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I am submitting herewith a thesis written by Paul Edmunds Easley entitled "A Mechanistic Study of Hydride Abstraction in Fluorosulfonic Acid and Other Media." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

Richard Pagni, Major Professor

We have read this thesis and recommend its acceptance:

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James Q Chambers

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A MECHANISTIC STUDY OF HYDRIDE ABSTRACTION IN FLUOROSULFONIC ACID AND OTHER MEDIA

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Paul Edmunds Easley

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ABSTRACT

Evidence has been presented for carbenium ion formation from hydrocarbons in superacids by a process which is formally a hydride abstraction by a proton. Observation of carbenium ion formation in fluorosulfonic acid with the accompanying production of sulfur dioxide, together with the report of facile hydride abstraction by SbF_5, indicate the existence of a "new" process for cation formation from hydrocarbons in superacids.

Additional examples of this "new" process were obtained and in all cases the reactions were analyzed by nmr. Investigations into an electron transfer were conducted by deuterium incorporation using D_2SO_4.

Incorporation of deuterium into the phenalene and 7H-benz[d,e]anthracene systems supported an electron transfer mechanism. Also, apparent oxidation of the phenalenyl radical furnished additional support for the electron transfer process.

TABLE OF CONTENTS

CHAPTER		PAGE
I.	INTRODUCTION	1
	A. Carbocations: Carbenium Ions and Carbonium Ions	1
	B. Stable, Long-Lived Carbenium Ions	4
	C. Electrophilic Reactions at Single Bonds	5
	D. Insufficient Hydrogen Production	9
	E. Carbenium Ion Formation with Concomitant Production of Sulfur Dioxide	10
II.	RESULTS AND DISCUSSION	12
	A. Introductory Remarks	12
	B. Additional Examples of this Reaction	12
	C. An Electron Transfer Mechanism	15
	D. Deuterium Incorporation	21
	E. Conclusions	25
III.	EXPERIMENTAL SECTION	26
	A. General Techniques	26
	B. Preparation of Compounds	27
	1. Phenalene	27
	2. Benz[d,e]anthracylium perchlorate	27
	3. 9-Thioxanthenol	28
	4. Thioxanthylium perchlorate	28
	5. Phenalene-d_1	28
	6. Phenalenyl radical	29
	7. 7H-Benz[d,e]anthracene	29
	C. Product Identification	29
LIST OF REFERENCES		31
VITA		35

LIST OF FIGURES

FIGURE		PAGE
1.	Nmr Spectrum of Xanthylium Carbenium Ion Generated by Tl^{+3} Oxidation	16
2.	Nmr Spectrum of Benz[d,e]Anthracylium Carbenium Ion Generated by NO_2^+ Oxidation	17
3.	Nmr Spectrum of Thioxanthylium Carbenium Ion Generated by H_2SO_4 Oxidation	18
4.	Nmr Spectrum of Phenalenyl Carbenium Ion Generated by Tl^{+3} Oxidation	19
5.	Nmr Spectrum of Thioxanthylium Perchlorate in Trifluoroacetic Acid	20
6.	Nmr Spectrum of Phenalenyl Carbenium Ion Generated by D_2SO_4 Oxidation	23

CHAPTER I

INTRODUCTION

A. Carbocations: Carbenium Ions and Carbonium Ions

The concept of carbocations had its origin in the kinetic, stereochemical and product studies of a wide variety of reactions, especially unimolecular nucleophilic substitutions and eliminations. In 1922, while studying the kinetics of the rearrangement of camphene hydrochloride to isobornyl chloride, Meerwein reported the important observation that the reaction rate increased in a general way with the dielectric constant of the solvent (1). He also found that metal chlorides, such as $SbCl_5$, $SnCl_4$ and $SbCl_3$, which promote the ionization of triphenylmethyl chloride by formation of ionized complexes, considerably accelerate the rearrangement of camphene hydrochloride. Due to these observations, Meerwein concluded that the conversion of camphene hydrochloride into isobornyl chloride proceeds by rearrangement of a cationic intermediate instead of by way of migration of the chloride atom. Thus the modern concept of carbocations was born.

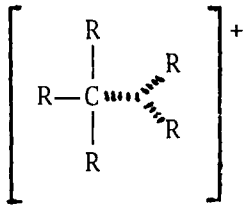
In the late 1920's, Ingold, Hughes et al. carried out kinetic investigations on what later became known as nucleophilic substitution at saturated carbon and on polar elimination reactions (2). The well-known work relating to S_N1 and later to E1 reactions established the carbocation concept. Meerwein's rearrangement theory was extended to many organic reactions by Whitmore in a series of papers, beginning

in 1932 (3). Bartlett, Nenitzescu, Winstein and other leading investigators have contributed fundamentally to the development of the modern carbenium ion theory, i.e., to the concept of electron deficient cationic intermediates.

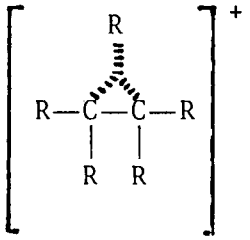
The trivalent carbenium ion contains an sp^2-hybridized electron deficient central carbon atom with six electrons in the valence shell. In the absence of constraining skeletal rigidity or steric interference, the carbenium ion tends to give a planar arrangement with the three directly bound atoms.

Ion stabilization via charge delocalization can occur by interaction of neighboring groups with the vacant p-orbital of the carbenium ion center. Such phenomena can involve atoms with unshared electron pairs (n-donors), C-H and C-C hyperconjugation, bent σ-bonds (as in cyclopropylcarbenium ions) and π-electron systems (direct conjugative or allylic stabilization).

Based on Olah's study of carbocations it became apparent that a second distinct class of carbocations exists, the penta- (or tetra) coordinated carbonium ion (4). Structurally, this ion contains five or four coordinated carbon atoms (having eight electrons in the valence shell) bound by three single bonds, and a two-electron, three-center bond (the latter being bound either to two additional bonding atoms or involving a carbon atom to which they are also bound by a single bond).



pentracoordinated
R = H or alkyl



tetracoordinated

It seems highly improbable that expansion of the carbon octet could take place via 3d-orbital participation and there can be only eight valence electrons in the outer shell of carbon. Thus the covalency of carbon cannot exceed four. Pentacoordination implies a species with five ligands at a reasonable bonding distance from the central atom. Recent studies on long-lived "nonclassical" ions in superacid solvent systems furnished direct observation of stable pentacoordinated species in solution (5).

