3	4.1×10^2	1.2×10^2
$C_6H_5NO_2$*	2.3×10^3	3.9×10^1	1.7×10^1
CH_2Cl_2*	3.3×10^3	8.2	5.4
$CH_2Cl_2/CF_3COOH/(CF_3\overset{\overset{O}{\|}}{C})_2O$ (45:1:5)	68	3.8	1.1
$CF_3COOH/(CF_3\overset{\overset{O}{\|}}{C})_2O$ (9:1)	2	2.5	1.1

* In the presence of suspended alumina.

Cyclization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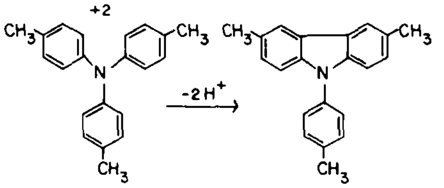
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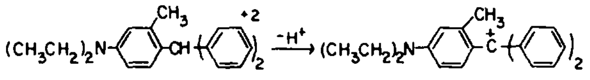
Deprotonation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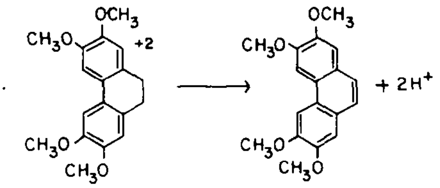
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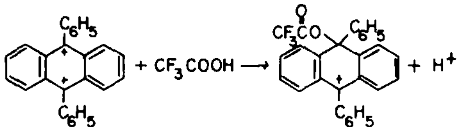
Reaction with a nucleophile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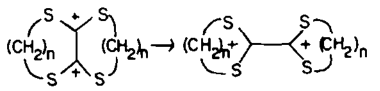
Pericyclic reaction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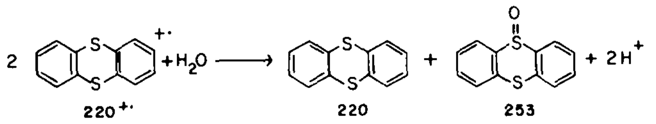
Without question the most controversy associated with the behavior of electrogenerated cations concerns the mechanism by which the thianthrene radical cation (**220**$^{+\cdot}$) (Th$^{+\cdot}$) reacts with H_2O to give thianthrene (**220**) (Th) and thianthrene monoxide (**253**) (ThO). In 1969 Shine and Murata reported on their kinetic studies of this reaction in CH_3CN/H_2O[172] and proposed a mechanism involving initial disproportionation of the radical cation followed by a reaction of the carbodication Th^{+2} with water.



Shine–Murata mechanism

$$2\,\mathrm{Th}^{+\cdot} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Th} + \mathrm{Th}^{+2}$$

$$\mathrm{Th}^{+2} + H_2O \xrightarrow{k_2} \mathrm{ThO} + 2H^+$$

$$\mathrm{Rate} = \frac{k_1}{k_{-1}} k_2 \frac{[\mathrm{Th}^{+\cdot}]^2[H_2O]}{[\mathrm{Th}]}.$$

Subsequently Eberson and Parker on the basis of voltammetric experiments suggested that the species reacting with water was not Th^{+2} but Th$^{+\cdot}$ and they proposed an alternate mechanism to explain the kinetic results.[173] Once it was possible to measure the reversible redox potential for Th$^{+\cdot}$ $\rightleftharpoons$ Th^{+2} + e,[145] the ratio of Th$^{+\cdot}$ to Th^{+2} in various media could be calculated from the known initial concentration of Th$^{+\cdot}$ and the value of K_{dis} (Table 7). Even though Th^{+2} is much more reactive with H_2O than $Th^{+\cdot}$,[173] its concentration is much too low to account for the observed rate of reaction of $Th^{+\cdot}$ with water.

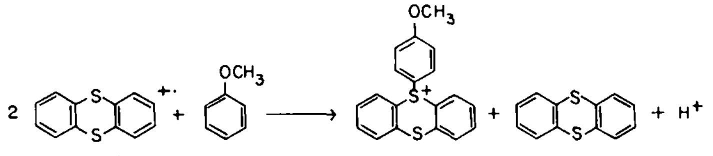
Parker–Eberson mechanism

$$Th^{+\cdot} + H_2O \rightleftharpoons ThOH\cdot + H^+$$

$$ThOH\cdot + Th^{+\cdot} \rightleftharpoons ThOH^+ + Th$$

$$ThOH^+ \rightarrow ThO + H^+.$$

In an attempt to look at this reaction in a different way, Parker and his students investigated the reaction of $Th^{+\cdot}$ with anisole (AnH) which is known to yield Th and the cation **254**.[174] Parker's kinetic studies of this reaction led to a mechanism in which the key step is the reaction of the $Th^{+\cdot}$-anisole intermediate (Th-$AnH^{+\cdot}$) with $Th^{+\cdot}$ to give the dication $ThAnH^{+2}$. If one were to substitute H_2O for AnH, one would have a new mechanism for the reaction of $Th^{+\cdot}$ with H_2O that is consistent with prior kinetic studies. In fact this type of mechanism has recently been proposed for the reaction of $Th^{+\cdot}$ with H_2O in methylene chloride containing trifluoroacetic acid.[175]



220$^{+\cdot}$ 254 220

Anisylation mechanism

$$Th^{+\cdot} + AnH \rightleftharpoons Th-AnH^{+\cdot}$$

$$Th-AnH^{+\cdot} + Th^{+\cdot} \rightarrow ThAnH^{+2} + Th$$

$$ThAnH^{+2} \rightarrow Th-An^{+} + H^{+}.$$

In 1977 Evans and Blount reported on their electrochemical and stopped flow absorption spectroscopic kinetic study of the $Th^{+\cdot}/H_2O$ reaction.[176] Notable was their observation of a third order dependence of the reaction rate on water and an inhibition of the rate by acid. They proposed the following mechanism which they believe yielded the correct rate law.

Evans–Blount mechanism

$$Th^{+\cdot} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ThOH_2^{+\cdot}$$

$$ThOH_2^{+\cdot} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ThOH\cdot + H_3O^+$$

$$ThOH_2^{+\cdot} + ThOH\cdot \xrightarrow{k_3} Th + H_2O + ThOH^+$$

$$ThOH^+ + H_2O \xrightarrow{fast} ThO + H_3O^+$$

$$Rate = K_{obs}[Th^{+\cdot}]^2[H_2O]^3/[H_3O^+] \quad \text{if} \quad k_{-2}[H_3O^+] \gg k_3[ThOH_2^{+\cdot}].$$

The Evans–Blount mechanism has recently been criticized by Hammerich and Parker.[175,177] They have no qualms with the experimental data but only with inconsistencies in the proposed mechanism. For a variety of reasons, in order for the rate law to be valid, Hammerich and Parker feel that the equilibrium in the first and second steps must lie far to the left. If so, the concentration of $ThOH_2^{+\cdot}$ will be too low for it to compete with $Th^{+\cdot}$ as an electron acceptor in the third step of the mechanism. Furthermore, uncomplexed $Th^{+\cdot}$ should be a better electron acceptor than $ThOH_2^{+\cdot}$ is. When they replace step three of the Evans–Blount mechanism with the "better" $Th^{+\cdot} + ThOH\cdot \rightarrow Th + ThOH^+$ step, the predicted rate law becomes second order in $[H_2O]$. If Parker and Hammerich are correct, how does one then explain the observed third order dependence in H_2O? A mechanism involving the reaction of $Th^{+\cdot}$ with water aggregates may be responsible.[177]