In contrast to the rather well-defined trivalent ("classical") carbenium ions, "nonclassical ions" have been more loosely defined. The classical-nonclassical carbonium ion problem has induced a lively controversy in recent years (6). The literature contains many contributions to the topic, but no generally accepted definition of nonclassical ions has emerged. Furthermore, no direct experimental means have been recognized for the differentiation of classical and nonclassical ions.

It is suggested by Olah and others that unequivocal experimental evidence has since been obtained for nonclassical ions such as the norbornyl cation (7), and that the bonding concept required to define

these "nonclassical ions" is to consider them as penta- or tetracoordinated carbonium ions, of which CH_5^+ (methonium ion) is the parent, in the same way as CH_3^+ (methenium ion) is the parent for trivalent carbenium ions.

B. Stable, Long-Lived Carbenium Ions

Until recently, simple alkylcarbenium ions were detected by electron impact measurements. Mass spectrometry has been used to investigate the formation of organic cations in the gaseous phase by electron bombardment of alkanes, haloalkanes, and other precursors (8).

Only in recent years has it been possible to directly observe stable, long-lived carbenium ions in solution, generally in highly acidic (superacid) solvent systems (9). The transient nature of carbocations in chemical reactions arises from their extreme reactivity with nucleophiles. Reactions leading to covalent products can be prevented by the use of highly acidic and very weakly nucleophilic solvents. In the last decade it has been possible in this way to observe a wide range of stable, long-lived carbocations.

Observation of alkylcarbenium ions (trivalent alkyl cations) has been a long standing challenge for many research workers. Attempts by Symons, Finch, Deno, and others to prove the existence of well-defined, stable alkylcarbenium ions were unsuccessful, both in experiments with sulfuric acid solutions as well as with systems from alkyl halides and Lewis acid halides (10, 11).

In 1962 Olah reported the first direct observation of stable alkylcarbenium ions in solution (12). He obtained the trimethylcarbenium ion when tert-butyl fluoride was dissolved in excess antimony pentafluoride, which served both as Lewis acid and solvent:

$$(CH_3)_3CF + 2SbF_5 \longrightarrow (CH_3)_3C^+Sb_2F_{11}^- \qquad (1)$$

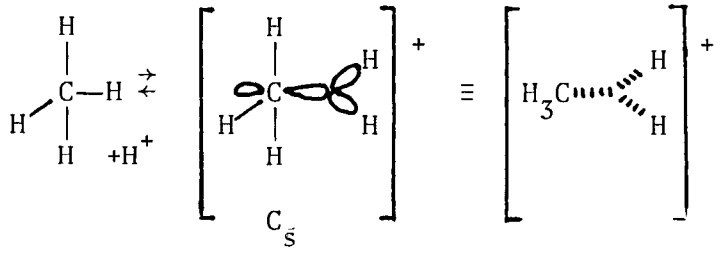
Olah investigated in detail the possibility of obtaining stable alkylcarbenium fluoroantimonate salts from alkyl fluorides (and subsequently other halides) in antimony pentafluoride solution (neat or diluted with sulfur dioxide, sulfuryl chloride fluoride, or sulfuryl fluoride) or in other superacids. His studies extended to all isomeric C_3, C_4, and C_5 alkyl fluorides, as well as to a number of higher alkyl halides and alcohols (13). The most stable tertiary or secondary carbenium ions were eventually observed by Olah starting from any of the isomeric alkyl fluorides or alcohols in superacidic solvent systems. Olah also studied the rearrangement to these more stable ions starting at very low temperatures.

C. Electrophilic Reactions at Single Bonds

It is commonly known that trivalent carbenium ions play an important role in acid-catalyzed rearrangements of hydrocarbons (isomerization, alkylation, cyclization, polymerization, etc.), as well as in a large variety of electrophilic reactions including those of the generalized Friedel-Crafts type. Olah proposes, however, that only ionization of

lone (nonbonding) electron pair donor precursors (n-bases) or protonation of singlet carbenes can lead directly to carbenium ions (14). He suggests that other (σ- or π-) donors always interact first via their bonding electron pairs with the electrophilic reagents, forming two electron three-center bound carbonium ions which subsequently yield the trivalent carbenium ions.

Olah considers the bonding of a carbonium ion center to involve three covalent, two-electron bonds with the fourth bond being a two-electron three-center bond (15). The existence of the methonium ion CH_5^+ is based on mass spectrometric studies (16) as well as on the chemistry of methane in superacids and with strong electrophiles (17). Thus, Olah reasons that the interaction involves the main lobes of the covalent bonds (frontal attack) and since an electrophile will attack the points of highest electron density, attack will occur on the covalent bonds themselves and not on the relatively unimportant back lobes.



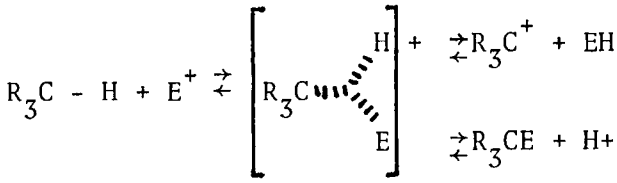
(2)

There are a number of possible structures for the methonium ion (D_{3h}, C_{4v}, C_s, D_{2h} or C_{3v} symmetry). Olah suggests preference for the C_s front-side protonated form based on consideration of the observed chemistry of methane in superacids (hydrogen-deuterium exchange

and polycondensation indicating ease of cleavage of CH_3^+ and H_2) and also on the basis of self-consistent field (SCF) calculations (18). More extensive calculations, including ab initio calculations utilizing an "all-geometry" parameter search (19) appear to confirm the favored structure with C_s symmetry.

Olah has proposed that pentacoordinated carbonium ions play an important role in the general area of electrophilic reactions at single bonds, e.g., in the aliphatic substitution of alkanes and cycloaklanes (20). Such reactions include acid-catalyzed hydrocarbon isomerizations, fragmentations, cyclizations, and other transformation reactions, electrophilic substitutions of alkanes and cycloalkanes and related electrophilic reactions.

In recent years, Olah has presented evidence for the general reactivity of covalent C-H and C-C single bonds of alkanes and cycloalkanes in various electrophilic substitution reactions such as protolytic processes, hydrogen-deuterium exchange (21), alkylation (22), nitration (23), etc. This reactivity is due to what Olah considers, alongside n- and π-donor ability, the third major type of electron donor ability, i.e., the σ-donor ability (sigma basicity) of bonded electron pairs (i.e., single bonds) to share their electron pairs with an electron deficient reagent through two-electron, three-center bond formation (24). Olah states that the reactivity of single bonds stems from their ability to participate in the formation of pentacoordinated carbonium ions (25). Subsequent cleavage of the three-center bond results in formation of trivalent carbenium ions and substitution products, or hydrogen (alkyl) transfer takes place.