It is interesting to note that Hammerich and Parker have recently found evidence (kinetic and isotope effects) that the Evans–Blount mechanism with the already noted alteration of the third step is valid for the reaction of $Th^{+\cdot}$ with H_2O in buffered acetonitrile.[177]

Reaction mechanism in buffered acetonitrile

$$Th^{+\cdot} + H_2O \rightleftharpoons ThOH_2^{+\cdot}$$

$$ThOH_2^{+\cdot} + B \rightleftharpoons ThOH\cdot + BH^+$$

$$ThOH\cdot + Th^{+\cdot} \rightleftharpoons ThOH^+ + Th$$

$$ThOH^+ + B \rightarrow ThO + BH^+$$

$$B - \text{base.}$$

It's clear that the only point of agreement among researches about the mechanism of $Th^{+\cdot}/H_2O$ reaction is that in CH_3CN and CH_2Cl_2 it is $Th^{+\cdot}$ and not Th^{+2} that reacts with H_2O. Even though Th^{+2} is more reactive than $Th^{+\cdot}$ with water, when the reaction begins with a solution of $Th^{+\cdot}$, the concentration of Th^{+2} is too low for it to contribute significantly to the overall reaction. This brings up the remarkable recent observations of Tinker and Bard.[178] When generated in liquid SO_2 at −40° where it is stable, $Th^{+\cdot}$ does not react with either water or anisole for at least one hour. On the other hand Th^{+2} reacts with both. In the case of water, the rate of reaction is first order in Th^{+2} and H_2O and the product of the reaction is ThO. Clearly solvent and temperature play a significant role in determining the reactivity of $Th^{+\cdot}$ with H_2O.

Behavior of Th *ions in liquid* SO_2

$$Th^{+\cdot} + H_2O \rightarrow \text{No reaction}$$

$$Th^{+2} + H_2O \rightarrow ThO + 2H^+.$$

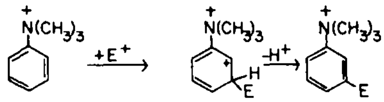
REACTIONS INVOLVING CARBODICATIONS

Introductory remarks

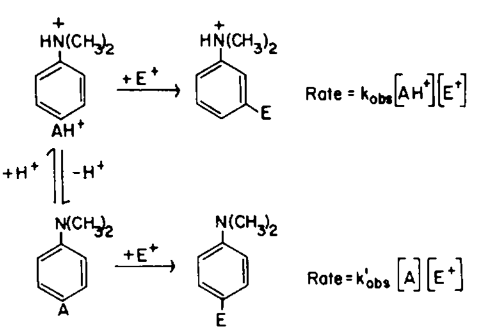
As attested by examples already mentioned in this article, the chemical behavior of carbodications has been known for many years but described only occasionally in the literature. Until recently the observed chemistry was usually a sidelight of some other project and, as a result, this chemistry was neglected. Only in the last couple of years has this area of research come into its own. Being such a new area of research, however, not enough information has been accumulated to come to many generalizations. It is difficult to know at this time if there are any significant differences between the chemistry of carbodications and monocations. Furthermore, as will become clear below, often not enough data is available to say with certainty that a carbodication is the active chemical intermediate in a given transformation.

Carbodications as sigma complexes in electrophilic aromatic substitution

Electrophilic aromatic substitution reactions involving trialkylanilinium and arysulfonium ions, which proceed via dicationic (if not carbodicationic) sigma complexes, have been studied in detail, notably by Ridd *et al.* in England.[179] Not surprisingly, the interest in this work has not centered on the generation of dications but on the directing ability of the cationic substituents.

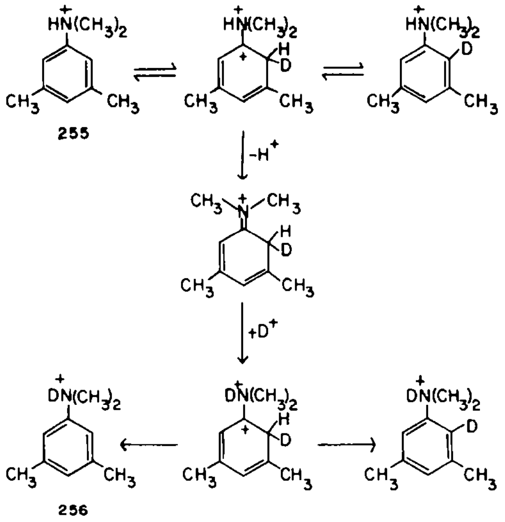


A much more interesting situation arises when the aromatic substrate such as N,N-dimethylaniline in certain solvents exists in both cationic and neutral forms that are in equilibrium with one another. In typical acidic media (Lewis and/or Bronsted–Lowry) used for electrophilic aromatic substitution, the cationic form predominates but is poorly reactive, whereas the neutral molecule which exists in very low concentration is highly reactive. Which of the aromatic substrates react? It is usually found that the reaction of the neutral species predominates. Furthermore, the aromatic substrates often react by a pre-association mechanism in which only those neutral aromatic substrates that are formed in close proximity to the electrophile undergo electrophilic aromatic substitution.[180]

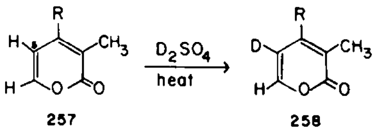


$[AH^+] >> [A]$, $k'_{obs} >> k_{obs}$

Some anilines do undergo electrophilic aromatic substitution in their ionic forms under certain conditions. Consider the behavior of N,N-dimethyl-3,5-xylidinium ion (**255**) and N-deutero-N,N-dimethyl-3,5-xylidinium ion (**256**) in aqueous H_2SO_4 and D_2SO_4.[181] In media containing up to 83% sulfuric acid, the ions undergo the expected base-catalyzed H–D exchange on the nitrogen atom, with the rate of exchange decreasing as the amount of acid increases. Above 83% acid, however, the rate of exchange on the nitrogen increases as the acid concentration goes up. In the acid range above 83%, ring exchange also occurs with its rate of exchange increasing as the amount of acid goes up. The parallel behavior of nitrogen and ring exchange above 83% sulfuric acid suggested to Ridd a commonality of mechanism involving initial attack of proton or deuterium ion onto the ring to give a dicationic intermediate as shown below. That this scheme is probably correct was borne out by the observation that in 98% H_2SO_4, the 3,5-xylidinium ion (**255**) undergoes N–H exchange about 450 times faster than the N,N-dimethyl-3-toluidinium ion. This is the rate increase expected if the initial reaction were ring protonation and it were rate determining. Furthermore, N,N-dimethyl-2,6-xylidinium ion undergoes ring exchange at one third the rate of the 3,5-isomer, but undergoes no N–H exchange. If the exchange at nitrogen requires initial protonation at C-2/6, it is not surprising that the 2,6 isomer does not undergo exchange at the N atom.

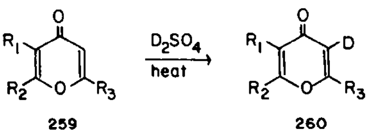


Exchange phenomena involving aromatic cations are surprisingly common. In connection with a photochemical study of hydroxypyrylium ions in sulfuric acid, Barltrop *et al.* have deuterated a series of dialkyl-2- and 4-pyrones (**257** and **259**) by heating the substrates in D_2SO_4.[182] The 4-pyrones were deuterated at the carbon(s) adjacent to the CO group and the 2-pyrones at C-5. 4-Ethyl-3-methyl-2-pyrone (**257b**), for example, yielded 4-ethyl-5-deutero-3-methyl-2-pyrone (**258b**) when heated at 140°. Interestingly 3,5-dimethyl-4-pyrone (**261**) which has the carbons adjacent to the CO group "blocked" with methyl groups did not exchange in D_2SO_4, even when heated at 200°.



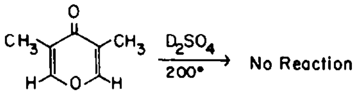
257 258

a) R=CH_3
b) R=CH_2CH_3



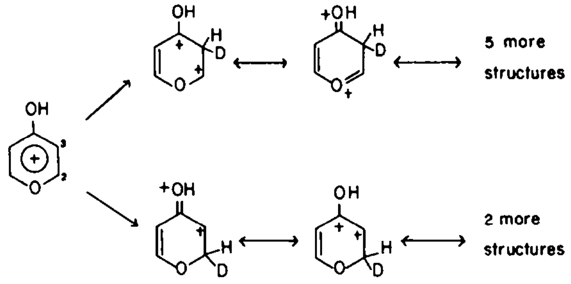
259 260

a) R_1=R_3=CH_3, R_2=H
b) R_1=H, R_2=R_3=CH_3
c) R_1=CH_3, R_2=CH_2CH_3, R_3=H

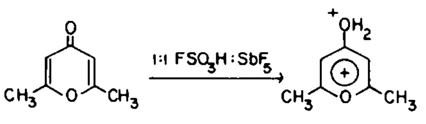


261

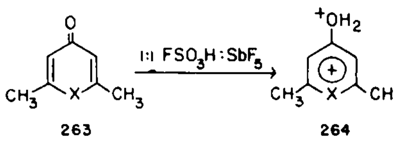
How can these results be explained? In strong acid the pyrones should exist predominantly as hydroxypyrylium ions. If a 4-hydroxypyrylium ion were to undergo exchange, it should occur at C-3 because the resultant carbodication has a resonance structure in which all atoms have the rare gas configuration. Attack at C-2 yields a dication in which this is not possible. A similar analysis also rationalizes the results for deuteration of the 2-pyrones. Although this basic mechanism is reasonable, with the data available at this time, one cannot disprove that the neutral pyrones undergo exchange, even though the molecules are present in extremely low concentrations.



The medium in which the pyrone is dissolved affects the site of the second protonation. When 2,6-dimethyl-4-pyrone (**259b**) was dissolved in the very strong acid 1 : 1 FSO_3H/SbF_5, careful ^1H- and ^{13}C-NMR analysis of the resulting solution demonstrated that the ketone is irreversibly doubly protonated on the carbonyl O atom to give **262**.^{183} Under these circumstances this dication is the most stable organic species. From these observations one can also conclude that in sulfuric acid either this dication is not formed or, if it is, it is formed reversibly and remains undetected. It follows then that in H_2SO_4 dication **262** is not the most stable organic species. The difference in acidity of the two acids, i.e. H_2SO_4 and 1 : 1 FSO_3H/SbF_5, clearly is instrumental in explaining the observed difference of behavior. Finally, it should be noted that the pyridone **263a** and thiopyrone **263b** were also doubly protonated on the CO oxygen in 1 : 1 FSO_3H/SbF_5.^{183}



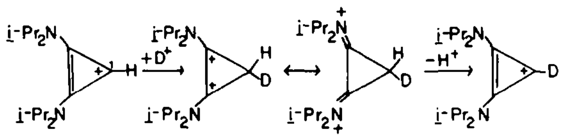
259b 262



263 264

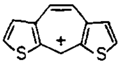
a) X=NCH_3
b) X=S

In several cases evidence for exchange reactions occurring by the reaction of two positively charged species is less ambiguous than in the pyrone examples. When the cyclopropenyl cation (**97a**) was treated with D_2SO_4 for a few minutes at room temperature, the monodeuterated ion **97a–d$_1$** was formed.^{68} The two dialkylamino substituents clearly are responsible for making this reaction so facile. First of all, the unit charge on the reactant must reside primarily on the two nitrogen atoms. The ^{13}C chemical shift of C-1 of ion **97a**, for example, is approximately 75 ppm higher field than the corresponding C in the unsubstituted cyclopropenyl ion. Secondly, the two nitrogens will also disperse charge in the dication intermediate **265**. Both of these premises were corroborated by *ab initio* MO calculations on this system.[184] As expected, the calculations show that the addition of the two amino substituents to the cyclopropenyl cation dramatically lowers the energy of activation for the reaction.[184]



97a 265 97a-d1

The heterocyclic fused tropylium ions **266**, **267** and **268** were all found to undergo exchange in their 5-membered rings at the positions β to the heteroatom when treated with D_2SO_4 at 68°.[185] The exchange rates were much slower than for **97a**, occurring with half lives of about 5 hr at 68°. Superdelocalizabilities (calculated from Hückel theory), a measure of the relative reactivity of the ring positions in electrophilic aromatic substitution, were in complete accord with the experimental observations.[185] Even though special conditions of high acidity and low nucleophilicity are required to facilitate the reactions, what is unusual is not that the reactions are electrophilic aromatic substitutions but that the intermediate carbodications are formed by the reaction of two positively charged species with each other.