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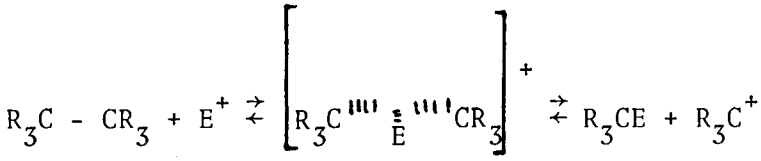
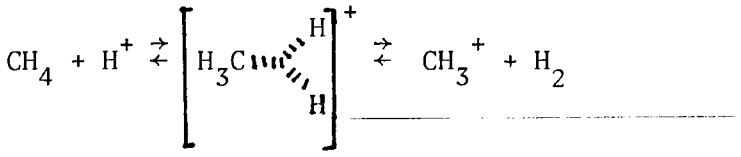


(4)

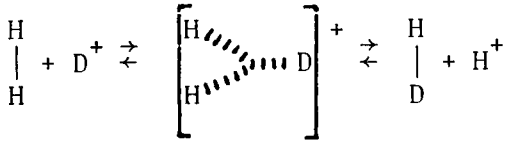
$E^+ = D^+, H^+, R^+, NO_2^+, Hal^+$

In 1967, Lukas and Olah reported the protolytic ionization and hydrogen-deuterium exchange of alkanes and cycloalkanes in superacids such as FSO_3H-$SbF_5(SO_2ClF)$ (26). These studies demonstrated that in the new superacid systems not only tertiary and secondary, but also primary C-H bonds as well as C-C bonds undergo facile protolytic cleavage. To account for the observed protolytic reactions of alkanes, Olah suggested that protolysis preferentially involved "front-side" attack through formation of triangular carbonium ions as shown in the case of protonation of methane to CH_5^+:



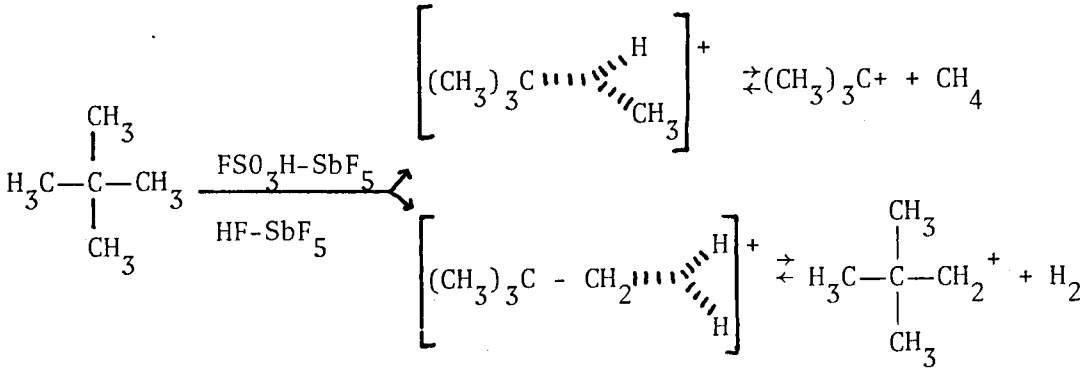
(5)

Olah later showed that molecular hydrogen itself readily undergoes hydrogen-deuterium exchange in superacids (27). He assumed that a triangular H_3^+-transition state (28) was involved in the protolytic process:



(6)

In Olah's continued investigations it became obvious that protolysis of single bonds, including C-H as well as C-C bonds was a general reaction (29). As an example, the protolysis of neopentane (30) may be mentioned, where there is both C-C and C-H bond reactivity:



(7)

In FSO_3H-SbF_5 or SbF_5 (which generally always contains HF) C-H cleavage is favored at low temperatures (-80°C). At higher temperatures or in HF-SbF_5, on the other hand, C-C cleavage predominated.

D. Insufficient Hydrogen Production

The fate of the abstracted hydride ion is not yet fully determined in these reactions. According to Olah's mechanism, hydrogen would be generated by electrophilic attack of a proton on a C-H bond. Part of this hydrogen has actually been observed to escape from the reaction mixture. However, Olah states that, "the bulk of the nascent hydrogen seems to reduce the acid solvent system" (31).

Neat antimony pentafluoride without added FSO_3H or HF acts as a very effective solvent system in which alkanes readily form alkylcarbenium ions (32). Olah assumes the proton acid impurities in the system are responsible for hydride abstraction as molecular hydrogen (H_2) is formed in the reactions. He proposes that since a "minimal proton acid impurity always seems to be present, the "neat" SbF_5 system must be indeed considered as an HF-SbF_5 system, with relatively low HF concentration. Thus the overall reaction is not

$$RH + SbF_5 \rightarrow R^+SbF_5H^- \quad (8)$$

but

$$RH + H^+SbF_6^- \rightarrow R^+SbF_6^- + H_2 \quad (9)$$

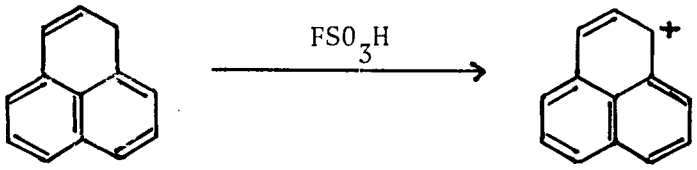
H_2 is readily reducing SbF_5 to SbF_3 and HF

$$SbF_5 + H_2 \rightarrow SbF_3 + 2HF \quad (10)$$

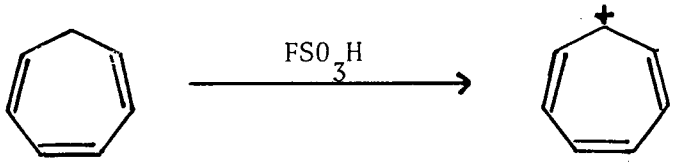
The system initiated by small proton acid impurities produces more acid as the reaction proceeds" (33).

E. Carbenium Ion Formation with Concomitant Production of Sulfur Dioxide

In 1973, Pagni and Larsen reported the oxidation of cycloheptatriene and phenalene in FSO_3H, both in the presence and absence of SbF_5, to the corresponding carbenium ion with the concomitant production of sulfur dioxide (34). SO_3 in liquid SO_2 also oxides these hydrocarbons.