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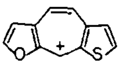

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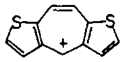
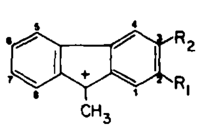


268

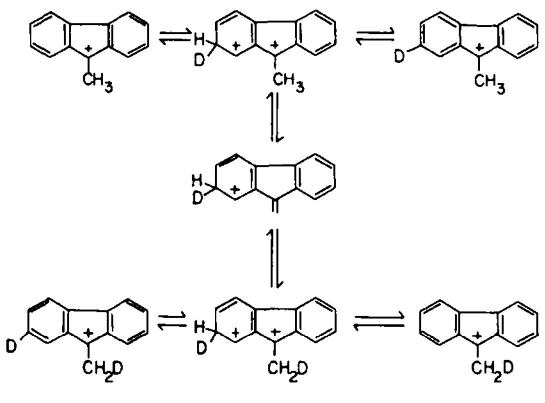
The carbocation undergoing exchange need not be an isolable one. In 1980 Olah, Schleyer and students reported the ^{1}H- and ^{13}C-NMR spectra of a series of 9-substituted fluorenyl cations which had been prepared by treatment of 9-fluorenols with FSO_3H/SbF_5 and SbF_5/SO_2ClF at $-78°$.[186] When a solution of cation **269b** having a D at C-2 was allowed to stand at $-30°$ for 15 min in FSO_3H/SO_2ClF, ^{1}H-NMR spectroscopy indicated that the D had been completely washed out of the ion. Likewise **269c** lost its D at C-3 under the same conditions. When the nondeuterated carbocation **269a** was generated at $-78°$, warmed to 0° and allowed to stand for 1 day in FSO_3D/SO_2ClF, ^{13}C-NMR spectroscopy revealed that exchange had occurred on the ion at C-2/7, C-4/5 and the Me carbon. Surprisingly no mention was made by the authors of exchange occurring at C-3/6 on **269a** which had been observed on **269c**. These results can be rationalized by a protonation-deprotonation mechanism involving carbodications. A second mechanism involving reversible loss of a proton from the Me group to give dibenzfulvene (**270**) followed by D exchange on this nonbenzenoid hydrocarbon at first glance also seems plausible. This latter mechanism can be discounted on the basis of a simple Hückel calculation. Superdelocalizabilities calculated for the fluorenyl cation are in complete agreement with the observed exchange at C-2/7 and C-4/5. Superdelocalizabilities calculated for dibenzfulvene suggest that ring exchange at C-4/5 and C-1/8 should be most facile; exchange at C-1/8, of course, was not observed. An experimental observation also rules out the dibenzfulvene mechanism. When **269a** was prepared in the stronger acid FSO_3D/SbF_5, exchange at the methyl position was completely suppressed and the rate of aromatic exchange sharply reduced. If the equilibrium **269a** $\rightleftarrows$ **270** + H^+ were shifted greatly to the left in FSO_3D/SbF_5 but the exchange occurred on the dibenzfulvene **270**, the ring exchange should also have been totally suppressed. If this be the case and the protonation-deprotonation is correct, one can rationalize the suppression of exchange at the methyl position, but it is not clear why the ring exchange is retarded. Perhaps the mechanisms of exchange in the two media are different; solvation effects may also be important in explaining the difference in behavior. It is clear that additional work will be required to understand this exchange phenomenon completely.



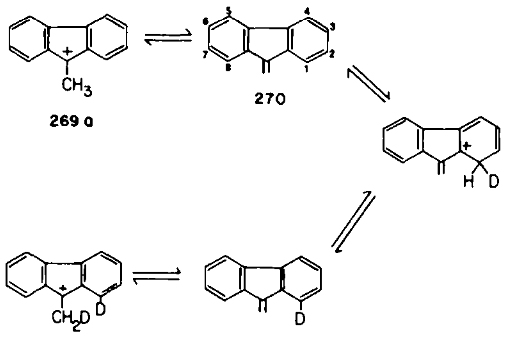
269

a) $R_1=R_2=H$
b) $R_1=D$, $R_2=H$
c) $R_1=H$, $R_2=D$

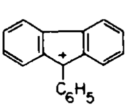
Protonation–deprotonation mechanism



Deprotonation–protonation mechanism



It should be noted that Olah reported that fluorenyl ions **271** and **272** also underwent exchange in deuterated acid.[186] In the case of the unsymmetrical ion **272** exchange at C-2 and C-4 occurred much more rapidly than at C-5 and C-7, attesting to the ability of the Me group at C-3 to stabilize a positive charge.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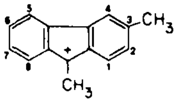
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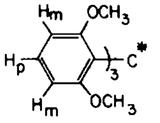
Undoubtedly the most facile exchange reaction on a carbocation was discovered serendipitously.[187] In a project designed to see if aryl radicals will undergo electrophilic aromatic substitution, the 2,2′,2″,6,6′,6″-hexamethoxytriphenylmethyl radical (**273**) was synthesized and subjected to the nonaqueous, nonoxidizing acids CF_3COOD and CF_3SO_3D.[188] In order to determine if the radical had undergone exchange, it was oxidized to the trityl cation **274** and ^{1}H-NMR spectrum of the resulting ion compared to the known spectrum of the ion. To insure that only the radical had exchanged, it was necessary to show that the trityl cation **274** was stable and did not exchange. In CF_3COOH, the ion gave a spectrum virtually identical to that reported by Martin,[189] with the *para* hydrogens appearing as a low field doublet and the *meta* hydrogens as an upfield triplet.[187] In the much stronger acid CF_3SO_3H,[190] however, the NMR spectrum was strikingly different, with the low field doublet collapsing to a singlet and the higher field triplet completely disappearing. This phenomenon was observed at temperatures as low as $-40°$. A variety of experiments demonstrated that these observations were due to cation **274** undergoing very rapid exchange at its meta positions with protons in the acid medium.[187,191]

It is remarkable that the reaction of two positively charged species, i.e. the carbocation and a proton, with each other can occur so rapidly, but there are several features of this system which makes this possible. First of all, the medium is highly acidic and of low nucleophilicity. A high acid pressure is required to help overcome charge repulsion between the two reacting ions. Secondly, the 6 methoxy groups help disperse charge in both the reacting carbocation and intermediate carbodication. Lastly, models show that the aryl rings in **274** are twisted considerably away from planarity. As a result not much positive charge actually resides on any one ring. Twisting of the rings in the dication intermediate also helps to insure that the two unit charges are localized in different parts of the intermediate. It is striking that prior to this work exchange on trityl cations had not been observed because trityl cations are so common and they are such good candidates for this reaction.

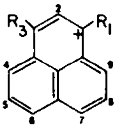


273 * = ·

274 * = +

[Exchange Rate in $CF_3COOH(D)$: $H_m > H_p$]

The exchange behavior of phenalenyl cations has been studied in detail.[187,191–193] When the phenalenyl carbocations **275a** through **275d**, all of which have two alkoxyl and/or OH substituents at activating positions, were generated in CF_3SO_3H, ^1H-NMR spectra of the resulting solutions were those expected for static, nonexchanging ions.[187,192] Either the ions are not undergoing the exchange or it is too slow to be detected by NMR spectroscopy. When the ions were generated in CF_3SO_3D, however, NMR spectroscopy revealed that all these ions underwent a rapid exchange at C-2 ($\tau_{1/2} \leqslant 3$ min) at room temperature and an extremely slow exchange at C-5/7 (detectable only when reaction was run at 100° for several hours); no exchange at C-4/9 and C-6/7 was observed.[187,192] These results are exactly those expected on the basis of resonance theory for an "ordinary" electrophilic aromatic substitution reaction; calculated superdelocalizabilities concur with this conclusion.[191] The 1-hydroxyphenalenyl ion (**275e**) which has a single activating group exchanged only at C-2 in CF_3SO_3D and at a rate thousands of times slower than for exchange at the same position in those ions with two activating groups. The unsubstituted phenalenyl cation (**275f**) did not exchange at all in triflic acid. These observations on the effect that zero, one and two activating substituents have on the rate of exchange are those anticipated for electrophilic aromatic substitution on the basis of resonance theory and Hückel MO theory.[191]