(11)



(12)

In all cases examined, SO_2 yields were within experimental error (± 1%) of the cation yields determined by nmr. It was determined that the formation of sulfur dioxide during the generation of carbenium ions from hydrocarbons in fluorosulfonic acid does not arise by reduction of SO_3 or FSO_3H by hydrogen. Obviously, the mechanism of oxidation in these reactions must be different from the process by which alkanes such as isobutane or neopentane are oxidized. Much work remains to be done in order to unequivocally establish the mechanisms by which hydrocarbons form carbenium ions in superacids and aprotic media.

CHAPTER II

RESULTS AND DISCUSSION

A. Introductory Remarks

The report of the oxidation of phenalene and cycloheptatriene by fluorosulfonic acid to the corresponding carbenium ions and the concomitant production of sulfur dioxide indicates the existence of a "new" process by which cations are formed from hydrocarbons in superacid. The formation of the tert-butyl carbenium ion from isobutane in mixtures of fluorosulfonic acid and antimony pentafluoride has been presented both as a hydride abstraction by a proton (35), and as an oxidation by antimony pentafluoride (36). Sulfur dioxide is generated during the formation of the tropylium ion from cycloheptatriene in these media. Therefore, it is clear that cation formation from alkanes is proceeding by a mechanism different from that reported by Pagni and Larsen (37). The purpose of the remaining portion of this thesis is to describe the experimental evidence for the involvement of an electron transfer mechanism in the oxidation of these hydrocarbons.

B. Additional Examples of this Reaction

The particular feature that obviously distinguishes cycloheptatriene or phenalene from saturated alkanes is the extensive π-system. Therefore, these two molecules form very stable carbenium ions, while saturated alkanes do not.

In Table I are listed some of the oxidations attempted, both in FSO_3H at -78° and H_2SO_4 at room temperature. In all cases the reactions were analyzed by nmr and identification of the cationic product was based on one or more of the following: (1) independent synthesis, (2) literature nmr values, and (3) a detailed analysis of the reaction nmr.

If the cation formed, it formed cleanly; no other products were observed except in the cases of cycloheptatriene, where there is extensive polymerization, thioxanthene, where there is some sulfonation (38), and 1,2,5,6-dibenzcycloheptatriene, where extensive sulfonation is observed in both FSO_3H and H_2SO_4. Tris(p-Anisyl)methane underwent a cleavage in FSO_3H to give anisole and 4,4´-dimethoxybenzhydryl carbenium ion (39).

Work by Deno in 1961 involving hydride transfers to generate arylcarbenium and alkycarbenium ions demonstrated that there should be a linear relationship between the rate of direct hydride abstraction and the stability of the cation formed (40). As can be seen in Table I, there is no obvious connection between ion stability (pK_R+) and whether the hydride abstraction occurs. Therefore, this evidence tends to make such a process unlikely in these oxidation reactions (41).

Because all the molecules which are oxidized in FSO_3H and H_2SO_4 have extensive π-systems, the oxidizing agent is behaving either as an electron acceptor or as an electrophile, and there should be nothing unique about FSO_3H, H_2SO_4 or SO_3 in this regard. As can be seen in Table 1, certain of the compounds were also oxidized to the corresponding carbenium ion by $NO_2{}^+BF_4{}^-$ in acetonitrile and $Tl(O_2CCF_3)_3$ in

Table I

Attempted Oxidations

Compound	Ion Formation in				pK_{R+}
	FSO_3H	H_2SO_4	Tl^{+3} CF_3COOH	NO_2^+, CH_3CN	
Fluorene	No	No	No	No	-14[a]
Diphenylmethane	No	No	No	No	-13.3[a]
Triphenylmethane	No	No	No	No	- 6.63[a]
7H-Benz[d,e]anthracene	Yes	Yes	Yes	Yes	- 6[b]
1,2,5,6-Dibenzcycloheptatriene	Yes	Yes	No	Yes	- 5.8[c]
Xanthene	No	No	Yes	Yes	-0.84[c,d]
Thioxanthene	Yes	Yes[e]	Yes	Yes	-0.21[d]
Phenalene	Yes	Yes	Yes	Yes	0-2[a]
Tris(p-Anisyl)methane	No	No	-	-	0.82[c]
Cycloheptatriene	Yes	Yes	No	No	4.7[c]

[a]Experimental value cited in Reference 48.

[b]Computed from MO theory by the method described in Reference 48.

[c]Experimental value cited in Reference 49.

[d]See Reference 50.

[e]See Reference 51.

trifluoroacetic acid. Treatment of 1,2,5,6-dibenzcycloheptatriene with NO_2^+ did generate the cation, but other products were also formed. In all other cases, if the ion was generated, it was generated cleanly and no other products were observed. The diverse nature of the oxidants used, reenforces the unlikelihood of a direct hydride transfer mechanism.

Nuclear magnetic resonance spectra of carbenium ions generated under various oxidation conditions are shown in Figures 1-4. Figure 5 is a nmr spectrum of the thioxanthylium carbenium ion which was independently synthesized.

C. An Electron Transfer Mechanism

Recently, Kochi found that paramagnetic species, the arene cation radicals, are readily formed in solution under thallation conditions (42). This was the first direct evidence that Tl^{+3} can act thermally as a one-electron oxidant. The formation of arene cation radicals with $Tl(O_2CCF_3)_3$ may implicate them as common intermediates in the thallation process. In view of this evidence along with the preparation of the cation radical of 9,9-dimethylthioxanthene in H_2SO_4 (43), the oxidation of [16]annulene to [16]annulenediyl dication by FSO_3H (44) and the electrochemical oxidation of thioxanthrene (45) and cycloheptatriene (46), an electron transfer mechanism, as shown below for Tl^{+3}, represents an attractive explanation for most of these "hydride" abstraction reactions.

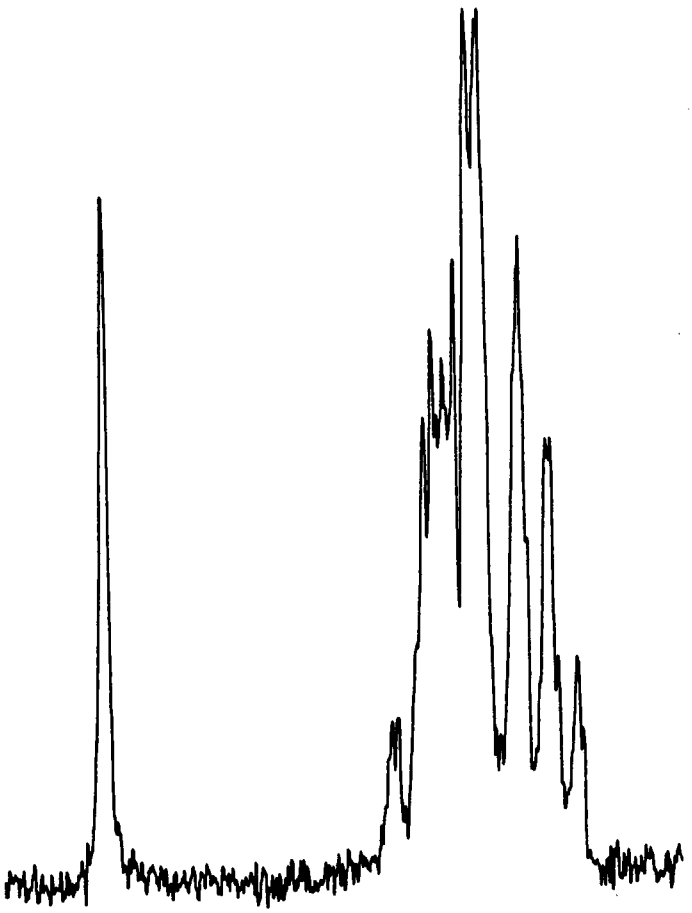


Figure 1. Nmr spectrum of xanthylium carbenium ion generated by Tl^{+3} oxidation.

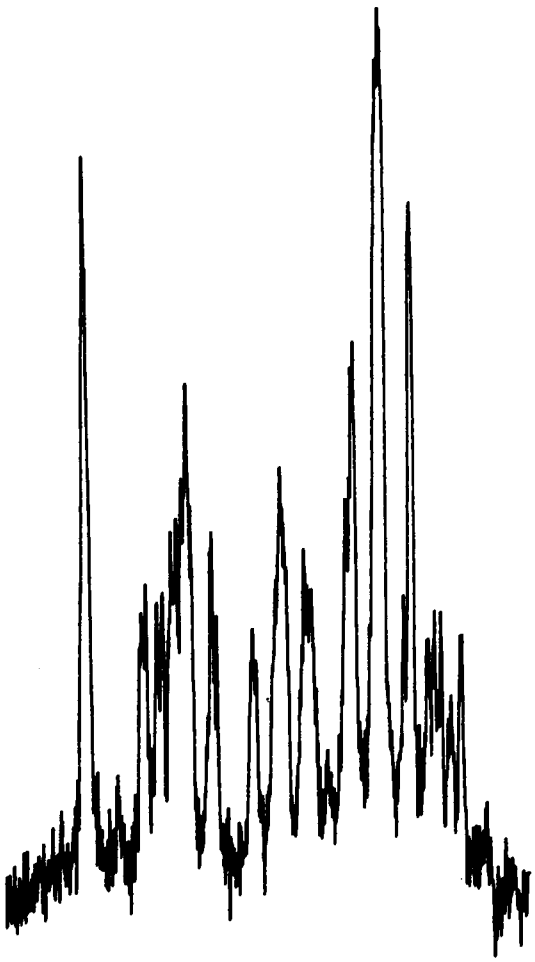


Figure 2. Nmr spectrum of benz[d,e]anthracylium carbenium ion generated by NO_2^+ oxidation.

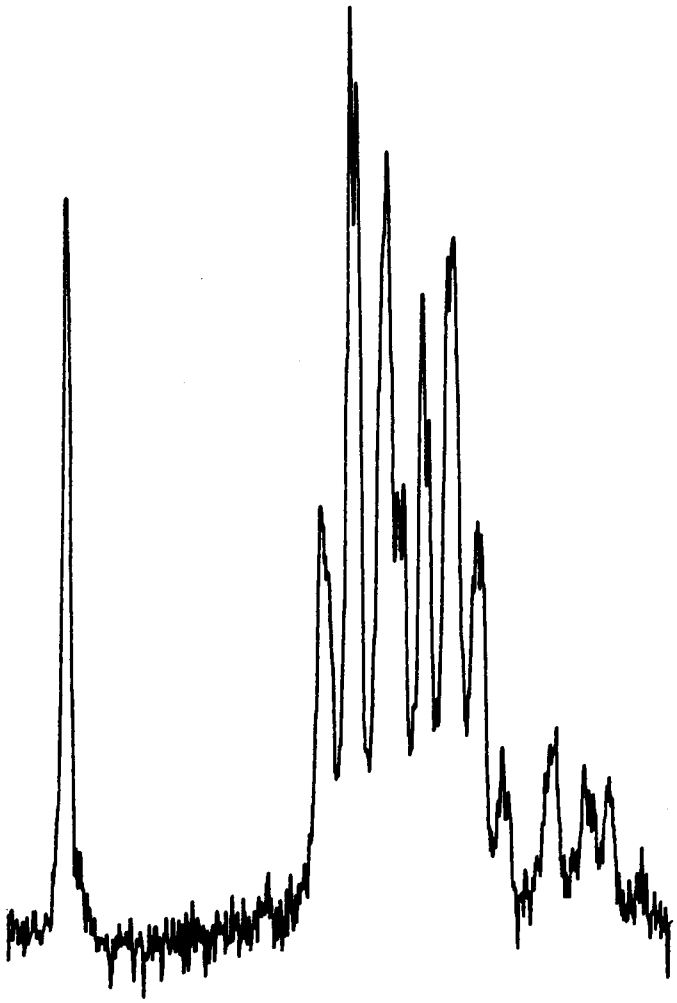


Figure 3. Nmr spectrum of thioxanthylium carbenium ion generated by H_2SO_4 oxidation.

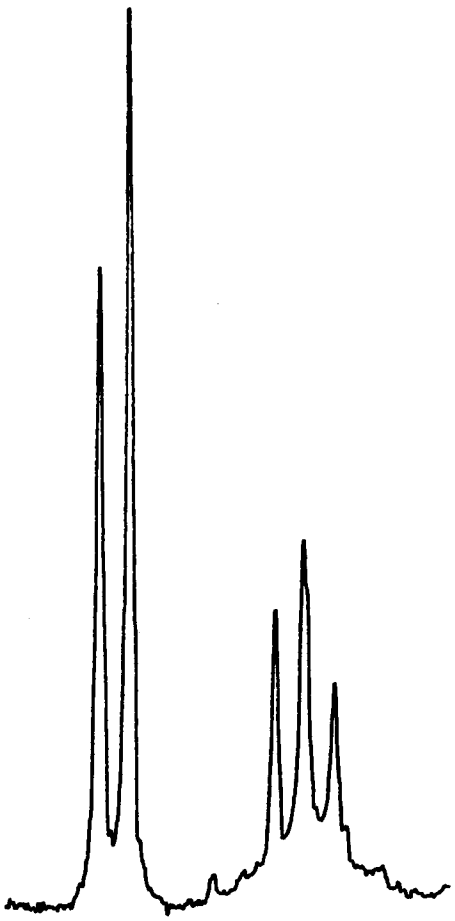


Figure 4. Nmr spectrum of phenalenyl carbenium ion generated by Tl^{+3} oxidation.