275

a) $R_1 = R_3 = OCH_2CH_3$

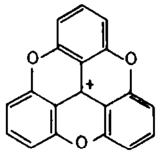
b) $R_1 = OH$, $R_3 = OCH_2CH_3$

c) $R_1 = OH$, $R_3 = OCH_3$

d) $R_1 = R_3 = OH$

e) $R_1 = OH$, $R_3 = H$

f) $R_1 = R_3 = H$



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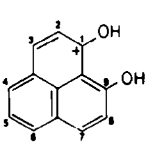

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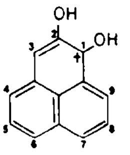


278

If the premise that the above exchange reactions occur by a protonation–deprotonation mechanism, i.e. by electrophilic aromatic substitution, is correct, altering the positions of the substituents on the phenalenyl ring should affect the rate and regiochemistry of exchange in a predictable manner. One would expect carbocation **277** with activating hydroxyl groups at C-1 and C-9 to exchange at C-2, C-5 and C-8 at rates comparable to the rate of exchange at C-2 in ion **275d**. Carbocation **278** with one activating OH group at C-1 and one deactivating OH group at C-2 should exchange slower than either **275d** or **277**, although the sites of exchange are difficult to predict qualitatively. The results of the exchange reactions in CF_3SO_3D are in good agreement with these qualitative predictions (Table 8); the agreement is even better when the experiments are compared to calculated superdelocalizabilities.[191,193] The only deviation from the predictions is the regiochemistry

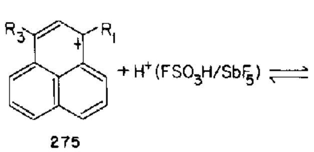
Table 8. Calculated and experimental exchange behavior of three dihydroxyphenalenyl cations in triflic acid

		275d (1,3-Dihydroxy)	**277** (1,9-Dihydroxy)	**278** (1,2-Dihydroxy)
Regiochemistry	*Calcd.*	2 > 5/8	2/8 > 5	5 ~ 8 > 3
	Exp.	2 > 5/8	2/8 ~ 5	3 ≫ 5 > 4 ~ 6
Reactivity	*Calcd.*		**275d** > **277** > **278**	
	Exp.		**275d** > **277** > **278**	

of exchange for 1,2-dihydroxyphenalenyl cation (**278**). This system exchanges so slowly ($\tau_{1/2} \sim 1.5$ days at 100°) that low concentrations of 2-hydroxyphenalenone, the precursor to **278**, may be the species undergoing exchange.

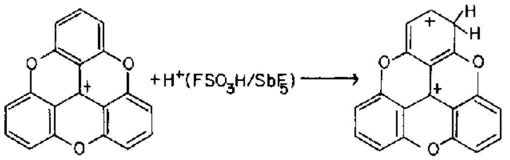
In spite of the excellent agreement between the experimental results and the expectations of a protonation–deprotonation mechanism for the phenalenyl cation exchange reactions, a large number of alternate mechanisms were considered.[191] The mechanisms included exchange occurring on phenalenyl radicals present in low concentration, occurring on uncharged phenalenes and/or phenalenones also present in very low concentrations and via a deprotonation reprotonation scheme. All of these were discounted because either the mechanism predicted the wrong site of exchange or the mechanism was incompatible with the observed rate of exchange.

A direct proof for the protonation mechanism only came when several of the phenalenyl cations were generated in acids considerably stronger than triflic acid. It was hoped that in these more acidic media the proton pressure would drive the reaction to the dication side, making it detectable by NMR. When **275d** was generated at −78° in 1 : 1 FSO_3H/SbF_5 diluted with SO_2, for example, the proton NMR spectrum at −60° showed an upfield singlet integrating for two hydrogens and three signals assigned to aromatic hydrogens but lower field than anticipated for **275d** in this medium.[191–192] These signals were assigned to the dication **279d**. Barely perceptable in the spectrum at −60° were signals due to **275d**. Raising the temperature increased the signals due to the monocation and relowering the temperature reduced their intensity. Thus one is observing directly the reversible protonation of **275d** at C-2 in this strong acid. In the still stronger acid 1 : 1 FSO_3H/SbF_5 diluted with SO_2ClF[194] only the carbodication was detected by NMR spectroscopy.[191–192] Cation **275a** behaved similarly, i.e. reversible protonation in 1 : 1 $FSO_3H/SbF_5/SO_2$ and irreversible protonation in 1 : 1 $FSO_3H/SbF_5/SO_2ClF$, while cation **275b** was protonated reversible in both media.[191,192] On the other hand, NMR spectroscopy of cations **275e** and **275f**, both of which have fewer activating groups than **275a**, **275b** and **275d**, and **277** and **278**, both of which have OH groups at other positions, yielded only the monocarbocations in both superacid media.[191] It is striking that the behavior of these ions in superacids parallels remarkably well the exchange behavior of the ions in CF_3SO_3D. The sesquixanthyl ion (**276**) which underwent rapid exchange at C-1 in CF_3SO_3D was protonated irreversibly at this position in both 1 : 1 FSO_3H/SbF_5 diluted with SO_2 and SO_2ClF.[191,192]



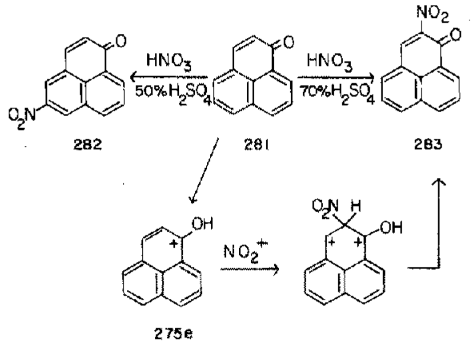
275 279

a) R_1=R_3=OCH_2CH_3
b) R_1=OH, R_3=OCH_2CH_3
d) R_1=R_3=OH

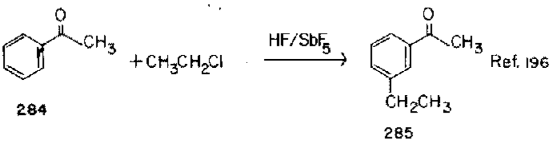


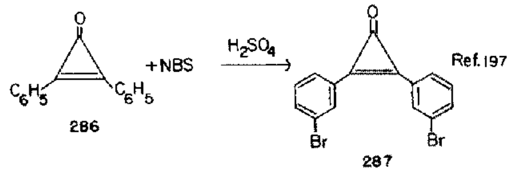
276 280

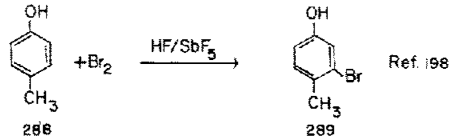
Based on the large body of data just described for the behavior of phenalenyl cations in strong acid, there can be no doubt as to when and how they react with the electrophiles H^+ and D^+. It is reasonable to inquire if other positively charged electrophiles undergo electrophilic aromatic substitution with phenalenyl cations. There is one report in the literature where this is a distinct possibility. A group of Russian chemists have shown[195] that, when phenalenone (**281**) is treated with nitric acid in 50% aqueous sulfuric acid, 5-nitrophenalenone (**282**) is produced. In 70% sulfuric acid, the reaction changes course dramatically and 2-nitrophenalenone (**283**) is formed. When fuming nitric acid in acetic acid, nitromethane or methylene chloride is used as the nitrating agent, 2-nitrophenalenone (**283**) is formed exclusively. In the stronger acid media one can assume that phenalenone is protonated first to give **275e** which then reacts with NO_2^+ to give **283**. Recall that **275e** underwent deuterium exchange at C-2 in CF_3SO_3D. In the less acidic medium nitration probably occurs on phenalenone itself.