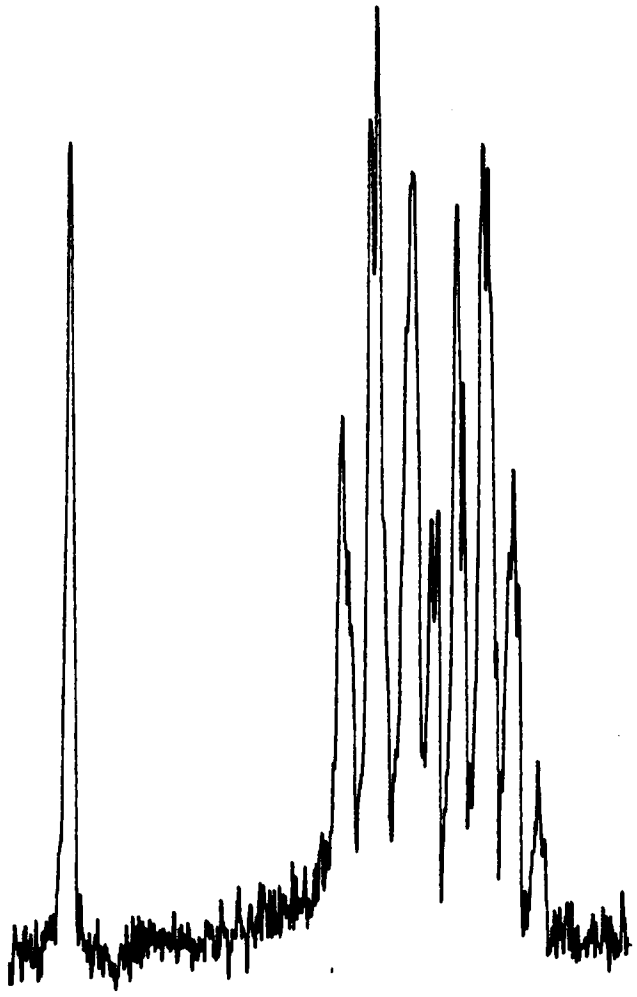
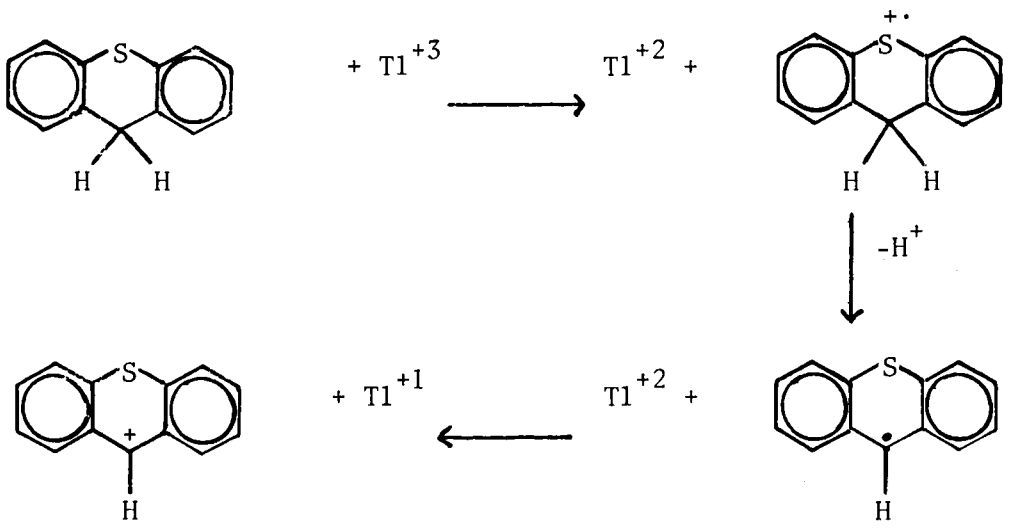


Figure 5. Nmr spectrum of thioxanthylium perchlorate in trifluoroacetic acid.

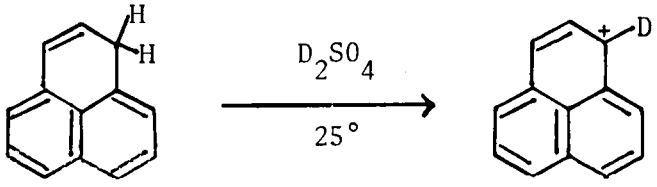


(13)

D. Deuterium Incorporation

As a preliminary investigation into the possibility of an electron transfer mechanism, oxidations of phenalene, 7H-benz[d,e]anthracene and thioxanthene were conducted using D_2SO_4 as the oxidant. Reversibility of the second step in the electron transfer mechanism would result in deuterium incorporation into the cationic product.

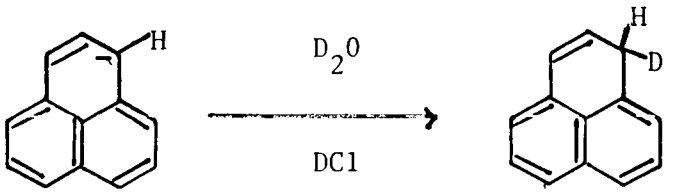
Oxidation of phenalene by D_2SO_4 to the carbenium ion resulted in deuterium incorporation into the phenalene system. Remarkably, the site of incorporation, determined by nmr, was the "shoulder" position(s)"



(14)

A nmr spectrum of the deuterated ion is shown in Figure 6. Oxidation of 7H-benz[d,e]anthracene by D_2SO_4 resulted in deuterium incorporation, but the site(s) of incorporation could not be determined by nmr because of the complexity of the spectrum. The nmr spectrum of the thioxanthylium carbenium ion generated by D_2SO_4 oxidation indicated no apparent incorporation of deuterium.

Phenalene-d_1, prepared by quenching the phenalenyl anion with DCl/D_2O, when treated with H_2SO_4, D_2SO_4 and FSO_3H also demonstrated exchange at the "shoulder" position.