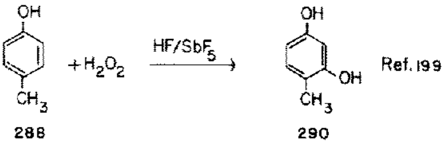


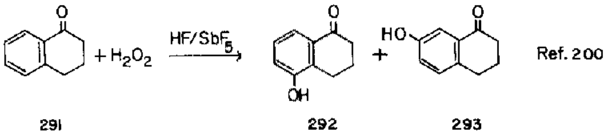
Several electrophilic substitution reactions known to occur in superacids are summarized below. Although virtually nothing is known about their mechanisms, it is safe to say that many of them proceed through dicationic intermediates. These reactions appear to have genuine synthetic utility, because the directing ability of a substituent is altered in these solvents. An OH group which is ordinarily a powerful o,p director clearly does not have this effect here. This area of research deserves much more attention.

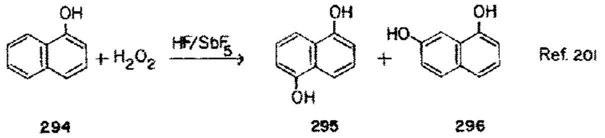




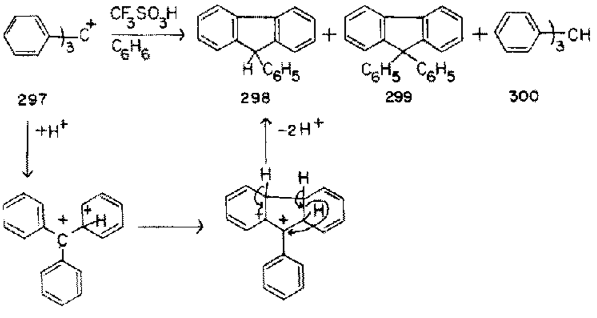






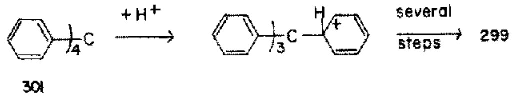


Suitable carbocations, usually having phenyl substituents, often undergo intramolecular cyclization reactions. Several examples have already been described in this article. An interesting example of this kind of chemistry has recently been described by Okamoto *et al.*[202] Heating a solution of 1 part triphenylmethyl cation (**297**) in a solution 2 parts of trifluoromethanesulfonic acid and 60 parts benzene at 80° for 2 hr yielded 9-phenylfluorene (**298**), 2,2-diphenylfluorene (**299**) and triphenylmethane (**300**) in 20%, 24% and 21% yield, respectively; 27% of unreacted **297** was also recovered. Because the trityl cation (**297**) does not react in the absence of CF_3SO_3H and reacts much more slowly in the presence of the weaker acid CF_3COOH, the authors proposed a mechanism for the formation of **298** involving initial protonation of the trityl ion (**297**) at the *ipso* position.

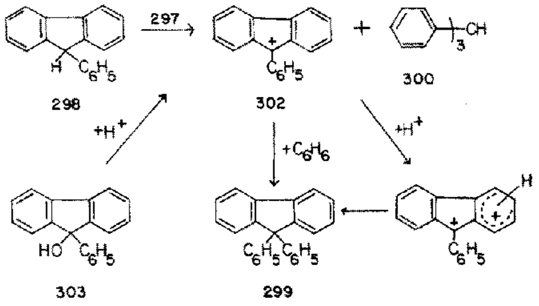


The 9,9-diphenylfluorene (**299**) was originally thought to arise by a Scholl-type reaction on tetraphenylmethane (**301**) formed by electrophilic attack of either the trityl cation or its protonated form on benzene. Control experiments demonstrated that **301** reacts too slowly in CF_3SO_3H/C_6H_6 to account for the formation of **299**. An alternate mechanism involving initial hydride abstraction by **297** on **298** to form the 9-fluorenylcation (**302**) followed by electrophilic aromatic substitution of it on benzene was also considered. This scheme has the virtue of explaining how triphenylmethane (**300**) is formed. The authors preferred, however, a slightly different scheme in which the 9-phenylfluorenyl cation (**302**) is first protonated before it reacts with benzene. The reason for this preference was the observation that 9-phenyl-9-fluorenol (**303**), a precursor to **302**, yielded **299** when treated with CF_3SO_3H in benzene, but did not yield **299** when treated with CF_3COOH in benzene. It is also possible that CF_3COOH is not a sufficiently strong acid to ionize **303** and generate **302**. Although it is clear that acid has a strong bearing on the chemical behavior of the trityl cation, additional work is required to prove that carbodications are reactive intermediates here.

Scholl mechanism



Hydride abstraction mechanism

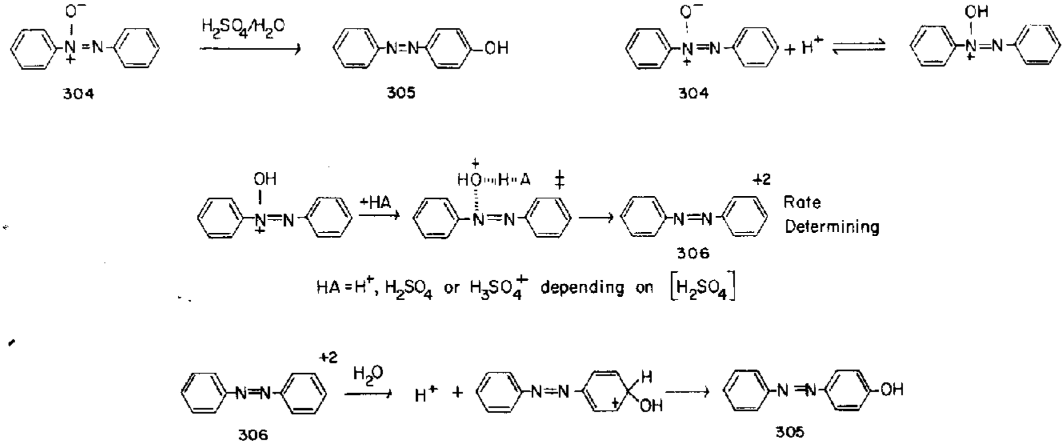


In the above chemistry of the trityl cation, CF_3SO_3H played a pivotal role. Not only is CF_3SO_3H a very strong acid, but, unlike H_2SO_4, FSO_3H and SbF_5, it is nonoxidizing and it will not sulfonate aromatic rings. In its pure state CF_3SO_3H is not unduly viscous which facilitates NMR spectroscopy. It is clear that CF_3SO_3H will play a significant part in the developing chemistry of carbodications.

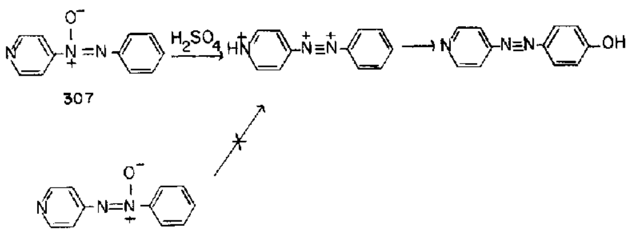
Chemistry of carbodications stabilized by nitrogen atoms

The Wallach rearrangement which involves the conversion of an azoxybenzene such as the parent **304** into a 4-hydroxyazobenzene such as **305** is probably the oldest reaction known to proceed through a dicationic intermediate. The rearrangement has been vigorously studied, notable by Buncel, and is the subject of a recent review by him.[203] Nonetheless, in the context of this article it is worth examining briefly the evidence for a dication in this interesting reaction and what the structure of this dication is. From the known pKa of azoxybenzene (**304**) in aqueous sulfuric acid, it is easy to demonstrate that in media with greater than 90% H_2SO_4 the molecule is completely protonated. If the rearrangement were to occur from this O-protonated intermediate, increasing the acidity above 90% H_2SO_4 should have little or no effect on the rate of rearrangement. The rate in fact increases almost six hundred fold in going from 90.37% to 99.99% H_2SO_4. The involvement of a second proton is clearly indicated. ^{15}N-labelling studies also indicate that at least one of the intermediates between reactant and product has a plane of symmetry. Although there are several symmetrical dicationic species that one can draw, it is generally agreed that this intermediate is the azobenzene dication (**306**). This dication has been observed spectroscopically by Olah *et al.* in their study of the Wallach rearrangement in superacids.[204] Based on these results and other kinetic studies not described here, the generally accepted mechanism shown below can be written.

Mechanism of Wallach rearrangement

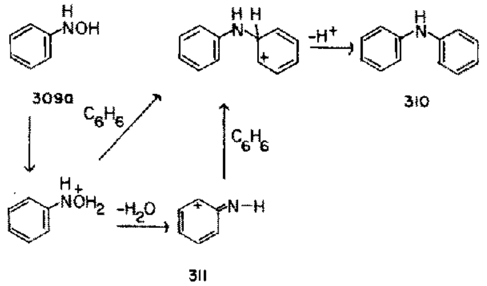


In a recent report Buncel and Keum have described the Wallach rearrangement of **307** which occurs via a tricationic intermediate.[205] The isomeric azoxy compound (**308**) was found unexpectedly to be totally unreactive. The difference in behavior of the isomers can be attributed to the difference in ability of the benzene and pyridinium ion rings in **307** and **308**, respectively, to disperse the developing third positive charge in the rate determining step of the rearrangement.

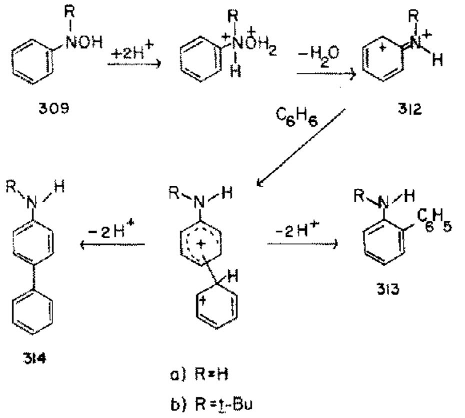


Other N-stabilized dications seem to play a role in electrophilic aromatic substitution. Okamoto and students have shown that N-phenylhydroxylamine (**309a**) yields primarily diphenylamine (**310**) when treated with four equivalents of trifluoroacetic acid in benzene.[206] This product can arise by attack of either protonated **309a** or the anilenium ion **311** on benzene. When **309a** was treated with excess trifluoromethanesulfonic acid in benzene, on the other hand, the reaction yielded as major products 2- and 4-aminobiphenyl (**313a** and **314a**).[206] Experiments with varying amounts of the two acids demonstrated that the presence of the highly acidic trifluoromethanesulfonic acid, and not the polarity of the medium, is responsible for the formation of the biphenyls. Although a mechanism involving monocations is possible, the results suggest that the reaction with trifluoromethanesulfonic acid proceeds through dicationic intermediates such as the protonated anilenium ion **312**. Similar results were obtained when N-t-butyl-N-phenylhydroxylamine (**309b**) was treated with CF_3SO_3H/C_6H_6.[206]

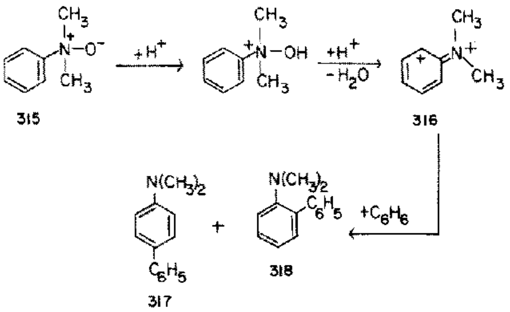
Mechanism with CF_3COOH



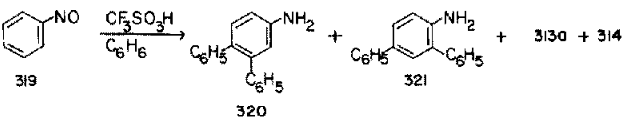
Mechanism with CF_3SO_3H

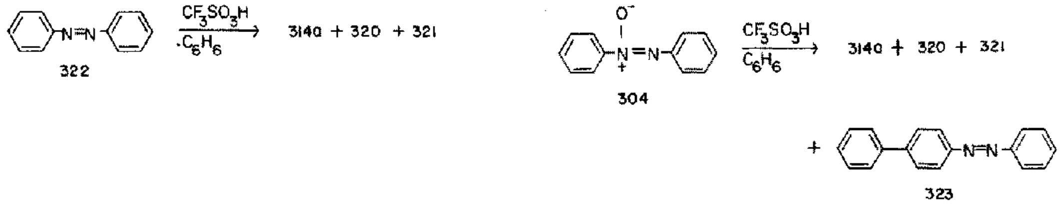


Protonated anilenium ions could be generated in other ways. When N,N-dimethylaniline N-oxide (**315**) was treated with CF_3SO_3H/C_6H_6, the biphenyls **317** and **318** were formed. A mechanism invoking the dicationic anilenium ion **316** as an intermediate can be written. Unlike the transformations of the hydroxylamines with CF_3SO_3H, there can be little doubt that dications are intermediates in this transformation.



Nitrosobenzene (**319**), azobenzene (**322**) and azoxybenzene (**304**) all reacted with CF_3SO_3H/C_6H_6 to give the products shown below. Although the details in the specific cases vary, the formation of these products can be explained by mechanisms involving dicationic intermediates. In the azoxybenzene example, it is interesting to note, the *p*-phenylazobenzene (**323**) likely arises from the reaction of the azobenzene dication (**306**), the intermediate in the Wallach rearrangement, with benzene.