(15)

The results of the oxidations of phenalene by D_2SO_4 and phenalene-d_1 by D_2SO_4, H_2SO_4 and FSO_3H are shown in Table II in terms of the relative areas of the nmr peaks.

Incorporation of deuterium by reversibility of the second step in the electron transfer mechanism requires protonation of the radical intermediate. The phenalenyl radical was prepared and subsequently added to D_2SO_4. The preliminary results suggested the following: (1) it was oxidized by D_2SO_4 to the phenalenyl carbenium ion and (2) apparently deuterium was incorporated. However, traces of phenalene present in the radical were identified by thin-layer chromatography and all attempts to remove the impurity were unsuccessful.

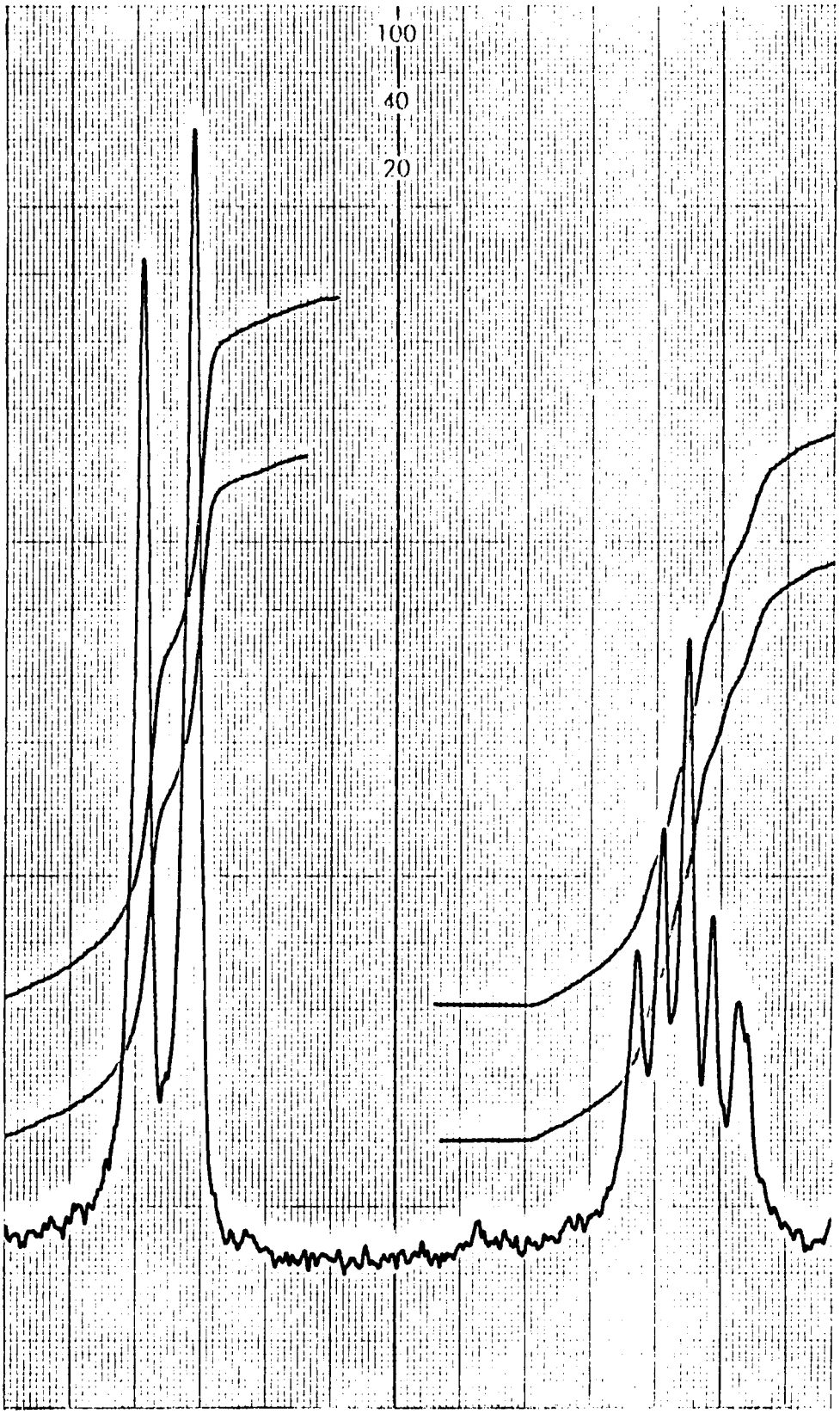


Figure 6. Nmr spectrum of phenalenyl carbenium ion generated by D_2SO_4 oxidation.

Table II

Relative Areas of Nmr Peaks

Conditions	Chemical Shifts in Hz						
	561	554	516	512	508	504	500
Phenalene/D_2SO_4	3.8	4.3	1.4	1.0	2.1	1.3	1.1
Phenalene-d_1/D_2SO_4	1.5	1.5	1.0	1.5	2.2	1.2	1.0
Phenalene-d_1/H_2SO_4	3.0	3.2	1.8	1.8	3.3	1.3	1.0
Phenalene-d_1/FSO_3H	4.7	6.4	2.4	1.5	3.6	1.0	1.5

E. Conclusions

Three mechanisms were given careful consideration in the investigation into the process by which hydrocarbons with extensive π-systems are oxidized by FSO_3H, H_2SO_4, Tl^{+3} and NO_2^+: (1) a protonation-hydride abstraction mechanism, (2) a direct hydride abstraction mechanism and (3) and an electron transfer mechanism.

One could argue that at least for phenalene, cycloheptatriene and 1,2,5,6-dibenzcycloheptatriene, where there is a classic double bond, oxidation could be attributed to a protonation-hydride abstraction process. However, experiments reported by Pagni, Bouis and Easley (47) refute this mechanism.

A direct hydride abstraction process seems unlikely because of the lack of correlation between ion stability (pK_{R^+}) and the rate of direct hydride abstraction. Also, the diverse nature of the oxidants used, reenforces the unlikelihood of this mechanism occurring.

At the present time, an electron transfer process represents the best explanation for the oxidation of these hydrocarbons. Not only the evidence presented in Section C, Chapter II, but also the deuterium incorporation and especially the oxidation of the phenalenyl radical by D_2SO_4 lend support to this mechanism. However, much work remains to be done in order to either refute or to establish unequivocally the electron transfer mechanism.

CHAPTER III

EXPERIMENTAL SECTION

A. General Techniques

Nuclear magnetic resonance (nmr) spectroscopy was used for analysis of the product mixtures. Nmr spectra were recorded on a Varian A-60, T-60 or HA-100 spectrometer. Either tetramethylsilane or tetramethylammonium bromide was used as an internal standard.

The cationic products were formed in the following manner, depending upon the oxidant used:

1. FSO_3H—approximately .3g of the compound to be oxidized was added to 1.5 ml of FSO_3H cooled to -78°. The reaction mixture was either analyzed at -78° or allowed to warm to room termperature and subsequently analyzed by nmr.

2. $H_2SO_4(D_2SO_4)$—approximately .3g of the compound to be oxidized was added to 1.5 ml of $H_2SO_4(D_2SO_4)$ at room temperature and/or -78°. The product mixture was analyzed by nmr.

3. Tl^{+3} - .2g of $Tl(O_2CCF_3)_3$ was dissolved in 1.5 ml of trifluoroacetic acid at room temperature. Approximately .2g of the compound was then added and the reaction mixture was subsequently analyzed by nmr.

4. NO_2^+ - .4g of $NO_2^+BF_4^-$ was dissolved in 1.5 ml of acetonitrile at room temperature. Approximately .2g of the compound was then added and the reaction mixture was analyzed by nmr.

B. Preparation of Compounds

1. Phenalene

The procedure of Pagni and Watson (52) was used to prepare phenalene.

A thimble containing 12.25g (0.074 mol) of phenalenone was placed in a Soxhlet extractor over a 2 liter flask and the apparatus was flushed with nitrogen. One liter of anhydrous ether 3.25g (0.024 mol) of fresh aluminum chloride and 3.25g (0.86 mol) of lithium aluminum hydride were added to the flask. The solution was refluxed for approximately 2 hrs. The reaction mixture was allowed to cool and 500 ml of water was added. The organic layer was separated and the solvent removed *in vacuo*. The product mixture was placed on an alumina column and eluted with ligroine to give 5.3g (64.7%) of white plates of phenalene, mp 85-86°.

2. Benz[d,e]anthracylium perchlorate

A modified procedure of Reid and Sutherland (53) was used to prepare benz[d,e]anthracylium perchlorate.

A solution of 7H-benz[d,e]anthracene (216 mg, 1 mmol) in 1 ml of acetic acid was added to a solution of 1,4-benzoquinone (108 mg, 1 mmol) and .2 ml of perchloric acid in 4 ml acetic acid, all at room temperature. Benz[d,e]anthracylium perchlorate at once deposited, was filtered, washed with anhydrous ether, and dried over phosphoric anhydride and potassium hydroxide. The perchlorate does not melt but decomposes slowly on being heated.

3. 9-Thioxanthenol

A modified procedure of Oehleschager and MacGregor (54) was used to prepare 9-thioxanthenol.

A mixture of 375g of mercury, 13.8g (0.65 mol) of thioxanthenone and 80 ml of 95% ethanol was placed in a pressure bottle. Small pieces of sodium (4.6g, 0.2 mol) were added during a period of 20 minutes while the mixture was being shaken. After the mixture had been shaken mechanically for an additional 15 minutes, the alcohol layer was decanted. The mercury amalgam was washed with two 15 ml portions of hot ethanol and the combined alcoholic solutions were centrifuged, filtered, and poured into one liter of water. A white, finely crystalline precipitate was collected and air dried. A yield of 12.1g was obtained (87.1%).

4. Thioxanthylium perchlorate

The procedure of Price, Hori, Parasaran and Polk (55) was used to prepare thioxanthylium perchlorate.

9-thioxanthenol (1g, 4.65 mmol) dissolved in 10 ml of ether was treated with 1.5 ml of 70% perchloric acid initially cooled to -78°. After warming to room temperature, the red solid was collected and recrystallized twice from acetic acid to give .85g (61%) of red plates, mp 229° dec.

5. Phenalene-d_1

Phenalene (1g, 6 mmol) was dissolved in 300 ml of anhydrous ether under nitrogen. Butyl lithium was added dropwise until a light

pink colored solution persisted. Then 3.8 ml of 1.6M butyl lithium was added and the solution was stirred for 1 hr. The anion was quenched by the addition to a solution of .7 ml of 38% DCl in 50 ml of D_2O. The reaction mixture was washed with water, dried ($CaCl_2$) and the solvent was removed to yield phenalene-d_1: nmr(CCl_4) δ 6.90(m,6H), 6.31(d,1H, J=10Hz), 5.61(d of d,1H,J=10Hz,J=4Hz), 3.65(s,1H).

6. Phenalenyl radical

Phenalene (.3g, 1.8 mmol) was dissolved in 50 ml of carbon tetachloride under nitrogen and .1g (.93 mmol) of quinone was added. The reaction mixture was refluxed for 30 mins., cooled and poured onto an alumina-carbon tetrachloride column. The bright blue phenalenyl radical was collected and the solvent removed in vacuo (58).

7. 7H-Benz[d,e]anthracene

7H-Benz[d,e]anthracene was prepared by reduction of benzanthrone with lithium aluminum hydride and aluminum chloride; alumina chromatography and recrystallization from ethanol gave mp 83.5-84.5° (56).

C. Product Identification

As stated in Chapter II, identification of the cationic product was based on one or more of the following: (1) independent synthesis, (2) literature nmr values, and (3) a detailed analysis of the reaction nmr.

The carbenium ions of 7H-benz[d,e]anthracene and thioxanthene were synthesized independently as discussed in Section B, Preparation of

Compounds, in Chapter III (page 27). Nmr spectra of these perchlorates in trifluoroacetic acid confirmed the cationic products of 7H-benz[d,e]anthracene and thioxanthene. The carbenium ions of 1,2,5,6-dibenzcycloheptatriene and xanthene were also synthesized independently by addition of the corresponding alcohol to FSO_3H. Literature nmr values of the phenalenyl carbenium ion and the tropylium ion have been reported (57).

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VITA

Paul Edmunds Easley was born in Reidsville, North Carolina on January 7, 1951. He obtained his elementary education in Burlington, North Carolina and graduated from Alliance Academy in Quito, Ecuador, South America in May, 1969. His first year of college was spent at John Brown University in Arkansas, after which he transferred to Appalachian State University in Boone, North Carolina, where he was awarded the Bachelor of Arts degree in Chemistry in June, 1973. The author took his graduate studies at the University of Tennessee, Knoxville, from September 1973 to August 1976, and held a graduate teaching assistantship throughout that time. In the midst of his graduate studies, he married the former Sherry Ann Govett of Tulsa, Oklahoma. In August, 1976, the author enters the Bowman Gray School of Medicine in Winston-Salem, North Carolina.