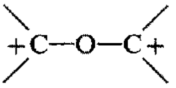




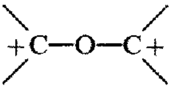
Recent developments

Since the completion of this report several interesting articles on multiply charged cations have appeared in the literature or come to the attention of the author. A short description of these is presented below.

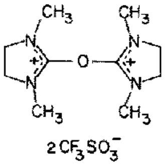
Another paper has appeared on the preparation of dication ethers by the reaction of carbonyl compounds (amides and ureas) with trifluoromethane-sulfonic anhydride.[207] X-ray crystallographic structures have been reported for the three dication ethers shown below.[208,209] Most significantly all the dications are bent about the

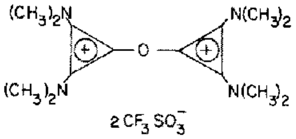


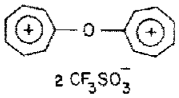
linkage. Furthermore, in the three dications all the rings are titled out of the



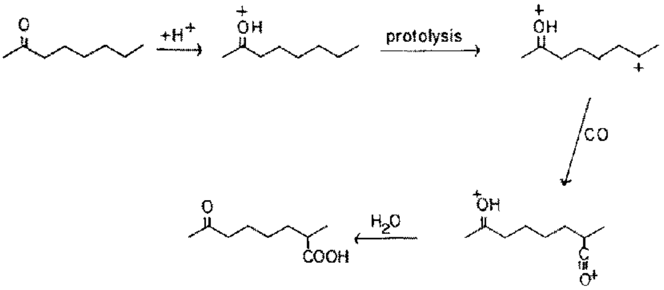
plane. The ditropylium dication ether has C_2 symmetry;[209] the other two dications lack symmetry.[208]



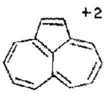


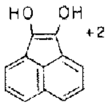


Yoneda *et al.* have shown that methyl alkyl ketones having five or more carbons in the alkyl chain react between −20° and +30° with HF/SbF_5 in the presence of CO to give, on workup, ketoacids.[210] The reaction undoubtedly occurs by protolysis of a saturated C—H or C—C bond of the protonated ketone followed by reaction with CO to form an acylium ion. The lack of reactivity of the smaller aliphatic ketones can be attributed to charge repulsion.

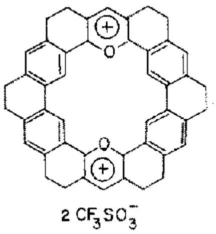


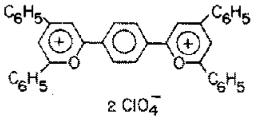
Rabinovitz has continued his research on the nature of dications such as the ones shown below and dianions.[211] A careful analysis of the ^1H- and ^{13}C-NMR spectra of these pericondensed systems demonstrated that the systems tend to sustain aromaticity, or, if that is not possible, to avoid antiaromaticity. A recent review describes these ideas in detail.[212]

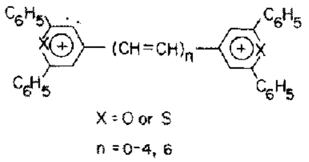


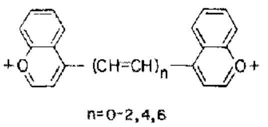


Several publications have appeared which describe the synthesis and/or physical properties (NMR and UV-Vis spectroscopy and redox potentials) of bispyrylium dication salts and related species.[213–215] Several of these dications are shown below.

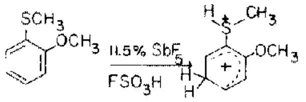




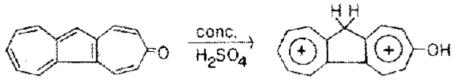




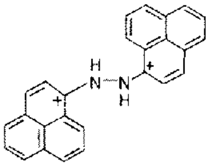
Maksic has discussed the behavior of *o*-, *m*-, and *p*-methoxythioanisole is 11.5% SbF_5/FSO_3H.[216] ^1H- and ^{13}C-NMR spectra of the *ortho* isomer clearly indicated that it is doubly protonated. Interestingly, the meta and para isomers are only monoprotonated (on S) in the same acid.



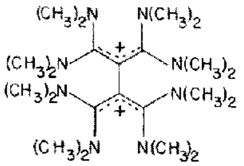
Takase *et al.* have prepared azuleno[1,2-d]tropone (shown below) and studied its behavior in several acids.[217] Spectroscopic studies demonstrated that the ketone is monoprotonated on O in CF_3COOH and diluted H_2SO_4 and doubly protonated in concentrated H_2SO_4.



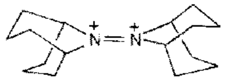
Several N-containing dications have come to the attention of the author and these are shown below.



Ref. 218

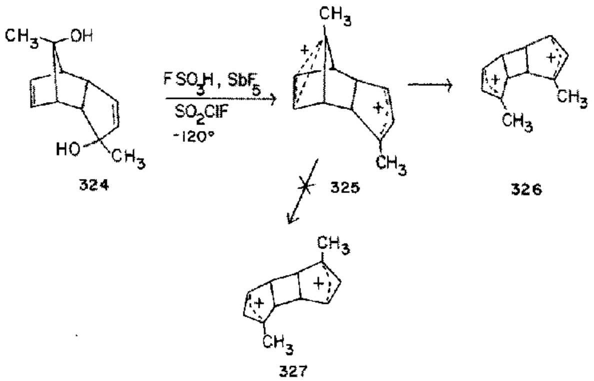


Ref. 219



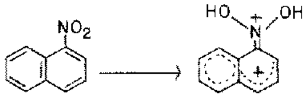
Ref. 220

Olah *et al.* have recently shown that carbodications may undergo 1,3-sigmatropic shifts just as the 7-norbornadienyl cation does.[221] Treatment of diol **324** with FSO_3H/SbF_5 in SO_2ClF at −120° results in the formation of dication **325** which, on warming to −40°, isomerized to dication **326**.[221] It is interesting to note that a similar 1,3-sigmatropic shift to give **327** did not occur.



More recently, Olah and Singh have synthesized a series of anthracene dications by oxidation of the corresponding anthracenes by SbF_5 in SO_2ClF at low temperature and studied their ^{13}C-NMR spectral properties.[222]

Shudo *et al.* have recently demonstrated the formation of a dihydroxyiminiumnaphthalene dication when 1-nitronaphthalene is dissolved in trifluoromethanesulfonic acid.[223] Although electronic and ^1H-, ^{13}C- (coupled and decoupled), and ^{15}N-NMR spectra and isotopic experiments were reported, the structure proof hinged on cryoscopic measurements which suggested the formation of three ions per molecule of 1-nitronaphthalene. Several substituted 1-nitronaphthalenes behaved accordingly.



Acknowledgement—The author wishes to thank Professors James Q. Chambers and John W. Larsen and Dr. Patricia Pagni for their help in the preparation of this manuscript.

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